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Ammonium Phenylphosphonamidodiselenoates and Phenylphosphonamidodi-selenoic Diamides from the Selenation of Primary and Secondary Amines

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In Memory of Professor Kurt Dehnicke, A Fine Scientist in the Best Tradition of German Chemistry

Keywords: Woollins' reagent; Amines; Ammonium phenylphosphonamidodiselenoates; Phenylphosphonamidodiselenoic diamides; X-ray diffraction

Abstract. By reacting two equivalents of primary or secondary amines with 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (*Woollins*' reagent) at room temperature a series of new ammonium phenylphosphonamidodiselenoates **1**–**7** have been obtained in good to excellent yields (70–99 %). The first metal complex of phenylphosphonamidodiselenoate, the complex of Cd_2L_4 (L = $[Se_2PPh(NCH(CH_3)_2]^-$) (**8**) has been prepared from the reaction of diisopropylamine *N*-isopropyl-*P*-phenylphosphonamidodiselenoate with $Cd(CH_3COO)_2$ in dichloromethane. Upon heating to 130 °C the ammonium phenylphosphonamidodiselenoates lose hydrogen selenide leading to the corresponding phenylphosphonamidodiselenoic diamides **9**–**11** in almost quantitative yields. The same products **9**–**11** can also be prepared directly from the reaction of primary amines with *Woollins*' reagent in refluxing toluene. Three representative X-ray structures are described.

Introduction

Despite their toxic nature in general, selenium compounds have now found applications in many areas such as organic synthesis,[1] biochemistry,[2] xerography,[3] the synthesis of conducting materials[4] and semiconductors,[5] and ligand synthesis.[6] A wide range of selenation reagents can introduce selenium into organic substrates by both nucleophilic and electrophilic pathways, and the resulting selenium-containing products can be further converted into useful targets that may or may not retain the selenium atom.[7] 2,4-Bis(phenyl)-1,3-diselenadiphosphethane-2,4-diselenide [{PhP(Se)(μ-Se)}$_2$] (*Woollins*' reagent, **WR**, a selenium counterpart of *Lawesson*'s reagent) has proved to be an efficient selenation reagent in organic synthetic chemistry in part due to its relatively pleasant chemical properties and ready preparation.[8] Reactions of *Woollins*' reagent with organic substrates display a wide spectrum ranging from simple oxygen-selenium exchange to the formation of complex phosphorus-selenium heterocycles as well as surprising phosphorus-selenium-free products.[9–17] Herein, as part of our investigation into the reactivity of *Woollins*' reagent towards different organic substrates, we report the synthesis of a series of novel ammonium phenylphosphonamidodiselenoates and phenylphosphonamidodiselenoic diamides from the selenation of primary/secondary amines, the complex of Cd_2L_4 (L = $[Se_2PPh(NCH(CH_3)_2]^-$) and three representative related single-crystal X-ray structures. To the best of our knowledge this is the first reported synthesis and characterisation of ammonium phenylphosphonamidodiselenoates and phenylphosphonamidodiselenoic diamides and the representative coordination compound, providing a valuable addition to the library of phosphodiselenoate compounds known.

Results and Discussion

The ammonium phenylphosphonamidodiselenoates **1**–**6** were synthesised by reaction of *Woollins*' reagent with two molar equivalents of primary or secondary amines (Scheme 1). However, the reaction of *Woollins*' reagent with two molar equivalents of isoproplyamine gave a mixed ammonium phenylphosphonamidodiselenoate **7** (Scheme 2). It was found that isoproplyamine was not pure but mixed with some diisoproplyamine (ca. 5 %), which was formed during the purification process with CaH_2 (Scheme 3).

Breaking the four-membered ring in *Woollins*' reagent forms the ammonium phenylphosphonamidodiselenoates **1**–**7** in 70–99 % yields as either off-white solids or pale yellow pastes, which are soluble in polar and chlorinated solvents such as alcohols, dichloromethane and chloroform but are insoluble in less polar solvents such as ethers and hexane. Compounds **1**–**7** are air stable for several weeks, after that obvious signs of degradation occur including reddening of the powders due to the expulsion of elemental selenium; this decomposition is accompanied by the evolution of foul smelling gas. The charac-

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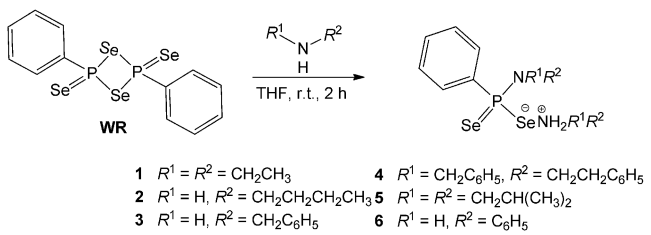
terisation of **1**–**7** is based on elemental analyses, ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectroscopy, IR spectroscopy and mass spectrometry. The elemental analyses for all compounds were satisfactory. The ^{31}P NMR spectra of **1**–**7** showed sharp singlet signals in the range of 42.0–70.0 ppm, flanked by a single pair of selenium satellites with ^{31}P–^{77}Se coupling constants in the range of 612–636 Hz, which are much smaller than the values in sodium phosphonodiselenoate salts (667–675 Hz),[18] indicating a P–Se bond order of approximately 1.5 as expected. This was further substantiated by the ^{77}Se NMR spectra which exhibited doublets in the range of 31.6–62.8 ppm, with matching ^{31}P–^{77}Se coupling constants.

