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Novel organo phosphorus–selenium heteroatom compounds from selenation of diamines

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ABSTRACT

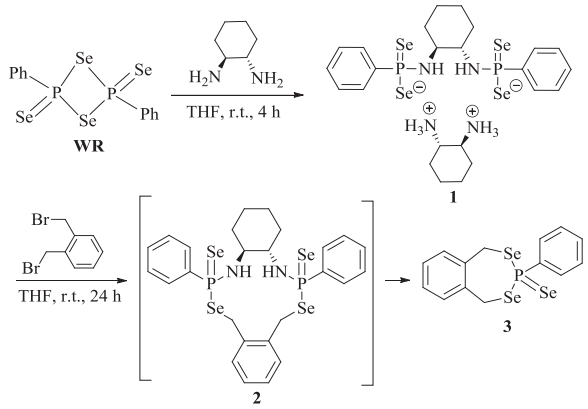
Reaction of Woollins' reagent (**WR**) with *trans*-1,2-cyclohexanediamine or 1,3-cyclohexanediamine, followed by treatment with *o*-xylylenedibromide in THF at room temperature surprisingly led to 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide (**3**). However, using *o*-phenylenediamine, the same product together with 1,4-dihydrobenzo[*d*][1,2]diselenine (**9**) was obtained. Furthermore, treating **WR** with *N*,*N*′-dibenzylethane-1,2-diamine gave rise to 1,3-dibenzyl-2-phenyl-1,3,2-diazaphospholidine 2-selenide (**10**) and a zwitterionic product *N*-benzyl-*N*-(2-(benzylammonio)ethyl)-*P*-phenyl-phosphonamidodiselenoate (**11**). Unexpectedly, **WR** reacted with 2,2′-disulfanediyldianiline under identical conditions affording the known product: 2-phenyl-2,3-dihydrobenzo[*d*][1,3,2]thiazaphosphole 2-selenide (**13**). Three representative X-ray structures are reported.

1. Introduction

Selenium compounds have applications in areas, such as organic synthesis,[1] biochemistry,[2] xerography,[3] the synthesis of conducting materials,[4] semiconductors[5] and ligand synthesis.[6] A wide range of 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 Se atom.[7] 2,4-Bis(phenyl)-1,3-diselenadiphosphethane-2,4-diselenide [{PhP(Se)(μ-Se)}$_2$] (Woollins' reagent, **WR**) has become known as an efficient selenation reagent in organic synthetic chemistry since it is not particularly malodorous or air sensitive.[8] Reactions of **WR** with organic substrates range from simple oxygen–selenium exchange to the formation of complex phosphorus–selenium heterocycles as well as surprising phosphorus–selenium-free products.[9–21] Recently, we reported the synthesis of a series of ammonium phenylphosphonamidodiselenoates and phenyl-phosphonamidodiselenoic diamides from the selenation of primary/secondary amines.[22] As part of our study into the reactivity of **WR** towards different organic nucleophiles, we herein report the synthesis of a series of novel diammonium phenyl-phosphonamidodiselenoates and their derivatives including three representative X-ray structures.

2. Results and discussion

Reaction of **WR** with 2 equiv of *trans*-1,2-cyclohexanediamine in THF at room temperature proceeded readily leading to the formation of (1*S*,2*S*)-cyclohexane-1,2-diaminium *N*,*N*′-(1*S*,2*S*)-cyclohexane-1,2-diylbis(*P*-phenylphosphonamido-diselenoate) **1** in 62% yield (Scheme 1). As expected, its ^{31}P NMR spectrum consists of a singlet (δ_P=124.6 ppm) accompanied by ^{77}Se satellites (J(P,Se)=799 Hz), considerably higher in magnitude than that in sodium



Scheme 1. Synthesis of (1*S*,2*S*)-cyclohexane-1,2-diaminium *N*,*N*′-(1*S*,2*S*)-cyclohexane-1,2-diylbis(*P*-phenylphosphonamidodiselenoate) (**1**) and its derivative (**3**).

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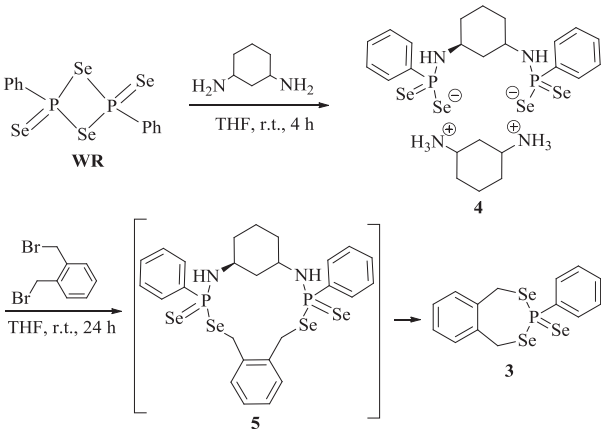
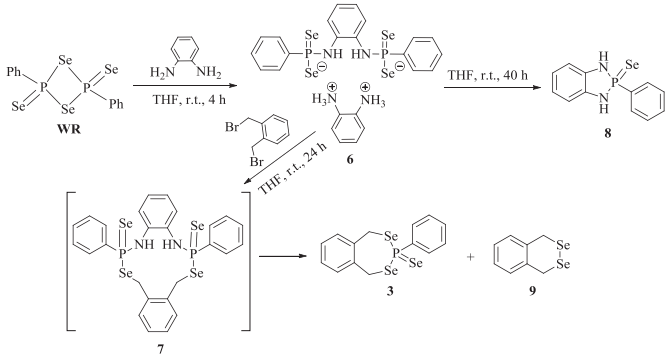
phosphonodiselenoate salts (667–675 Hz),[23] indicating a P–Se bond order of approximately 1.5. This was further substantiated by the ^{77}Se NMR spectrum, which exhibits a doublet δ_{Se}=−178.2 ppm with matching ^{31}P–^{77}Se coupling.

