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New P–Se compounds from the reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide with alkyl-diols

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1,3,2-Dioxaphosphorinane-2-phenyl-2-selenide

ABSTRACT

Reaction of alkyl-diols [$HO(CH_2)_nOH$, n=2–6, 8 and 10] with 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [$(PhP(\mu\text{-}Se)Se)_2$ Woollins' reagent, WR] in dry dichloromethane gave a series of bis-diselenophosphonic acids at room temperature. Treatment of the acids with butylamine in tetrahydrofuran afforded the corresponding ammonium salts **1**–**7** in excellent yields (91–97%). Esterification of the salts with methyl iodide led to Se,Se-dimethyl esters **8**–**14** in medium to excellent yields (50–86%). Alternatively, heating the toluene solution of alkyl-diols [$HO(CH_2)_nOH$, n=2–4] and WR at reflux, afforded 1,3,2-dioxaphosphorinane-2-phenyl-2-selenides **16**, **18** and **20** in reasonable to good yield. Meanwhile, when 1,2-ethylene glycol was used, a heterocycle containing a selenium atom, 2,4-bisphenyl-2,4-diseleno-1,5-dioxa-3-seleno-2,4-diphosphetane **15** was formed. In the case of 1,3-propanediol or 1,4-butanediol, the heterocycles containing two neighbouring selenium atoms, 2,5-diphenyl-(1,6,3,4,2,5)-dioxadiselenadiphosphocane-2,5-disulfides **17** and **19** were obtained together with **18** and **20**. Perhaps due to a steric effect, pinacol and WR in toluene at reflux gave 1,3,2-dioxaphosphorinane-2-selenide **21** as the only product. One representative X-ray crystal structure of an ammonium salt is described.

1. Introduction

Lawesson's reagent has been widely used for the transformation of carbonyl functional groups into thiocarbonyls as well as for the synthesis of sulfur-containing heterocyclic compounds since the beginning of the last quarter of the 20th century.[1,2] Its selenium counterpart, 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$, Woollins' reagent (WR) is receiving increasing attention due to its efficiency in selenation. For example, WR has been used to prepare a wide range of selenium-containing compounds, such as large P/Se molecular aggregates or metal complexes by nucleophilic ring-opening reactions with alkali-metal thiolates,[3] selenoamides and selenoaldehydes by simple oxygen/selenium exchange or reaction with ArCN followed by hydrolysis as well as a variety of P–Se heterocycles by simple one-step selenation.[4] Recently, we have reported the use of WR for the syntheses of symmetrical and unsymmetrical (*E*)-olefins from ketones or aldehydes and to deoxygenate sulfoxides to give sulfides under relatively mild conditions.[5,6]

Interaction of Lawesson's reagent with aliphatic diols gives bisdithiophosphonic acids, which can be converted into the corresponding ammonium salts or used as tetradentate bisdithiophosphonate ligands with a wide range of metal ions.[7] Lawesson's reagent also reacts with dihydric alcohols at higher temperature leading to the formation of cyclic trithiopyrophosphonate and 1,3-dioxaphosphorinane.[8] However, similar reactions have not been tried yet for WR and complexation of phosphinodiselenoate and phosphorodiselenoate ligands has only been reported sparsely since 1964[9] whilst studies on the metal complexes of selenium compounds have been concentrated on the field of metal cluster chemistry.[10,11] Here, we report a series of new species bearing the P(Se)–Se or P=Se motif obtained by reaction of WR with alkyl-diols at both room temperature and in refluxing toluene. The new ammonium salts and methyl esters of the bisdiselenophosphonic acids, and the cyclic selenium-containing compounds gained at higher temperature provides a valuable addition to the phosphodiselenoate family.

2. Results and discussion

WR was prepared as described previously in high yield (>80%)[4d] and further purified by Soxhlet extraction. Cleavage of the four-membered P_2Se_2 ring in WR by 1 equiv of diol in dichloromethane at room temperature afforded the bisdiselenophosphonic acids [quantitatively as yellow oils], which were converted into the

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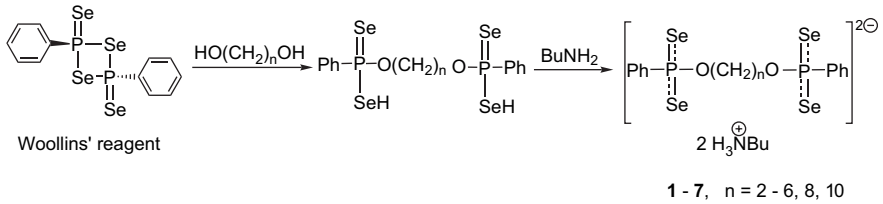


Scheme 1. Synthesis of amine salts of bisdiselenophosphonic acid **1**–**7**.