Attempts to crystallise ammonium salts proved unsuccessful apart from compound **7**, which was obtained by diffusion of the dichloromethane solution into hexane at room temperature. The building block for compound **7** is shown in Figure 1 and Table 1. The P–Se bond lengths [2.1545(9) and 2.1537(8) Å] are slightly shorter than those found in amine salts of bisdiselenophosphonic acid [2.1280(11)–2.1350(12) Å][19] and other symmetrical phosphenium salts [ca. 2.13 Å],[20] however, being still intermediate between single bond [ca. 2.38 Å] and double bond [P=Se double bond length ca. 2.08 Å],[21] indicating significant delocalisation of the negative charge over the Se–P–Se fragment. It should be noted that the two Se···N distances between the anion and cation are significantly different [6.024(2) Å for N(2)···Se(1) and 3.424(2) Å for N(2)···Se(2)].



Scheme 1. Synthesis of ammonium phenylphosphonamidodiselenoates **1**–**6**.

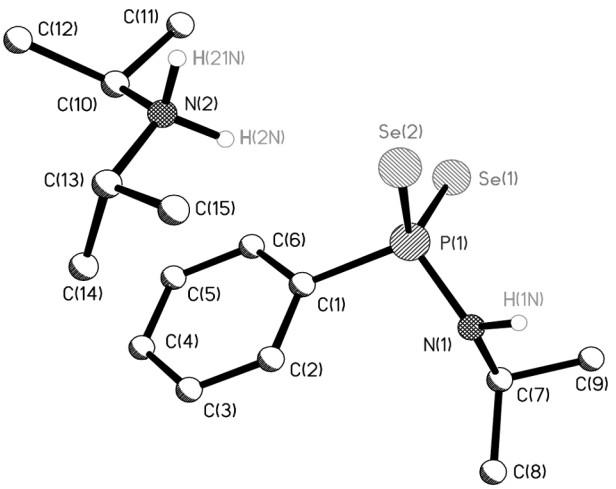
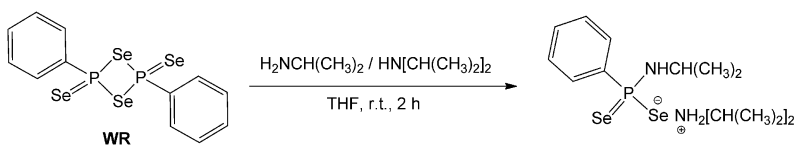
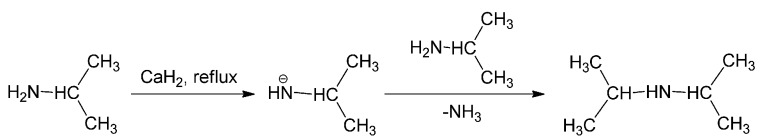


Figure 1. Single crystal structure of compound **7** (Hydrogen atoms on carbon atoms omitted for clarity). Selected bond lengths /Å and angles /° (esds in parentheses): Se(1)–P(1) 2.1545(9), Se(2)–P(1) 2.1537(8), P(1)–N(1) 1.665(2), P(1)–C(1) 1.830(2), N(1)–C(7) 1.474(4), N(2)–C(10) 1.507(3), N(2)–C(13) 1.504(4); Se(1)–P(1)–Se(2) 116.57(4), Se(1)–P(1)–N(1) 114.62(9), Se(1)–P(1)–C(1) 106.76(10), Se(2)–P(1)–N(1) 105.79(9), Se(2)–P(1)–C(1) 109.15(10), N(1)–P(1)–C(1) 103.05(14), P(1)–N(1)–C(7) 121.39(19), C(10)–N(2)–C(10) 118.0(2).

The preparation of the first metal complex of ammonium phenylphosphonamidodiselenoate has been carried out. Cadmium acetate dihydrate was stirred with two equivalents of **7** in dichloromethane at room temperature to generate the complex **8** (Scheme 4). The complex was obtained in high yield (98 %) as a white solid soluble in dichloromethane. The ^{31}P NMR spectrum of **8** displays a sharp singlet at δ_P = 35.7, flanked by a single pair of selenium satellites with a ^{31}P–^{77}Se coupling constant of 554 Hz. Meanwhile the ^{77}Se NMR spectrum showed a doublet at δ_{Se} = 225.5 with a matching coupling constant. The results show that upon complexation there is not only a change in chemical shift (a decrease at δ_P from 42.0 to 35.7 and an increase at δ_{Se} from 70.7 to 225.5) but also a significant decrease in the ^{31}P–^{77}Se coupling constant (a de-



Scheme 2. Synthesis of ammonium phenylphosphonamidodiselenoate **7**.



Scheme 3. Formation of small amount of diisopropylamine (ca. 5 % based on ^{1}H NMR spectroscopic analysis) in isopropylamine purification process.

Table 1. Details of the X-ray data collections and refinements for compounds **7**, **8**, and **11**.