Reaction of **1** with an equimolar amount of *o*-xylylenedibromide in THF at room temperature for 24 h surprisingly gave 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide **3** (Scheme 1) rather than 12-membered N–P–Se heterocycle **2**. We surmised that the intermediate **2** was first formed, then, decomposed to the seven-membered ring compound **3**. To test this presumption, **WR** reacted with 2 equiv of 1,3-cyclohexanediamine (cis and trans isomers mixture) to afford cyclohexane-1,3-diaminium *N*,*N*′-cyclohexane-1,3-diylbis(*P*-phenylphosphonamido-diselenoate) **4** [three isomers: δ_P=74.9 (s, *J*(P,Se)=786 Hz), 42.2 (s, *J*(P,Se)=788 Hz) and 41.0 (s, *J*(P,Se)=788 Hz) ppm], the latter was followed by in situ treatment with an equimolar amount of *o*-xylylenedibromide (Scheme 2). Once again, 3-phenyl-1,5 dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide **3** was separated as a unique product rather than the 13-membered N–P–Se intermediate **5**. The seven-membered heterocycle **3** might be more stable and its formation preferable over the 13-membered heterocycle **5** in the reaction.



Scheme 2. Synthesis of heterocycle (**3**).

However, in the case of using phenylenediamine in place of cyclohexanediamine gave little bit different story. The reaction of **WR** with an equimolar amount of *o*-phenylenediamine generating an intermediate **6** [δ_P=40.5 (s, *J*(P,Se)=770 Hz) ppm], followed by treatment with 1 equiv of *o*-xylylenedibromide under identical conditions produced two species: 1,4-dihydrobenzo[*d*][1,2]diselenine **9** and **3** after purification by silica gel column (Scheme 3). We speculate the presence of unstable **7** as an intermediate, which eventually degrades to compounds **3** and **9** in this reaction. Furthermore, the reaction of **WR** with 2 equiv of benzene-1,2-diamine

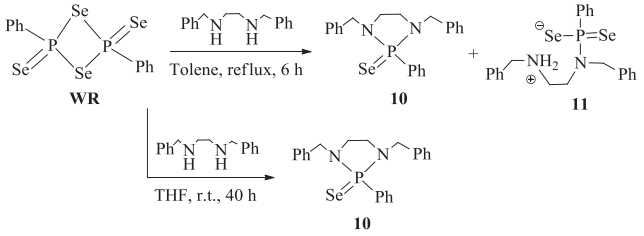


Scheme 3. Synthesis of heterocycles **3**, **8** and **9**.

in THF at room temperature for 43 h led to the formation of 2-phenyl-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-selenide **8**, which was one uniquely isolable product in 16% yield after work-up purification.

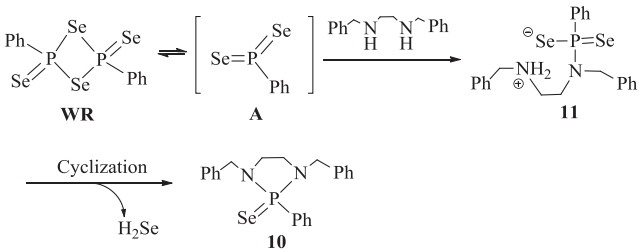
The synthesis and X-ray structure of compound **8** has been reported previously.[24] Heterocycles **3** and **9** are quite stable as solids and in solution in air and moist atmospheres, and are soluble in normal organic solvents. Both compounds were fully characterized by ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR, IR spectroscopy, mass spectrometry. Both compounds showed the anticipated molecular ion peaks $[M]^+$ or $[M+H]^+$ and satisfactory accurate mass measurement in their EI or CI mass spectra. The ^{31}P NMR spectrum of compound **3** shows a sharp singlet at 14.1 ppm, flanked by two sets of selenium satellites (770 and 360 Hz), being a very similar pattern to the analogous structure we previously reported,[12] indicating the presence of a typical P–Se single bond and a P=Se double bond in this compound. This is further supported by the ^{77}Se NMR spectrum of **3**, which consists of two doublets at 302.2 and −393.2 ppm. In compound **9**, the ^{77}Se NMR displayed one single peak at 306.2 ppm.

In contrast to the above results, **WR** reacts with *N*,*N*′-dibenylethane-1,2-diamine to give a different pattern of final products. Refluxing a toluene solution of **WR** with an equivalent of *N*,*N*′-dibenzylethane-1,2-diamine for 6 h gave the five-membered P–Se ring compound **10** in 23% yield and a zwitterionic product *N*-benzyl-*N*-(2-(benzylammonio)ethyl)-*P*-phenylphosphonamido-diselenoate **11** in 63% yield. However, carrying out the same reaction in THF at room temperature for 40 h gave only **10** in 80.5% isolated yield (Scheme 4).



Scheme 4. Synthesis of P–Se heteroatom compounds **10** and **11**.