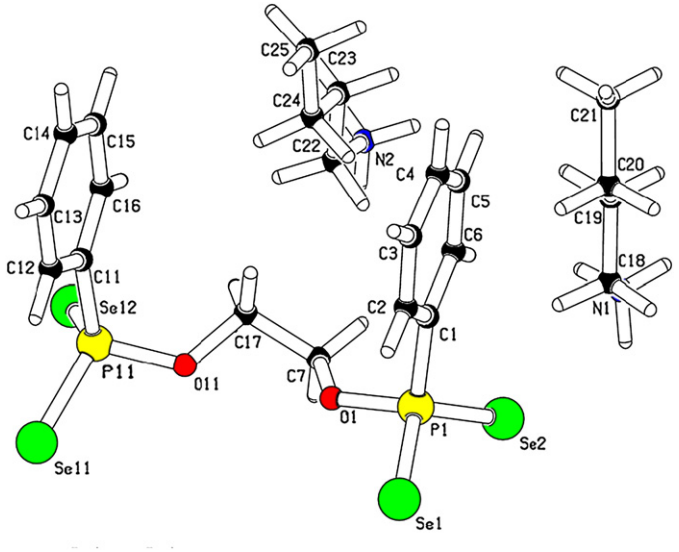
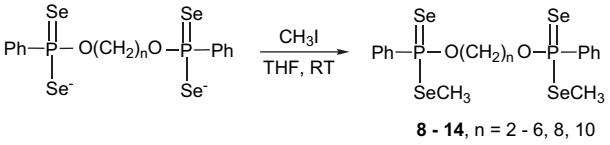


Figure 1. X-ray crystal structure of **1**, selected bond lengths (Å) and angles (°): Se(1)–P(1) 2.1366(12), Se(11)–P(11) 2.1280(11), P(1)–O(1) 1.630(3), P(11)–O(11) 1.619(2), P(1)–C(1) 1.817(4), P(11)–C(11) 1.827(4), O(1)–C(7) 1.454(5), O(11)–C(17) 2.439(4), Se(2)–P(1) 2.1350(12), Se(12)–P(11) 2.1490(13), Se(1)–P(1)–Se(2) 118.65(5), Se(11)–P(11)–Se(12) 117.22(5), Se(2)–P(1)–O(1) 110.97(12), Se(12)–P(11)–O(11) 111.21(12), Se(1)–P(1)–O(1) 102.65(11), Se(11)–P(11)–O(11) 103.08(10), P(1)–O(1)–C(7) 123.3(2), P(11)–O(11)–C(17) 122.9(2).



Scheme 2. Synthesis of Se,Se-dialkyl esters **8**–**14**.

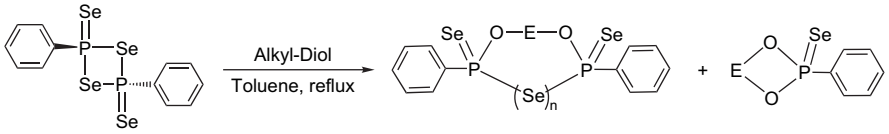
corresponding amine salts (**1**–**7**) by further treatment with butylamine at room temperature (Scheme 1).

Salts **1**–**7** were obtained in high yields as white solid or colourless pastes, which were moderately stable in air, degrading over a period of several weeks with the obvious signs of red elemental selenium accompanying the evolution of a foul-smelling gas. All salts are soluble in chloroform, dichloromethane, and tetrahydrofuran and insoluble in diethyl ether and hexane. The ^{31}P–$\{^{1}H\}$ NMR spectra of **1**–**7** display sharp singlets in the range of δ(P) 78.65–84.85 ppm, with the ^{31}P resonance moving slightly upfield as the $(CH_2)_n$ chain length increases. Each singlet is accompanied by selenium satellites [range 657–678 Hz] indicating, as expected, a P–Se bond order of approximately 1.5; **1** has the highest *J* value (average 18 Hz difference) possibly due to the close distance between two phosphorus atoms within **1**. The ^{77}Se–$\{^{1}H\}$ NMR spectra display doublets [δ(Se) 73.23, 91.34, 84.06, 87.81, 88.27, 84.75 and 87.81 ppm, respectively]. The ^{1}H and ^{13}C NMR spectra of **1**–**7** were as expected confirming the presence of the phenyl, $O(CH_2)_nO$ and H_3NBu moieties. Microanalysis results and mass spectra are in good agreement with theoretical values whilst IR spectra show bands at 560–543 and 522–501 cm^{-1} corresponding to $\nu(PSe)_{asym}$ and $\nu(PSe)_{sym}$ absorptions, respectively.