Compound	**7**	**8**	**11**
Formula	$C_{15}H_{29}N_2PSe_2$	$C_{18}H_{26}N_2P_2Se_4Cd$	$C_{20}H_{21}N_2PSe$
M	426.30	760.61	399.33
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a /Å	11.060(3)	8.5190(14)	5.687(10)
b /Å	11.767(3)	11.663(2)	10.2583(18)
c /Å	15.528(4)	13.167(2)	16.204(2)
α /°	90	90.897(4)	107.730(9)
β /°	108.299(7)	95.811(4)	90.680(5)
γ /°	90	96.400(4)	97.955(4)
V /A^3	945.81(7)	1238.2(4)	2209.4(7)
Z	4	2	2
μ /mm^{-1}	1.476	2.040	1.489
Reflections collected	14281	12299	9000
Independent reflections	3863	5604	4047
R_{int}	0.079	0.1819	0.0954
$R1$;	0.0429;	0.1036;	0.0594;
$wR2$ [$I > 2\sigma(I)$]	0.1137	0.2383	0.1065

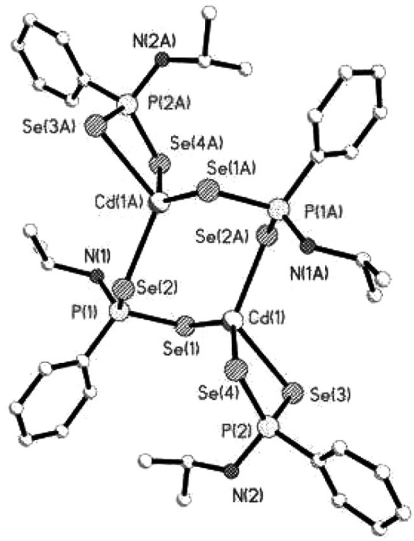


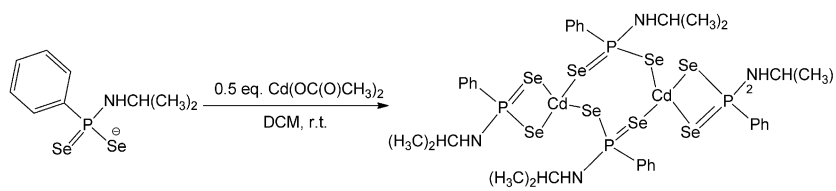
Figure 2. Single crystal structure of the complex **8** (Hydrogen atoms on carbon atoms omitted for clarity). Selected bond lengths /Å and angles /° (esds in parentheses): Cd(1)–Se(1) 2.668(2), Cd(1)–Se(2) 3.255(2), Cd(1)–Se(3) 2.794(2), Cd(1)–Se(4) 2.624(2), Se(1)–P(1) 2.151(5), Se(2)–P(1) 2.204(4), Se(3)–P(2) 2.161(5), Se(4)–P(2) 2.192(4), P(1)–N(1) 1.597(16), P(2)–N(2) 1.641(15), Cd(1)–Se(2A) 2.639(2); Se(1)–Cd(1)–Se(2) 73.80(6), Se(1)–Cd(1)–Se(2A) 99.68(7), Se(1)–Cd(1)–Se(3) 92.60(7), Se(1)–Cd(1)–Se(4) 136.40(8), Se(1)–Cd(1)–P(2) 112.75(10), Se(2A)–Cd(1)–Se(3) 147.11(7), Se(2A)–Cd(1)–Se(4) 87.80(6), Se(3)–Cd(1)–Se(4) 81.81(7), Cd(1)–Se(1)–P(1) 95.33(14), Cd(1)–Se(4)–P(2) 83.93(14), Se(1)–P(1)–Se(2) 110.9(2), Se(1)–P(1)–N(1) 106.6(5), Se(2)–P(1)–N(1) 117.4(5), Se(3)–P(2)–Se(4) 109.3(2), Se(3)–P(2)–N(2) 110.5(6), Se(4)–P(2)–N(2) 114.1(5).

crease from 615 to 554 Hz). A similar pattern was found in the ^{1}H and ^{13}C NMR spectra of **8** as in the starting material **7**. The mass spectrometry found the 1/2 expected parent ion at m/z = 761.

The single-crystal X-ray structure of **8** was determined (Figure 2 and Table 1). Although no literature example of structurally characterised cadmium complexes with such NP(Se)Se containing ligands have been found, one example of cadmium complex of a similar OP(Se)Se containing ligand[19] and many examples of OP(S)S containing ligands have been documented.[22] All examples exhibit a structural motif of an eight-membered $Cd_2P_2Se_4$ or $Cd_2P_2S_4$ ring with two terminal bidentate ligands each bound to one cadmium atom via both selenium/sulfur atoms and the other two acting as bridging ligands with their selenium/sulfur atoms binding to two different cadmium atoms. Not surprisingly, the structure of compound **8** shows a dimeric complex in the solid state with an eight-membered $Cd_2P_2Se_4$ ring, flanked by two four-membered rings, which is very closely related to the similar OP(Se)Se complex.[18,23,24]

Heating a toluene solution of ammonium phenylphosphonamidodiselenoates to reflux for 12 h led to the corresponding phenylphosphonamidodiselenoic diamides **9**–**11** in almost quantitative isolated yields with evolution of hydrogen selenide (Scheme 5). The same products **9**–**11** could be also obtained in 90–95 % yields via the reaction of *Woollins*' reagent with two equivalents of the corresponding primary amine in refluxing toluene (Scheme 6).