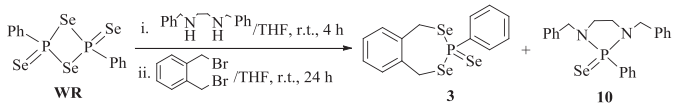
We propose a possible pathway for the formation of compounds **10** and **11** in Scheme 5. **WR** in toluene solution at elevated temperature or in THF solution at room temperature is in equilibrium with a diselenaphosphorane $PhP(Se)_2$ (**A**), which is believed to be a true reactive species.[25] The initial step for the formation of compounds **10** and **11** involves one of the NH groups of the diamine molecule reacting with a P=Se bond from diselenaphosphorane $PhP(Se)_2$ to give zwitterionic *N*-benzyl-*N*-(2-(benzylammonio) ethyl)-*P*-phenylphosphonamidodiselenoate, the latter can readily cyclize to give five-membered P–Se ring **10** by eliminating a molecule of H_2Se. When the reaction was performed in toluene solution at elevated temperature, both compounds **10** and **11** co-exist with compound **10** being dominant. In the case of THF used as a medium at room temperature, the reaction seemed to be performed completely from the conversion of zwitterionic *N*-benzyl-



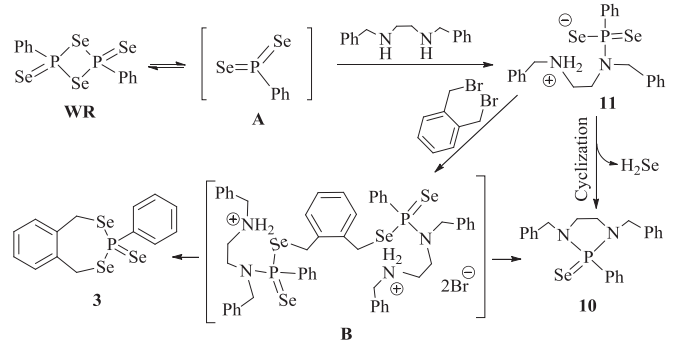
Scheme 5. A possible mechanism for the formation of compounds **10** and **11**.

N-(2-(benzylammonio)ethyl)-*P*-phenylphosphonamidodiselenoate (**11**) to five-membered ring **10**. It should be noted that in the case of THF as a donor solvent the low total outcome might contribute from the slow reaction of THF with **WR**.

We also carried out the reaction of **WR** with *N*,*N*′-dibenzylethane-1,2-diamine in THF at room temperature, followed by reaction with an equimolar amount of *o*-xylylenedibromide as shown in Scheme 6. Interestingly, once again, seven-membered ring **3** was obtained together with the five-membered ring **10**. It is presumed that the similar mechanism as the above is applied as shown in Scheme 7. It appears that the zwitterionic *N*-benzyl-*N*-(2-(benzylammonio)ethyl)-*P*-phenylphosphonamidodiselenoate **11** behaves as an intermediate in the reaction, which can either cyclize to give compound **10** by loss of a molecule of H_2Se or further reacts with *o*-xylylenedibromide to give another intermediate **B**, the latter was not stable and eventually decomposed to deliver one molecule of seven-membered ring **3** and another molecule of five-membered heterocycle **10** by loss of one molecule of *N*,*N*′-dibenzylethylenediamine dihydrobromide. To prove our presumption, we have carried out the reaction of compound **11** with an equivalent of *o*-xylylenedibromide at refluxing toluene for 3 h. Not surprisingly, both compounds **3** and **10** were isolated by silica gel chromatography column in respective 36.0% and 59.2% yields.



Scheme 6. Synthesis of P–Se heterocyclic compounds **3** and **10**.

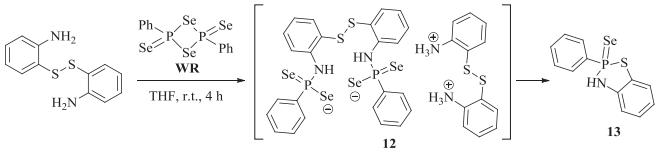


Scheme 7. Possible formation paths for the preparation of P–Se heterocyclic compounds **3** and **10**.

The release of H_2Se in the above reactions was observed in the bubbler (the formation of dark Se due to the decomposition of the H_2Se), which connects the N_2 line and the top of the condenser and could be trapped by sodium hydroxide as sodium selenate after the bubbler.

Compounds **10** and **11** are air and moisture stable and soluble in polar organic solvents. The identification of **10** and **11** is based on their ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR, IR spectroscopy, accurate mass spectrometry. Both compounds showed the anticipated molecular ion peaks $[M+H]^+$, and satisfactory accurate mass measurements. The ^{31}P NMR spectrum of compound **10** shows one singlet at 84.2 ppm, accompanied by selenium satellites (J(P,Se)=795 Hz), indicating the presence of a P=Se double bond. This was further confirmed by the ^{77}Se NMR spectrum of **9** displaying a doublet at −251.1 ppm with a marching coupling constant. The ^{31}P NMR spectrum of compound **11** also exhibits one singlet at 63.6 ppm (J(P,Se)=624 Hz), indicating a P–Se bond order of approximately 1.5. The value supports the presence of the zwitterionic structures in this compound. The ^{77}Se NMR spectrum of **11** reveals a doublet at 79.5 ppm supporting the presence of the zwitterionic conformation.

Finally, one more analogous reaction was carried out. **WR** reacted with an equimolar amount of 2,2′-disulfanediyldianiline under identical conditions leading to the formation of the unique product: 2-phenyl-2,3-dihydrobenzo[*d*][1,3,2]thiazaphosphole 2-selenide **13** in almost quantitative yield (Scheme 8). Once again we speculate the presence of intermediate **12**, which decomposed readily to the final stable 2-phenyl-2,3-dihydrobenzo[*d*][1,3,2] thiazaphosphole 2-selenide **13** via cleavage of the sulfur–sulfur single bond, followed by loss of a molecule of selenium and finally cyclization to form a stable five-membered heterocycle. The same product was obtained from the reaction of **WR** with 2-aminobenzenethiol and its characterization has been reported previouly.[12] Thus, the compound will not be discussed here in detail.