All attempts to crystallise salts proved unsuccessful apart from salt **1**. Single crystals of **1** were obtained by diffusion of the dichloromethane solution into hexane. The building block for **1** is displayed in Figure 1.[12] This compound exhibits a very interesting structural motif. It consists of a $[PhP(Se)(Se)OCH_2CH_2O(Se)(Se)PPh]^{2-}$ anion and two $[BuNH_3]^{+}$ cations, forming a wing-like structure with the two bulky phenyl groups oriented on the same side of the anion which has an approximate mirror plane bisecting the P–O–C–C–O–P axis. The P–Se bond lengths [2.1366(12), 2.1350(12), 2.1280(11) and 2.1490(13) Å] in line with other symmetrical phosphenium salts (typical bond length of 2.13 Å)[13] are intermediate between single [ca. 2.38 Å] and double [P=Se double bond ca. 2.08 Å].[14]

Replacement of the two H_3NBu cations in the amine salts of bisdiselenophosphonic acid **1**–**7** by 2 equiv of iodomethane generated bis(phenyl-diselenophosphonic acid Se,Se-dimethyl esters) **8**–**14** as yellow oils in high yields (Scheme 2), which are soluble in normal solvents such as chloroform, dichloromethane and acetone but are insoluble in strong polar solvents such as alcohols or amines. Esters **8**–**14** are stable to air and moisture for months at room temperature. As expected, the diesters **8**–**12** are mixtures of diastereoisomers. However, for **13** and **14,** only one major compound was obtained. These results were confirmed by analysis of ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra. Diester **8** consists of diastereomer pairs in approximately equal amounts, while **9**–**12** are a mixture of three diastereomers of random populations. All attempts to further purify these mixtures were unsuccessful. Despite the presence of two stereogenic centres in **13** and **14**, no separate signals assignable to either diastereoisomeric forms were observed in their ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra.

Interestingly, heating a toluene solution of WR with ethylene glycol at reflux led to new ring systems, a seven-membered ring triselenapyrophosphonate **15** and a five-membered ring 1,3-dioxaphosphorinane-2-selenide **16** (Scheme 3). Different ratios of



15, E = $(CH_2)_2$, n = 1
17, E = $(CH_2)_3$, n = 2
19, E = $(CH_2)_4$, n = 2

16, E = $(CH_2)_2$
18, E = $(CH_2)_3$
20, E = $(CH_2)_4$
21, E = $C(CH_3)_2C(CH_3)_2$

Scheme 3. Synthesis of P–Se heterocycles **15**–**21**.

Table 1
Proportion of **15** and **16** when various ratios of starting materials were applied

Entry	WR (mmol)	Ethylene glycol (mmol)	Yield of **15** (%)	Yield of **16** (%)
1	1.0	0.5	31	69
2	1.0	1.0	72	28
3	1.0	1.5	74	26
4	1.0	5.0	73	27

starting materials resulted in the same products **15** and **16** but with different proportions (Table 1). It is noted that using a large excess of ethylene glycol (entry 4) did not change the proportion of products **15** and **16**.

However, under the same reaction conditions, 1,3-propanediol or 1,4-butanediol reacts with WR to give cyclic tetraselenapyrophosphonates **17**, **19** containing diselenides [–Se–Se–] as part of ring, and 1,3-dioxaphosphorinane-2-selenides **18**, **20**, respectively. Surprisingly, only 1,3,2-dioxaphosphorinane-2-phenyl-2-selenide **21** was obtained as pale yellow solid by the reaction of pinacol with WR in toluene in 69% yield (Scheme 3).