Compounds **9**–**11** are soluble in common chlorinated solvents and air stable for several months as sticky oils or solid. Their formulations were confirmed by IR spectroscopy, MS (including accurate mass measurement), solution multinuclear NMR spectroscopy and one representative X-ray structure determination. The ^{31}P NMR spectra of **9**–**11** showed sharp singlet signals at δ_P = 60.3, 46.0 and 62.4, respectively, the singlet in each case was flanked by a single pair of selenium satellites with ^{31}P–^{77}Se coupling constants in the range of 763–813 Hz, indicating typical P=Se double bond character. This was further confirmed by the ^{77}Se NMR spectra which exhibited doublets at δ_{Se} = –243.2, –180.4 and –250.4, respectively with matching ^{31}P–^{77}Se coupling constants. The ^{1}H and ^{13}C NMR spectra of **9**–**11** were as expected confirming the presence of phenyl and NH moieties. Mass spectra for them showed the expected parent ions as [M + Na].



Scheme 4. Synthesis of the complex **8**.

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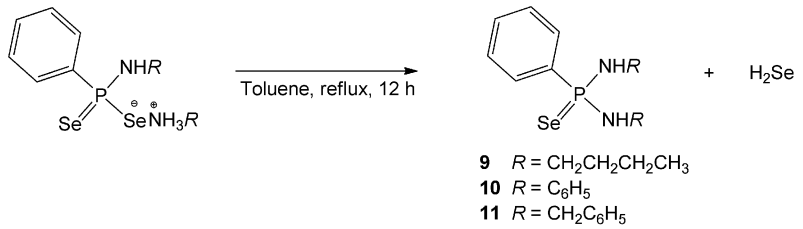
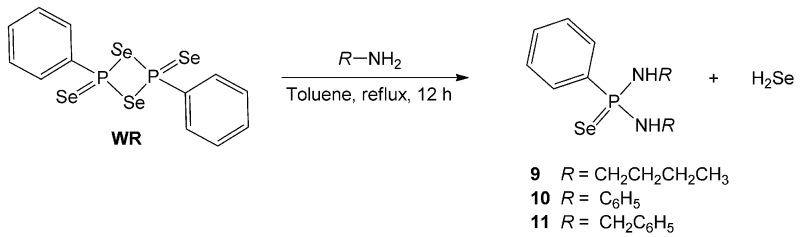


Scheme 5. Synthesis of phenylphosphonamidodiselenoic diamides **9**–**11** from ammonium phenylphosphonamidodiselenoates.



Scheme 6. Synthesis of phenylphosphonamidodiselenoic diamides **9**–**11** from the direct selenation of primary amines.

Compound **11** was crystallised by slow evaporation of dichloromethane solution to give transparent, colourless cubic crystals. The data for X-ray structure of compound **11** is shown in Figure 3 and Table 1 The phenyl rings attached to phosphorus atom via a CH_2–NH bridge are opposite positions with an inclined angle of 74.2° and being bent towards the different side of the phenyl ring directly attached phosphorus atom with angles of 61.8° and 76.5°, respectively. The single crystal structure shows maginally longer P–Se double bond length [2.1175(12) Å], compared to the normal double bond length [ca. 2.08 Å][21] and significant shorter P–N single bond lengths [1.652(3) and 1.664(3) Å], compared to the other typical P–N single bond system [ca. 1.80 Å],[25] suggesting the more or less extent of resonance delocalisation.

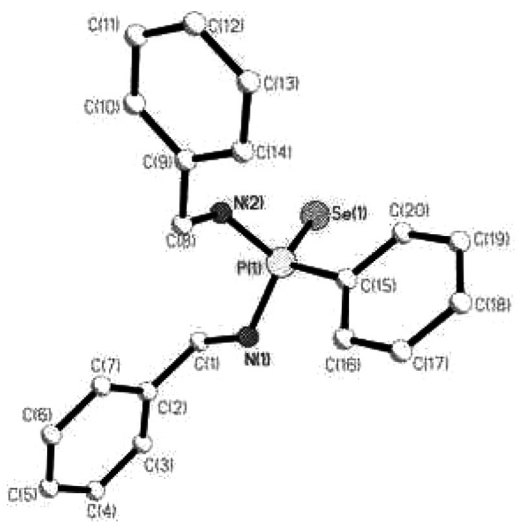


Figure 3. Single crystal structure of compound **11** (Hydrogen atoms on carbon atoms omitted for clarity). Selected bond lengths /Å and angles /° (esds in parentheses): Se(1)–P(1) 2.1175(12), P(1)–N(1) 1.652(3), P(1)–N(2) 1.664(3), P(1)–C(15) 1.811(5), N(1)–C(1) 1.475(6), N(2)–C(8) 1.449(5); Se(1)–P(1)–N(1) 116.50(12), Se(1)–P(1)–N(2) 107.49(13), Se(1)–P(1)–C(15) 115.34(15), N(1)–P(10)–N(2) 106.75(18), N(1)–P(1)–C(15) 102.21(20), N(2)–P(1)–C(15) 108.00(18), P(1)–N(1)–C(1) 118.2(3), P(1)–n(2)–C(8) 125.6(3).