Scheme 8. Synthesis of P–Se heterocycle **13**.

Perspective views of the X-ray structures of **3**, **10** and **11** with selected parameters are shown in Figs. 1–3. Crystal data and details of the structure determination are given in Table 1. In **3**, the newly formed seven-membered ring is folded and has a chair-like conformation; the phenyl ring at the phosphorus atom prefers an axial position; the P=Se bond lengths [2.1030(19) Å] and the P–Se single bond distances [2.2386(20) and 2.2559(19) Å] are in reasonable agreement with each other and are consistent with related P/Se heterocyclic compounds containing the P(Se)(μ-Se) units.[12,13,23–29] The internal Se(2)–P(1)–Se(3) angle (109.15(8)°) in **3** is almost ideally tetrahedral.

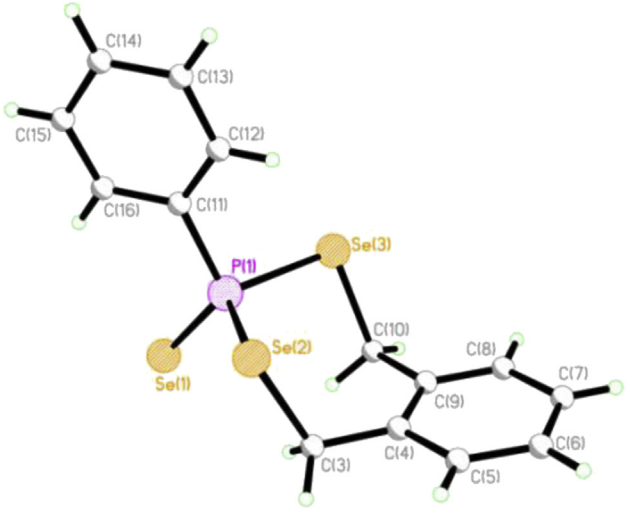


Fig. 1. X-ray structure of compound **3**. Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.1030(19), Se(2)–P(1) 2.2386(20), Se(3)–P(1) 2.2559(19), Se(2)–C(3) 1.987(7), Se(3)–C(10) 1.986(7), P(1)–C(11) 1.814(7), C(4)–C(9) 1.401(9); Se(1)–P(1)–Se(2), 114.21(8), Se(1)–P(1)–Se(3) 112.79(8), Se(2)–P(1)–Se(3) 109.15(8), P(1)–Se(2)–C(3) 96.0(2), P(1)–Se(3)–C(10) 94.2(2), Se(1)–P(1)–C(11) 116.3(2), Se(2)–P(1)–C(11) 100.6(2), Se(3)–P(1)–C(11) 102.5(2), Se(2)–C(3)–C(4) 112.6(5).

The structure of **10**, in contrast to the reported similar structures, which are essentially planar,[12] has a five-membered P–N–C–C–N ring, which is significantly distorted from planar. The P=Se distance (2.0895(16) Å) is normal,[24–27] while the P–N

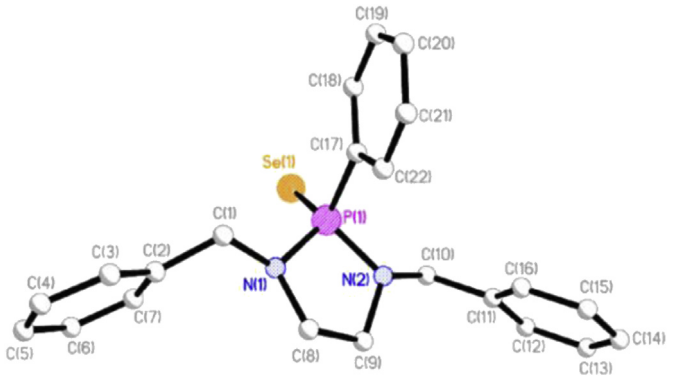


Fig. 2. X-ray structure of compound **10** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.0895(16), P(1)–N(1) 1.682(5), P(1)–N(2) 1.658(5), P(1)–C(17) 1.820(6), N(1)–C(1) 1.470(7), N(1)–C(8) 1.462(7), N(2)–C(9) 1.463(7), N(2)–C(10) 1.475(7); Se(1)–P(1)–N(1) 116.11(18), Se(1)–P(1)–N(2) 117.90(18), Se(1)–P(1)–C(17) 112.62(18), N(1)–P(1)–N(2) 93.9(2), N(1)–P(1)–C(17) 107.4(2), N(2)–P(1)–C(17) 107.1(3), P(1)–N(1)–C(1) 119.2(4), P(1)–N(1)–C(8) 111.7(3), C(1)–N(1)–C(8) 118.0(5), P(1)–N(2)–C(9) 113.1(4), P(1)–N(2)–C(10) 121.3(4), C(9)–N(2)–C(10) 115.9(4).