Compound **15** was isolated as yellow oil. The $^{31}P–\{^1H\}$ NMR spectrum obtained in dichloromethane consists of a singlet at δ_P 75.02 ppm with two sets of ^{77}Se satellites (vide infra), arising from two distinct isotopomers with one ^{77}Se atom in the *exo*- or *endo*-position of the ring. For these two sets of systems A_2X (Se_{endo}) and AA′X (Se_{exo}) (A, A′=^{31}P, X=^{77}Se), iterative simulation allowed for complete analysis of chemical shifts and coupling constants, e.g., ^2J(P,P) (14.1 Hz). The magnitudes of J(P,Se) are as expected. The $^{77}Se–\{^1H\}$ spectrum of **15** showed two signals: a triplet at δ_{Se}=696.24 ppm with $^1J(P,Se_{endo})$=396 Hz, a doublet of doublets at δ_{Se}=5.37 ppm with $^1J(P,Se_{exo})$=851 Hz and $^3J(P,Se_{exo})$=9.8 Hz. The MS, ^1H and ^{13}C NMR spectra also confirmed the identity of **15**. In the ^{13}C NMR spectrum the endocyclic carbon gave a doublet at δ_C 135.4 ppm with ^1J(P,C)=104 Hz, ^3J(P,C)=12.5 Hz.

We have recently published the first synthesis and characterisation of the compounds **17** and **19**, as 9- and 10-membered heterocycles containing the O–P–Se–Se–P–O linkage,[15] therefore the two compounds will not be discussed here in detail. Compounds **16, 18, 20** and **21**, which are homologues of **17** and **19** were isolated as white pastes. All are soluble in polar solvents such as alcohols and acetone but are insoluble in less polar solvents. They are quite stable to air and moisture. The $^{31}P–\{^1H\}$ NMR spectra of **16, 18, 20** and **21** display sharp singlets [δ_P 111.60, 93.27, 93.09, 99.19 ppm, $J(^{31}P–^{77}Se)$ 876–911 Hz] indicating the presence of a P=Se double bond in each molecule as anticipated. The results were further substantiated by the $^{77}Se–\{^1H\}$ NMR spectra, which showed doublets [δ_{Se} −203.95, −247.17, −212.44 and −84.14 ppm] with matching $^{31}P–\{^1H\}–^{77}Se–\{^1H\}$ coupling constants. The ^1H and ^{13}C NMR spectra of **16**, **18**, **20** and **21** confirm the presence of the phenyl and $O(CH_2)_nO$ (n=2, 3 and 4) or $OC(CH_3)_2C(CH_3)_2O$ moieties and mass spectrometry showed the parent ions (ESI^+ or CI^+ mode) as $[M+Na]^+$ or $[M+H]^+$.

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. Solvents were dried, purified, and stored according to common procedures. ^1H (270 Hz), ^{13}C (67.9 Hz), $^{31}P–\{^1H\}$ (109 Hz) and $^{77}Se–\{^1H\}$ (51.4 Hz 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. Microanalysis was performed by the University of St Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea (UK) and the University of St Andrews Mass Spectrometry Service. We compared observed isotopomer distributions with calculated patterns to confirm assignments. X-ray crystal data for compound **1** was collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Intensities were corrected for Lorentz-polarisation and for absorption. The structure was solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinement was obtained with full-matrix least-squares based on F^2 using SHELXTL. CCDC 681330 contains 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. General procedure for synthesis of dibutylammonium bisdiselenophosphonates

A mixture of diol (1.0 mmol) and WR (0.54 g, 1.0 mmol) in dry dichloromethane (20 ml) was stirred at room temperature for 20 h. The red suspension disappeared and a greenish yellow solution was formed along with a trace precipitate of grey elemental selenium. The resulting mixture was filtered. The filtrate was concentrated in vacuo leading to a green paste. The residue was dissolved in tetrahydrofuran (50 ml) (yellow solution) and butylamine (0.5 ml) was added dropwise. This resulted in the formation of a brown suspension and then a grey or pale grey suspension after 4 h stirring at room temperature. Compounds **1–7** were filtered off and washed with dichloromethane and diethyl ether.