Conclusions

The reaction of *Woollins*' reagent with the primary or secondary amines gives the non-symmetric phosphoronamidodiselenoate anions $[Ph(R^1R^2N)PSe_2]^-$ as their ammonium salts in good to excellent yields. The latter can be converted into the corresponding phenylphosphonamido-diselenoic diamides in almost quantitative yields with evolution of hydrogen selenide. The same products, phenylphosphonamido-diselenoic diamides, can be directly obtained via the reaction of *Woollins*' reagent with two equivalents of primary amine in excellent yields. The first metal complex of a phosphoronamidodiselenoate anion shows a conformation with a dimeric nature, which is very closely related to the known OP(Se)Se system.

Experimental Section

Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air. ^1H (270 MHz), ^{13}C (67.9 MHz), $^{31}P\{^1H\}$ (109 MHz) and $^{77}Se\text{-}\{^1H\}$ (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise) with a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} with a Perkin–Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St-Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service. X-ray crystal data for **7**, were collected using the Rigaku STANDARD system[26] and for **8** and **11** using a Rigaku SCXMIni Mercury CCD system. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were cor-

rected for Lorentz polarisation effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 by using the program SHELXTL.[27] Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries. CCDC-829188 (**7**), -829187 (**8**), -829186 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk.

General Procedure for the Formation of Ammonium Phenylphosphonamidodiselenoates 1–7

A mixture of *Woollins*' reagent (0.54 g, 1.0 mmol) and primary or secondary amine (4.0 mmol) in dry tetrahydrofuran (50 mL) was stirred at room temperature. While the red suspension disappeared gradually and a greyish white suspension formed after stirring at room temperature for 2 h. Upon evaporating to remove the solvent the residue was dissolved in dichloromethane. After removal of insoluble solid with a celite pad, the filtrate was dried in vacuo to give ammonium phenylphosphonamidodiselenoates **1–7**.

Diethylamine *N*,*N*-diethyl-*P*-phenylphosphonamidodiselenoate (1): A pale yellow paste (0.800 g, 97 % yield). $C_{14}H_{42}N_2PSe_2$ (427.39): C, 39.34; H, 9.91; N, 6.55. Found: C, 39.70; H, 10.01; N, 6.70. Selected **IR** (KBr): 1565(w), 1458(m), 1434(s), 1381(s), 1167(s), 1090(m), 1055(s), 1013(s), 905(m), 745(m), 691(s), 547(vs, P–Se), 500(s) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.17–8.09 (m, 2 H, Ar–H), 7.33–7.32 (m, 3 H, Ar–H), 6.84 (wide peak, 2 H, NH), 3.20–3.08 (m, 4 H, CH_2), 3.03–2.95 (m, 4 H, CH_2), 1.31 (t, J(H,H) = 7.2 Hz, 6 H, CH_3), 1.02 (t, J(H,H) = 6.9 Hz, 6 H, CH_3) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 130.9 (Ar–C), 130.7 (Ar–C), 129.6 (Ar–C), 127.2 (d, J(P,C) = 12.5 Hz, (Ar–C)), 53.1 (CH_2), 41.5 (CH_2), 13.9 (CH_3), 11.2 (CH_3) ppm. **^{31}P NMR** (CD_2Cl_2, δ), 55.8 (s, J(P,Se) = 615 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), 62.8 (d, J(P,Se) = 616 Hz) ppm. **Mass spectrum** [ES$^-$, *m*/*z*]: 348 [M – $HN(C_2H_5)_2]^-$.

Butan-1-amine *N*-butyl-*P*-phenylphosphonamidodiselenoate (2): A pale yellow condensed oil (0.810 g, 98 % yield). $C_{14}H_{26}N_2PSe_2$ (411.26): C, 40.89; H, 6.37; N, 6.81. Found: C, 41.10; H, 6.55; N, 6.70. Selected **IR** (KBr): 1640(w), 1582(m), 1479(m), 1435(m), 1387(m), 1096(m), 1069(m), 740(m), 690(m), 554(s, P–Se), 496(s) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.12–8.06 (m, 2 H, Ar–H), 7.33–7.31 (m, 2 H, Ar–H), 6.05 (wide peak, 3 H, NH_3), 2.80 (t, J(H,H) = 6.9 Hz, 2 H, CH_2), 2.66 (t, J(H,H) = 7.2 Hz, 2 H, CH_2), 2.11 (wide peak, 1 H, NH), 1.57–1.21 (m, 8 H, CH_2), 0.92–0.79 (m, 6 H, CH_3) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 130.4 (Ar–C), 130.3 (Ar–C), 129.8 (d, J(P,C) = 3.1 Hz, Ar–C), 127.5 (d, J(P,C) = 12.5 Hz, Ar–C), 43.4 (d, J(P,C) = 5.2 Hz), 40.2, 33.2 (d, J(P,C) = 9.3 Hz), 32.1, 20.2, 20.0, 13.7, 13.5 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 44.3 (s, J(P,Se) = 613 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), 57.9 (d, J(P,Se) = 613 Hz) ppm. **Mass spectrum** [ES$^-$, *m*/*z*]: 340 [M – $H_2NC_4H_9]^-$.