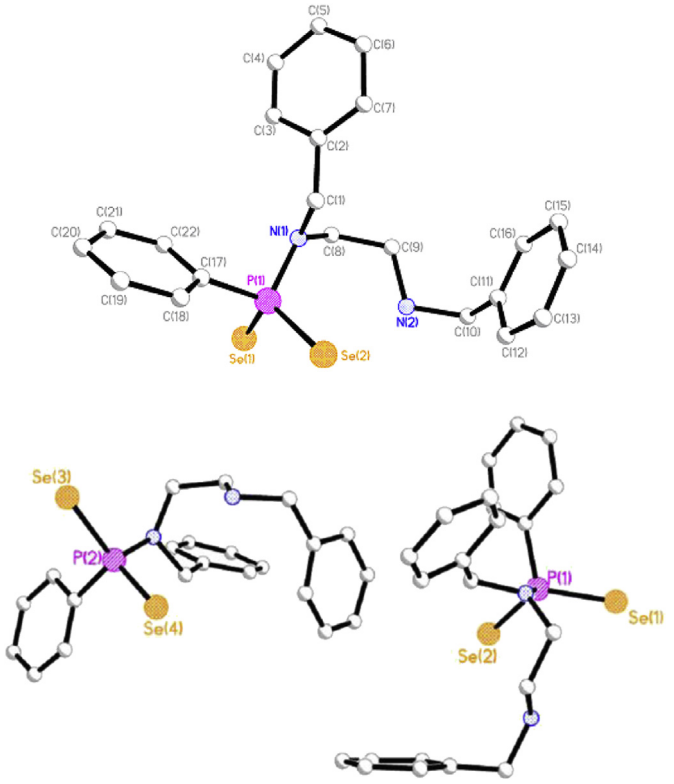


Fig. 3. X-ray structure of the anion in **11** (up picture: one representative molecule; below picture: two independent molecules per unit cell) (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses) (dimension for second independent molecule in square parentheses): Se(1)–P(1) 2.151(4) [2.151(3)], Se(2)–P(1) 2.152(3) [2.156(3)], P(1)–N(1) 1.696(11) [1.670(11)], P(1)–C(17) 1.811(13) [1.845(13)]; Se(1)–P(1)–Se(2) 115.74(15) [116.47(15)], Se(1)–P(1)–C(17) 107.9(5) [108.6(4)], Se(2)–P(1)–C(17) 110.5(4) [110.3(4)], P(1)–N(1)–C(1) 113.7(8) [113.9(8)], Se(1)–P(1)–N(1) 108.5(4) [109.4(4)], Se(2)–P(1)–N(1) 111.7(4) [109.6(4)], N(1)–P(1)–C(17) 101.6(6) [101.5(6)].

bond lengths (1.682(5) and 1.658(5) Å) are significant shorter than the typical P–N single bond length (1.77 Å) but much longer than the normal P=N double bond (1.57 Å)[30] indicating some multiple bond character present in this structure. The internal N–P–N angle N(1)–P(1)–N(2) 93.9(2) of the five-membered P–N–C–C–N ring is slightly bigger than the smallest angle [91.34(14)° and 92.3(2)°] at the phosphorus atom, while the exocyclic Se=P–X (X=C_{alkyl} or N) [112.62(18)–117.90(18)°] angles are amongst the widest angles for the P–N–C–C–N five-membered rings known.[31]

Table 1
Details of the X-ray data collections and refinements for compounds **3**, **10** and **11**

Compound	**3**	**10**	**11**
Formula	$C_{14}H_{13}PSe_3$	$C_{22}H_{23}N_2PSe$	$C_{22}H_{25}N_2PSe_2$
M	449.11	425.37	506.35
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$
a/Å	8.484(3)	15.288(4)	10.900(5)
b/Å	8.297(3)	11.936(3)	28.459(13)
c/Å	20.790(6)	21.964(5)	14.383(6)
α	90	90	90
β	90.104(8)	97.694(6)	92.161(15)
γ	90	90	90
U/A^3	1463.4(8)	3971.9(17)	4458(3)
Z	4	8	8
g/cm^{-3}	2.038	1.423	1.509
Reflections collected	10,949	15,788	29,799
Independent reflections	2643	4012	8089
R_{int}	0.0467	0.0806	0.1682
*R*1	0.0450	0.0797	0.1373
*wR*2 [$I>2\sigma(I)$]	0.2054	0.3215	0.4171

The structure of compound **11** contains two independent molecules within the unit cell. The P–N bond distances [1.696(11), 1.670(11) Å] are normal, and comparable with those observed in aminophosphazenes $N_4P_4(NMe_2)_8$ [1.69(1) Å][32] or $N_4P_4(NC_4H_8)_8$ [1.677(7) Å].[33] The P–Se bond distances [2.151(4) [2.151(3) Å], and 2.152(3) [2.156(3) Å] are considerably longer than those found in amine salts of bisdiselenophosphonic acid [2.1280(11)–2.1350(12) Å],[34] however, they are still intermediate between single bond [ca. 2.38 Å] and double bond [ca. 2.08 Å],[35] indicating delocalization of the negative charge over the PSe_2 fragment.

In conclusion, the reaction of **WR** with diamines (*trans*-1,2-cyclohexanediamine, 1,3-cyclohexanediamine, *o*-phenylenediamine, *N*,*N*′-dibenzylethane-1,2-diamine and 2,2′-disulfanediyldianiline) was investigated. The results showed that **WR** reacting with *trans*-1,2-cyclohexanediamine, 1,3-cyclohexanediamine and *o*-phenylenediamine, followed by further treatment with *o*-xylylenedibromide with formation of the same product: 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide. In the case of *o*-phenylenediamine, another product 1,4-dihydrobenzo[*d*][1,2,3,6]diselenadiazine was also obtained along with 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide. The reaction of **WR** with *N*,*N*′-dibenylethane-1,2-diamine gave a different pattern of final products: 1,3-dibenzyl-2-phenyl-1,3,2-diazaphospholidine 2-selenide and zwitterionic *N*-benzyl-*N*-(2-(benzylammonio)ethyl)-*P*-phenylphosphonamidodiselenoate; the reaction mixture was further treated with *o*-xylylenedibromide leading once again to the appearance of 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide. Furthermore, cleavage of the S–S single bond in 2,2′-disulfanediyldianiline by **WR** resulted in the formation of a known 2-phenyl-2,3-dihydrobenzo[*d*][1,3,2]thiazaphosphole 2-selenide.