*3.2.1. Dibutylammonium 1,2-dioxoethane-1,2-bis(phenyldiselenophosphonate) (**1**)*

White solid (701 mg) in 95% yield. Mp 96 °C. Found (calcd for $C_{22}H_{38}N_2O_2P_2Se_4$): C 35.35 (35.69), H 5.01 (5.17), N 3.50 (3.78). Selected IR (KBr, cm^{-1}): 2958 (s), 1467 (w), 1434 (m), 1048 (s), 973 (m), 934 (s), 745 (m), 692 (m), 560 (s), 522 (m). ^1H NMR ($CDCl_3$, δ), 8.05 (m, 6H, NH_3^+), 8.02 (dd, ^3J(P,H)=13 Hz, ^3J(P,H)=8 Hz, 4H, ArH), 7.82 (m, ^3J(P,H)=13 Hz, 2H, ArH), 7.36 (d, 2H, ArH), 6.81 (d, 2H, ArH), 3.82 (dd, ^3J(P,H)=26 Hz, ^3J(H,H)=6 Hz, 4H, OCH_2), 2.96 (t, ^3J(H,H)=7 Hz, 4H, NCH_2), 1.64 (m, ^3J(H,H)=7 Hz, 4H, CH_2), 1.29 (m, ^3J(H,H)=6 Hz, 4H, CH_2), 0.84 (t, ^3J(H,H)=7 Hz, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 140.8 (d, ^1J(P,C)=76 Hz), 130.9 (d, ^4J(P,C)=3.1 Hz), 130.2 (d, ^2J(P,C)=14.5 Hz), 127.9 (d, ^3J(P,C)=12.5 Hz), 63.0, 40.1, 30.5, 20.0, 13.7 ppm. $^{31}P–\{^1H\}$ NMR ($CDCl_3$, δ), 84.85 (s, ^1J(P,Se)=678 Hz) ppm. $^{77}Se–\{^1H\}$ NMR ($CDCl_3$, δ), 73.23 (d, ^1J(P,Se)=678 Hz) ppm. MS (ES^-, m/z): 588 $[M-C_4H_{12}NSe]^+$, 329 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, m/z): 742 $[M]^+$, 663 $[M-SeH]^+$.

*3.2.2. Dibutylammonium 1,3-dioxopropane-1,3-bis(phenyldiselenophosphonate) (**2**)*

Colourless paste (732 mg) in 97% yield. Found (calcd for $C_{23}H_{40}N_2O_2P_2Se_4$): C 36.32 (36.62), H 4.91 (5.34), N 3.59 (3.71). Selected IR (KBr, cm^{-1}): 2958 (s), 1588 (m), 1467 (m), 1435 (m), 1098 (m), 1040 (s), 949 (m), 748 (m), 693 (s), 543 (s), 501 (m). ^1H NMR ($CDCl_3$, δ), 8.11 (m, 6H, NH_3^+), 7.82 (m, ^3J(P,H)=13 Hz, ^3J(P,H)=8 Hz, 4H, ArH), 7.37 (d, ^3J(P,H)=13 Hz, 2H, ArH), 7.22 (d, 2H, ArH), 7.17 (d, 2H, ArH), 3.98 (dd, ^3J(P,H)=26 Hz, ^3J(H,H)=6 Hz, 4H, OCH_2), 3.01 (t, ^3J(H,H)=7 Hz, 4H, NCH_2), 1.97 (m, 2H, CH_2), 1.64 (m, ^3J(H,H)=7 Hz, 4H, CH_2), 1.30 (m, ^3J(H,H)=6 Hz, 4H, CH_2), 0.83 (t, ^3J(H,H)=7 Hz, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 141.7 (d, ^1J(P,C)=82 Hz), 131.8 (d, ^4J(P,C)=3.1 Hz), 128.5 (d, ^2J(P,C)=14.5 Hz), 127.9 (d, ^3J(P,C)=12.5 Hz), 63.5, 40.2, 30.7, 29.8, 19.9, 13.7 ppm. $^{31}P–\{^1H\}$ NMR ($CDCl_3$, δ), 81.14 (s, ^1J(P,Se)=660 Hz) ppm. $^{77}Se–\{^1H\}$ NMR ($CDCl_3$, δ), 91.34 (d, ^1J(P,Se)=660 Hz) ppm. MS (ES^-, m/z): 602

$[M-C_4H_{12}NSe]^+$, 343 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, *m*/*z*): 756 $[M]^+$, 677 $[M-SeH]^+$.