Benzylamine *N*-benzyl-*P*-phenylphosphonamidodiselenoate (3): An off-white solid (0.902 g, 99 % yield). M.p. 150–152 °C. $C_{20}H_{22}N_2PSe_2$ (479.30): C, 50.11; H, 4.63; N, 5.85. Found: C, 50.20; H, 4.95; N, 6.01. Selected **IR** (KBr): 1569(m), 1493(m), 1468(m), 1377(m), 1199(w), 1063(s), 732(m), 696(vs), 548(s), 483(s) cm^{-1}. **^{1}H NMR** ([D$_8$]THF, δ), 8.28 (dd, J(P,H) = 13.8, J(H,H) = 7.9 Hz, 2 H, Ar–H), 7.55–7.07 (m, 13 H, Ar–H), 6.72 (wide peak, 3 H, NH), 3.92 (d, J(P,H) = 9.3 Hz, 2 H, CH_2), 3.58 (s, 2 H, CH_2), 3.40 (wide peak, 1 H, NH) ppm. **^{13}C NMR** ([D$_8$]THF, δ), 145.0, 143.9, 141.6, 141.4, 134.9, 130.9, 130.8, 129.1, 128.6, 128.3, 128.0, 127.8, 126.6, 126.4, 126.1, 47.5, 43.2 ppm. **^{31}P NMR** ([D$_8$]THF, δ), 46.1 (s, J(P,Se) = 634 Hz) ppm. **^{77}Se NMR** ([D$_8$]THF, δ), 39.9 (d, J(P,Se) = 634 Hz) ppm. **Mass spectrum** [ES$^-$, *m*/*z*]: 374 [M – $H_2CH_2Se]^-$. [ES$^+$, *m*/*z*]: 108 [M–C_6H_5P(Se) $NHCH_2C_6H_5Se]^-$. Accurate mass measurement (ES$^-$MS): 373.9115, calculate mass for [$C_{20}H_{22}N_2PSe_2$–$C_6H_5CH_2NH_2$]: 373.9116.

***N*-Benzyl-2-phenylethanamine *N*-benzyl-*N*-phenethyl-*P*-phenylphosphonamidodiselenoate (4):** A reddish golden paste (1.280 g, 93 % yield). $C_{34}H_{38}N_2PSe_2$ (663.57): C, 61.54; H, 5.77; N, 4.22. Found: C, 61.52; H, 5.95; N, 4.41. Selected **IR** (KBr): 1601(w), 1494(m), 1434(m), 1454(m), 1092(m), 747(s), 696(vs), 544(m), 486(m) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.38 (dd, J(P,H) = 13.8, J(H,H) = 7.2 Hz, 2 H, Ar–H), 8.02 (wide peak, 2 H, NH), 7.47–6.81 (m, 13 H, Ar–H), 4.12 (s, 4 H, CH_2), 3.27–3.05 (m, 4 H, CH_2), 2.65–2.51 (m, 4 H, CH_2) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 140.3, 137.1, 131.8, 131.6, 131.4, 130.0, 129.0, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.9, 127.7, 127.5, 127.4, 126.9, 125.8, 51.7, 50.8, 47.5, 34.8, 32.7, 30.4 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 70.0 (s, J(P,Se) = 620 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), 56.1 (d, J(P,Se) = 620 Hz) ppm. **Mass spectrum** [ES$^-$, *m*/*z*]: 454 [M – $H_2N(CH_2C_6H_5)CH_2CH_2C_6H_5]^-$. Mass spectrum [ES$^+$, *m*/*z*]: 212 $[H_2N(CH_2C_6H_5)CH_2CH_2C_6H_5]^-$.

Diisobutylamine *N*,*N*-diisobutyl-*P*-phenylphosphonamidodiselenoate (5): An orange paste (1.000 g, 95 % yield). $C_{22}H_{42}N_2PSe_2$ (523.48): C, 50.48; H, 8.09; N, 5.35. Found: C, 50.69; H, 8.35; N, 5.70. Selected **IR** (KBr): 1560(m), 1468(s), 1435(m), 1388(m), 1368(m), 1092(m), 988(m), 769(m), 748(m), 695(s), 554(s), 511(s) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.24 (dd, J(P,H) = 13.9, J(H,H) = 7.2 Hz, 2 H, Ar–H), 7.90 (wide peak, 2 H, NH), 7.30–7.28 (m, 3 H, Ar–H), 2.82 (dd, J(H,H) = 7.2, J(H,H) = 7.7 Hz, 4 H, CH_2), 2.80 (d, J(H,H) = 7.2 Hz, 4 H, CH_2), 2.13 (septet, J(H,H) = 6.9 Hz, 2 H, CH), 1.81 (septet, J(H,H) = 6.6 Hz, 2 H, CH), 1.01 (d, J(H,H) = 6.6 Hz, 6 H, CH_3), 0.75 (d, J(H,H) = 6.6 Hz, 6 H, CH_3) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 142.8 (d, J(P,C) = 83.0 Hz), 131.8 (d, J(P,C) = 11.4 Hz), 129.4 (d, J(P,C) = 3.1 Hz), 126.8 (d, J(P,C) = 12.5 Hz), 56.9, 53.8, 27.2 (d, J(P,C) = 7.3 Hz), 25.1, 20.6, 20.2 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 63.9 (s, J(P,Se) = 617 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), 31.6 (d, J(P,Se) = 617 Hz) ppm. **Mass spectrum** [ES$^-$, *m*/*z*]: 396 [M – $HN(C_4H_9)_2]^-$, 129 $[HN(C_4H_9)_2]^-$.