3. Experimental section

3.1. General

Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work-up procedures were performed in air. ^{1}H (270 MHz), ^{13}C (67.9 MHz), ^{31}P–{^{1}H} (109 MHz) and ^{77}Se–{^{1}H} (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} on

a Perkin–Elmer 2000 FTIR/Raman spectrometer. 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 **3**, **10** and **11** were collected using the St Andrews Robotic diffractometer (Saturn724 CCD) at 125 K with graphite monochromated Mo Kα radiation (λ=0.71073 Å).[36,37] Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization 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.[38] Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. CCDC 916232 **3**, 916234 **10**, 916233 **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.

3.2. Synthesis

*3.2.1. Synthesis of trans-1,2-cyclohexanediamine N,N′-(1S,2S)-cyclohexane-1,2-diylbis(P-phenylphosphonamidodiselenoate) (**1**).* A mixture of *trans*-1,2-cyclohexanediamine (0.228 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature for 4 h. The red suspension disappeared and a bright yellow suspension formed. Upon filtration to remove unreacted solid the filtrate was dried in vacuo to give a golden solid (0.705 g, 93% yield), mp 160–162 °C. Selected IR (KBr, cm^{-1}): 2930(w), 2858(w), 1434(s), 1260(m), 1184(s), 1091(s), 1062(s), 888(m), 747(m), 692(s), 545(vs, P–Se). ^{1}H NMR (THF-d_8, δ), 8.31–7.97 (m, 4H, ArH), 7.38–7.25 (m, 6H, ArH), 6.21 (m, 6H, NH_3), 4.32 (d, J(P,H)=13.5 Hz, 2H, NH), 4.24–4.15 (m, 2H, CH), 3.64–3.58 (m, 2H, CH), 3.17–2.85 (m, 8H, CH_2), 1.79–1.73 (m, 8H, CH_2) ppm. ^{13}C NMR (THF-d_8, δ), 141.7 (d, J(P,C)=127.1 Hz), 130.7 (d, J(P,C)=12.5 Hz), 130.3 (d, J(P,C)=3.1 Hz), 127.3 (d, J(P,C)=13.5 Hz), 62.4 (d, J(P,C)=8.3 Hz), 54.4, 31.3 (d, J(P,C)=13.5 Hz), 30.5, 24.7, 24.1 ppm. ^{31}P NMR (THF-d_8, δ), 124.6 (s, J(P,Se)=799 Hz) ppm. ^{77}Se NMR (THF-d_8, δ), −178.2 (d, J(P,Se)=799 Hz) ppm. MS (ES^- m/z), 323 [1/2M]$^-$. Accurate mass measurement [ES^-, m/z]: 322.8965 [1/2M]$^-$, calculated mass for ½[$C_{18}H_{22}N_2P_2Se_4$]: 322.8969.

*3.2.2. Synthesis of 3-phenyl-1,5-dihydrobenzo[e][1,3,2]-diselenaphosphepine 3-selenide (**3**) from 1 and o-xylylenedibromide.* A brown suspension of (1*S*,2*S*)-cyclohexane-1,2-diamine (0.25 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature for 4 h, during which time a pale white suspension was formed. Then, *o*-xylylenedibromide (0.264 g, 1.0 mmol) was added. The mixture was stirred at room temperature for 24 h. Upon removing unreacted solid and solvent, the residue was purified by silica gel column chromatography (1:9 ethyl acetate/dichloromethane) to give 0.381 g of the title compound as a greenish yellow solid in 84% yield. Mp 196–197 °C. Selected IR (KBr, cm^{-1}): 1434(s), 1179(m), 1090(s), 745(s), 688(m), 535(vs), 488(m). ^{1}H NMR (CD_2Cl_2, δ), 8.18–7.24 (m, 9H, ArH), 4.67 (d, J(P,H)=13.5 Hz, 4H, $SeCH_2$) ppm. ^{13}C NMR (CD_2Cl_2, δ), 139.0, 133.3 (d, J(P,C)=3.1 Hz), 131.7 (d, J(P,C)=11.4 Hz), 130.4, 129.2 (d, J(P,C)=14.5 Hz), 128.4, 32.4 ppm. ^{31}P NMR (CD_2Cl_2, δ), 14.1 (s, J(P,Se)=369 Hz, J(P,Se)=770 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 302.2 (d, J(P,Se)=369 Hz), −393.2 (d, J(P,Se)=770 Hz) ppm. Accurate mass measurement [CI^+, m/z]: 452.8318 [M+H]$^+$, calculated mass for $C_{14}H_{13}PSe_3H$: 452.8329.

*3.2.3. Synthesis of 3-phenyl-1,5-dihydrobenzo[e][1,3,2]-diselenaphosphepine 3-selenide (**3**) from **WR**, m-cyclohexanediamine and o-xylylenedibromide.* A brown suspension of *m*-cyclohexanediamine (cis and trans isomer mixture, 0.23 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature for 4 h, during which time a pale white suspension was formed. Then, *o*-xylylenedibromide (0.264 g, 1.0 mmol) was added. The mixture was stirred at room temperature for 24 h. Upon removing unreacted solid and solvent, the residue was purified by silica gel column chromatography (1:9 ethyl acetate/dichloromethane) to give 0.360 g of the title compound as a greenish yellow solid in 81% isolated yield. The same product was obtained as above.