Benzenamine *N*,*P*-diphenylphosphonamidodiselenoate (6): A yellow paste (0.640 g, 70 % yield). $C_{18}H_{18}N_2PSe_2$ (451.24): C, 47.91; H, 4.02; N, 6.21. Found: C, 47.98; H, 4.25; N, 6.50. Selected **IR** (KBr): 1600(s), 1494(s), 1434(m), 1378(m), 1282(m), 1027(m), 905(s), 742(s), 689(s), 527(m), 478(m) cm^{-1}. **^{1}H NMR** (Tetrahydrofuran-d$_8$, δ), 8.02–6.90 (m, 15 H, Ar–H), 6.71 (d, J(P,H) = 7.7 Hz, 1 H, NH), 5.39 (wide peak, 3 H, NH) ppm. **^{13}C NMR** (Tetrahydrofuran-d$_8$, δ), 143.3 (d, J(P,C) = 87.2 Hz), 132.5 (d, J(P,C) = 3.1 Hz), 130.5, 126.8 (d, J(P,C) = 12.5 Hz), 129.5, 129.4, 129.2, 129.0, 128.8, 128.0, 127.8, 122.7, 119.6, 119.5, 119.0 ppm. ^{31}P NMR (Tetrahydrofuran-d$_8$, δ), 46.2 (s, J(P,Se) = 636 Hz) ppm. **^{77}Se NMR** (Tetrahydrofuran-d$_8$, δ), 39.0 (d, J(P,Se) = 636 Hz) ppm. **Mass spectrum** [ES$^-$, *m*/*z*]: 360 [M – $H_2NC_6H_5]^-$, 93 $[H_2NC_6H_5]^-$.

Diisopropylamine *N*-isopropyl-*P*-phenylphosphonamidodiselenoate (7): A yellow solid (0.810 g, 95 % yield). M.p. 119–120 °C. $C_{15}H_{29}N_2PSe_2$ (426.30): C, 42.26; H, 6.86; N, 6.57. Found: C, 42.40; H, 7.05; N, 6.70. Selected **IR** (KBr): 1578(m), 1434(m), 1406(m), 1129(m), 1093(m), 1023(m), 1020(m), 751(m), 694(m), 547(vs, P=Se), 500(m) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.15–8.08 (m, 2 H, Ar–H), 7.81 (wide peak, 2 H, NH), 7.32–7.27 (m, 3 H, Ar–H), 3.49–3.42 (m, 1 H, CH), 3.32–3.22 (m, 1 H, CH), 2.48 (wide peak, 1 H, NH), 1.46 (d, J(H,H) = 6.3 Hz, 12 H, CH_3), 0.99 (d, J(H,H) = 6.6 Hz, 6 H, CH_3)

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ppm. **^{13}C NMR** (CD_2Cl_2, δ), 130.5 (d, J(P,C) = 12.5 Hz, Ar–C), 129.4 (Ar–C), 127.3 Ar–C), 127.1 (Ar–C), 48.6, 46.1, 24.8, 20.0 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 42.0 (s, J(P,Se) = 615 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), 70.7 (d, J(P,Se) = 615 Hz) ppm. **Mass spectrum** [ES$^-$, m/z]: 326 [M – $H_2NC_6H_{14}$]$^-$.

Bis(*N*-isopropyl-*P*-phenylphosphonamidodiselenoato)cadmium (8): *N*-isopropyl-*P*-phenylphosphonamidodiselenoate (0.048 g, 0.1 mmol) and $Cd(CH_3COO)_2 \bullet 2H_2O$ (0.013 g, 0.05 mmol) in dichloromethane (10 mL) was stirred at room temperature for 2 h. A colourless solution formed. Upon filtering to remove unreacted solid, the filtrate was dried in vacuo to give as a white solid (0.036 g) in 97 % yield. Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a dichloromethane solution. $C_{36}H_{52}N_4P_4Se_8Cd_2$ (1521.22): C, 28.42; H, 3.45; N, 3.68. Found: C, 28.67; H, 3.70; N, 3.79. Selected **IR** (KBr): 1562(m), 1006(m), 880(s), 748(s), 692(s), 541(s) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.14–8.06 (m, 8 H, Ar–H), 7.41–7.38 (m, 12 H, Ar–H), 3.25 (q, J(H,H) = 6.6 Hz, 4 H, CH), 2.65 (very wide peak, 4 H, NH), 1.26 (d, J(H,H) = 6.6 Hz, 24 H, CH_3) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 138.8 (d, J(P,C) 83.0 Hz), 131.4 (d, J(P,C) = 3.1 Hz), 130.8 (d, J(P,C) = 13.5 Hz), 128.0 (d, J(P,C) = 13.5 Hz), 46.6, 19.3 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 35.7 (s, J(P,Se) = 514 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), 225.5 (d, J(P,Se) = 514 Hz) ppm. **Mass spectrum** [MALDI, m/z]: 761 [1/2M]$^+$, 440 [1/2M–$PSe_2NC_9H_{13}$]$^+$.