*3.2.4. Synthesis of 2-phenyl-2,3-dihydro-1H-benzo[d][1,3,2]-diazaphosphole 2-selenide (**8**).* A mixture of *o*-phenylenediamine (0.216 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in dry tetrahydrofuran (60 mL) was stirred at room temperature for 43 h. Upon removing unreacted solid and solvent, the residue was purified by silica gel column chromatography (eluent 1:9 ethyl acetate/dichloromethane) to give 0.095 g (16.2%) of 2-phenyl-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-selenide (**8**) as a pale yellow solid, mp 144–145 °C. Selected IR (KBr, cm^{-1}): 2141(s), 1489(s), 1435(m), 1381(s), 1272(s), 1248(m), 1103(s), 883(s), 743(s), 654(m), 562(s). ^{1}H NMR (CD_2Cl_2, δ), 7.91–7.85 (m, 4H, ArH), 7.44–7.34 (m, 5H, ArH), 6.71 (d, J(P,H)=19 Hz, 2H, NH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 138.2 (d, J(P,C)=110.5 Hz, Ar–C), 133.1 (d, J(P,C)=4.4 Hz, Ar–C), 132.5 (d, J(P,C)=3.4 Hz, Ar–C), 131.3 (d, J(P,C)=13.9 Hz, Ar–C), 128.2 (d, J(P,C)=14.9 Hz, Ar–C), 120.7 (Ar–C), 110.9 (Ar–C), 110.8 (Ar–C) ppm. ^{31}P NMR (CD_2Cl_2, δ), 70.7 (s, J(P,Se)=831 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −105.3 (d, J(P,Se)=830 Hz) ppm. MS (CI^+ m/z), 295 [M+H]$^+$. Accurate mass measurement [CI^+, m/z]: 288.9959 [M+H]$^+$, calculated mass for $C_{12}H_{11}N_2P^{74}SeH$: 288.9957.

*3.2.5. Synthesis of 3-phenyl-1,5-dihydrobenzo[e][1,3,2]-diselenaphosphepine 3-selenide (**3**) and 1,4-dihydrobenzo[d][1,2]diselenine (**9**) from **WR**, o-phenylenediamine and o-xylylenedibromide.* A suspension of *o*-phenylenediamine (0.216 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) and *o*-xylylenedibromide (0.264 g, 1.0 mmol) in dry tetrahydrofuran (60 mL) was stirred at room temperature for 24 h, during which time a pale white suspension was formed. Upon removing unreacted solid and solvent, the residue was purified by silica gel column chromatography to give 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide (**3**) as a pale yellow solid (eluent 1:1 hexane/dichloromethane) and 1,4-dihydrobenzo[*d*][1,2]diselenine (**9**) as a reddish yellow solid (eluent dichloromethane).

*3.2.5.1. 3-Phenyl-1,5-dihydrobenzo[e][1,3,2]diselenaphosphepine 3-selenide (**3**).* 0.100 g as a pale yellow solid in 22% isolated yield.

*3.2.5.2. 1,4-Dihydrobenzo[d][1,2]diselenine (**9**).* 0.400 g as a reddish yellow solid in 76% isolated yield, mp118–120 °C. Selected IR (KBr, cm^{-1}): 1484(m), 1159(m), 759(s), 579(m). ^{1}H NMR (CD_2Cl_2, δ), 7.39–7.30 (m, 4H, ArH), 3.94 (s, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 130.9 (Ar–C), 128.1 (Ar–C), 127.6 (Ar–C), 24.1 (CH_2) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 306.2 ppm. MS (EI^+ m/z), 266 [M]$^+$. Accurate mass measurement [EI^+, m/z]: 255.9003 [M]$^+$, calculated mass for $C_8H_8^{76}Se_2$: 255.9005.

*3.2.6. Synthesis of 1,3-dibenzyl-2-phenyl-1,3,2-diaza-phospholidine 2-selenide (**10**) from N,N′-dibenzylethylenediamine and **WR** in THF at room temperature.* A THF (50 mL) suspension of *N*,*N*′-dibenzylethylenediamine (0.46 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) was stirred at room temperature for 40 h to give a greyish yellow suspension. Upon filtering to remove unreacted solid and evaporating to remove solvent the residue was purified by silica gel column to provide 0.341 g of the title compound as an yellow solid (1:4 ethyl

acetate/dichloromethane as eluent). 80% isolated yield. Mp 100–102 °C. Selected IR (KBr, cm^{-1}): 1492(m), 1452(m), 1435(m), 1206(m), 1139(vs), 1098(s), 1064(s), 1027(m), 930(s), 737(vs), 695(s), 606(m), 511(s). ^1H NMR (CD_2Cl_2, δ), 8.02–7.94 (m, 2H, ArH), 7.53–7.43 (m, 4H, ArH), 7.30–7.19 (m, 9H, ArH), 4.08–3.88 (m, 4H, CH_2), 3.23–3.02 (m, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 137.6, 132.4, 132.2, 131.9, 128.5, 128.4, 128.3, 128.0, 127.4, 49.9 (d, J(P,C)=7.3 Hz), 46.5 (d, J(P,C)=7.3 Hz) ppm. ^{31}P NMR (CD_2Cl_2, δ), 84.2 (s, J(P,Se)=795 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −251.1 (d, J(P,Se)=795 Hz) ppm. MS (CI^+ m/z), 427 $[M+H]^+$. Accurate mass measurement [CI^+, m/z]: 427.0837 $[M+H]^+$, calculated mass for $C_{22}H_{23}PSeH$: 427.0837.