General Procedure for Formation of Phenylphosphonamido-Diselenoic Diamides 9–11

Route A: A toluene solution (20 mL) of ammonium phenylphosphonamidodiselenoate (0.05 mmol) was heated to reflux under N_2 gas for 12 h. Upon cooling to room temperature the mixture was evaporated to remove solvent and the residue was purified by silica gel column (dichloromethane as eluent) to afford the corresponding compounds **9–11**.

Route B: A suspension of primary amine (2.0 mmol) and *Woollins*' reagent (0.54 g, 1.0 mmol) in dry toluene (20 mL) was heated to reflux under N_2 for 12 h. The red suspension disappeared and a yellow suspension formed. Upon cooling to room temperature and removing the unreacted solid by filtration, the filtrate was evaporated and the residue was purified by silica gel column (dichloromethane as eluent) to give the corresponding compounds **9–11**.

***N*,*N*-Dibutyl-*P*-phenylphosphinoselenoic amide (9):** A yellow oil (99 % yield from *Route A* and 91 % yield from *Route B*). Selected **IR** (KBr): 1463(m), 1436(m), 1402(m), 1106(s), 1081(s), 755(m), 694(m) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 7.95 (dd, J(P,H) = 13.2, J(H,H) = 7.4 Hz ppm, 2 H, Ar–H), 7.47–7.44 (m, 3 H, Ar–H), 2.94–2.82 (m, 4 H, CH_2), 2.47 (wide peak, J(P,H) = 6.3 Hz, 2 H, NH), 1.60–1.25 (m, 4 H, CH_2), 0.87 (t, J(H,H) = 7.2 Hz, 6 H, CH_3) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 135.5 (d, J(P,C) = 112.1 Hz), 131.6, 130.9 (d, J(P,C) = 11.4 Hz), 128.3 (d, J(P,C) = 16,2 Hz), 41.6, 33.5, 20.1, 13.6 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 60.3 (s, J(P,Se) = 763 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), –243.2 (d, J(P,Se) = 763 Hz) ppm. **Mass spectrum** [ES$^+$, m/z]: 355 [M + Na]$^+$. Accurate mass measurement (ES$^+$MS): 355.0820, calculate mass for [$C_{14}H_{25}N_2PSeNa$]: 355.0818.

***N*,*N*-Diphenyl-*P*-phenylphosphinoselenoic amide (10):** A pale yellow solid (98 % yield from *Route A* and 95 % yield from *Route B*). Selected **IR** (KBr): 1597(s), 1495(s), 1389(m), 1281(m), 1221(m), 1100(m), 1028(m), 911(m), 745(s), 688(s) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.02–7.93 (m, 2 H, ArH), 7.58–7.44 (m, 3 H, Ar–H), 7.24–6.96 (m, 10 H, Ar–H), 5.38 (d, J(P,H) = 9.1 Hz, 2 H, NH) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 140.0 (d, J(P,C) = 3.1 Hz), 134.8 (d, J(P,C) = 113.1 Hz), 132.5 (d, J(P,C) = 3.1 Hz), 130.6 (d, J(P,C) = 11.4 Hz), 129.2, 129.1, 128.8, 122.7, 119.6, 119.5 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 46.0 (s, J(P,Se) = 812 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), –180.4 (d, J(P,Se) = 813 Hz) ppm. Mass spectrum [ES$^+$, m/z]: 395 [M + Na]$^+$. Accurate mass measurement (ES$^+$MS): 395.0195, calculate mass for $C_{18}H_{17}N_2PSe$ [M + Na]: 395.0192.

***N*,*N*-Dibenzyl-*P*-phenylphosphinoselenoic amide (11):** A yellow oil (99 % yield from *Route A* and 90 % yield from *Route B*). Selected **IR** (KBr): 1435(m), 1394(m), 1261(m), 1051(s), 800(s), 744(s), 695(vs), 550(m), 485(m) cm^{-1}. **^{1}H NMR** (CD_2Cl_2, δ), 8.14–7.97 (m, 2 H, Ar–H), 7.49–7.21(m, 13 H, Ar–H), 6.34 (wide peak, 2 H, NH), 4.16–4.06 (m, 4 H, CH_2) ppm. **^{13}C NMR** (CD_2Cl_2, δ), 139.6, 135.9, 132.9, 132.0, 131.1, 131.0, 130.6, 130.5, 130.2, 129.2, 129.0, 128.6, 128.4, 127.6, 127.4, 127.2, 127.0, 45.9 ppm. **^{31}P NMR** (CD_2Cl_2, δ), 62.4 (s, J(P,Se) = 775 Hz) ppm. **^{77}Se NMR** (CD_2Cl_2, δ), –250.4 (d, J(P,Se) = 775 Hz) ppm. **Mass spectrum** [ES$^+$, m/z]: 423 [M + Na]$^+$. Accurate mass measurement (ES$^+$MS): 423.0507, calculate mass for $C_{18}H_{18}N_2PSeNa$ [M + Na]: 423.0505.

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