*3.2.7. Synthesis of 1,3-dibenzyl-2-phenyl-1,3,2-diaza-phospholidine 2-selenide (**10**) and N-benzyl-N-(2-(benzylammonio)ethyl)-P-phenylphosphonamidodiselenoate (**11**) from N,N′-dibenzylethane-1,2-diamine and **WR** in refluxing toluene.* A solution of *N*,*N*′-dibenzylethane-1,2-diamine (0.46 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 6 h. A slightly green suspension was formed. Upon cooling to room temperature the mixture was filtered to remove unreacted solid and evaporating to remove solvent the residue was purified by silica gel column to afford compound **9** as an orange solid and compound **10** as a greenish white solid (1:4 ethyl acetate/dichloromethane as eluent).

*3.2.7.1. 1,3-Dibenzyl-2-phenyl-1,3,2-diazaphospholidine 2-selenide (**10**).* 0.121 g, 28% isolated yield.

*3.2.7.2. N-Benzyl-N-(2-(benzylammonio)ethyl)-P-phenyl-phosphonamidodiselenoate (**11**).* 0.314 g in 63% isolated yield. Mp 160–162 °C. Selected IR (KBr, cm^{-1}): 1433(s), 1240(m), 1140(m), 1092(m), 992(m), 951(m), 745(vs), 695(vs), 588(m), 552(s), 530(s), 493(m). ^1H NMR (CD_2Cl_2, δ), 8.30–7.15 (m, 15H, ArH), 6.83 (s, 2H, NH_2), 4.43 (s, 2H, CH_2), 3.86 (d, J(P,H)=8.3 Hz, CH_2), 3.70–3.54 (m, 2H, CH_2), 3.12–3.07 (m, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 140.7 (d, J(P,C)=82.6 Hz), 136.4 (d, J(P,C)=10.2 Hz), 131.9, 131.3, 130.8, 129.9, 129.5, 129.3, 128.8, 128.5, 128.0, 127.7, 51.7, 50.4, 43.0 (d, J(P,C)=16.0 Hz), 42.0 (d, J(P,C)=4.7 Hz) ppm. ^{31}P NMR (CD_2Cl_2, δ), 63.6 (s, J(P,Se)=624 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 79.5 (d, J(P,Se)=624 Hz) ppm. MS [CI^+, m/z]: 509 $[M+H]^+$. Accurate mass measurement [CI^+, m/z]: 509.0160 $[M+H]^+$, calculated mass for $C_{22}H_{25}N_2PSe_2H$: 509.0164.

*3.2.8. Synthesis of 3-phenyl-1,5-dihydrobenzo[e][1,3,2]-diselenaphosphepine 3-selenide (**3**) and 1,3-dibenzyl-2-phenyl-1,3,2-diazaphospholidine 2-selenide (**10**) from N,N′-dibenzylethane-1,2-diamine, **WR** and 1,2-bis(bromomethyl)-benzene.* A mixture of *N*,*N*′ dibenzylethane-1,2-diamine (0.48 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in dry THF (50 mL) was stirred at room temperature for 4 h. Then *o*-xylylenedibromide (0.264 g, 1.0 mmol) was added to the mixture and the mixture was continued stirring at room temperature for another 24 h. Upon filtration to remove unreacted solid and evaporating to remove the solvent the residue was purified by silica gel column chromatography to give 3-phenyl-1,5-dihydrobenzo[*e*][1,3,2]diselenaphosphepine 3-selenide (**3**) (0.140 g, 32%) as pale yellow solid (eluent 2:1 dichloromethane/hexane) and 1,3-dibenzyl-2-phenyl-1,3,2-diazaphospholidine 2-selenide (**9**) (0.240 g, 55%) (eluent dichloromethane) as an orange solid.

*3.2.9. Synthesis of 2-phenyl-2,3-dihydrobenzo[d][1,3,2]-thiazaphosphole 2-selenide (**13**).* A brown suspension of 2,2′-disulfanediyldianiline (0.496 g, 2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in dry THF(50 mL) was stirred at room temperature for 4 h. A grey suspension was formed. Upon filtering to remove unreacted solid and evaporating to remove solvent the residue was purified by silica gel column (eluented by dichloromethane) to give 310 mg of the title compound as a milky solid in 99% isolated yield, mp 160–162 °C. Selected IR (KBr, cm^{-1}): 1578(m), 1470(s), 1454(s), 1437(m), 1368(s), 1259(m), 1096(s), 892(s), 743(vs), 687(m), 554(s), 488(s). ^1H NMR (CD_2Cl_2, δ), 8.07–7.98 (m, 2H, ArH), 7.57–7.42 (m, 3H, ArH), 7.23–7.07 (m, 2H, ArH), 6.93–6.88 (m, 2H, ArH), 5.67 (d, J(P,H)=12.9 Hz, 1H, NH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 139.9 (d, J(P,C)=72.7 Hz), 132.7 (d, J(P,C)=3.1 Hz), 131.2 (d, J(P,C)=14.5 Hz), 128.4 (d, J(P,C)=14.5 Hz), 126.7, 124.2 (d, J(P,C)=6.2 Hz), 121.8, 112.9 (d, J(P,C)=11.4 Hz) ppm. ^{31}P NMR (CD_2Cl_2, δ), 74.5 (s, J(P,Se)=840 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −32.8 (d, J(P,Se)=840 Hz) ppm. MS (CI^+, m/z), 312 $[M+H]^+$. Accurate mass measurement [CI^+, m/z]: 311.9506 $[M+H]^+$, calculated mass for $C_{12}H_{10}NPSeH$: 311.9509.

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Supplementary data

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