3.2.3. Dibutylammonium 1,4-dioxobutane-1,4-bis(phenyl-diselenophosphonate) (**3**)

Colourless paste (695 mg) in 91% yield. Found (calcd for $C_{24}H_{42}N_2O_2P_2Se_4$): C 37.05 (37.51), H 5.12 (5.51), N 3.30 (3.65). Selected IR (KBr, cm^{-1}): 2958 (s), 2866 (w), 1590 (w), 1466 (m), 1436 (m), 1118 (m), 1095 (m), 1035 (s), 748 (m), 694 (m), 566 (s), 543 (s), 506 (m). ^1H NMR ($CDCl_3$, δ), 8.13 (m, 6H, NH_3^+), 7.82 (m, $^3J(P,H)=13$ Hz, $^3J(P,H)=8$ Hz, 4H, ArH), 7.42 (d, $^3J(P,H)=13$ Hz, 2H, ArH), 7.21 (d, 2H, ArH), 7.15 (d, 2H, ArH), 3.87 (dd, $^3J(P,H)=26$ Hz, $^3J(H,H)=6$ Hz, 4H, OCH_2), 2.88 (t, $^3J(H,H)=7$ Hz, 4H, NCH_2), 1.78 (m, 4H), 1.72 (m, $^3J(H,H)=7$ Hz, 4H, CH_2), 1.29 (m, $^3J(H,H)=6$ Hz, 4H, CH_2), 0.82 (t, $^3J(H,H)=7$ Hz, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 142.0 (d, $^1J(P,C)=84$ Hz), 131.8 (d, $^4J(P,C)=3.1$ Hz), 130.1 (d, $^2J(P,C)=14.5$ Hz), 127.9 (d, $^3J(P,C)=12.5$ Hz), 66.0, 40.2, 30.5, 26.7, 19.9, 13.7 ppm. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ), 81.12 (s, $^1J(P,Se)=662$ Hz) ppm. $^{77}Se-\{^1H\}$ NMR ($CDCl_3$, δ), 84.06 (d, $^1J(P,Se)=668$ Hz) ppm. MS (ES^-, *m*/*z*): 616 $[M-C_4H_{12}NSe]^+$, 357 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, *m*/*z*): 770 $[M]^+$, 691 $[M-SeH]^+$.

3.2.4. Dibutylammonium 1,5-dioxopantane-1,5-bis(phenyl-diselenophosphonate) (**4**)

Colourless paste (365 mg) in 93% yield. Found (calcd for $C_{25}H_{44}N_2O_2P_2Se_4$): C 37.97 (38.48), H 5.51 (5.67), N 3.43 (3.58). Selected IR (KBr, cm^{-1}): 2958 (vs), 2872 (m), 1588 (m), 1467 (m), 1435 (m), 1099 (m), 974 (m), 748 (m), 693 (m), 565 (s), 542 (s), 504 (m). ^1H NMR ($CDCl_3$, δ), 8.10 (m, 6H, NH_3^+), 7.81 (m, 4H, ArH), 7.36 (d, 2H, ArH), 7.25 (d, 2H, ArH), 7.08 (d, 2H, ArH), 3.78 (dd, 4H, OCH_2), 2.95 (t, 4H, NCH_2), 1.65 (m, 4H, CH_2), 1.47 (m, 2H, CH_2), 1.30–1.21 (m, 8H, CH_2), 0.82 (m, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 141.7 (d, $^1J(P,C)=80$ Hz), 131.8 (d, $^4J(P,C)=3.1$ Hz), 130.1 (d, $^2J(P,C)=14.5$ Hz), 127.9 (d, $^3J(P,C)=12.5$ Hz), 66.4, 40.1, 29.7, 29.5, 22.6, 19.9, 13.7 ppm. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ), 80.28 (s, $^1J(P,Se)=660$ Hz) ppm. $^{77}Se-\{^1H\}$ NMR ($CDCl_3$, δ), 87.81 (d, $^1J(P,Se)=658$ Hz) ppm. MS (ES^-, *m*/*z*): 630 $[M-C_4H_{12}NSe]^+$, 371 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, *m*/*z*): 784 $[M]^+$, 705 $[M-SeH]^+$.

3.2.5. Dibutylammonium 1,6-dioxohexane-1,6-bis(phenyl-diselenophosphonate) (**5**)

Colourless paste (370 mg) in 93% yield. Found (calcd for $C_{26}H_{46}N_2O_2P_2Se_4$): C 39.01 (39.21), H 5.43 (5.82), N 3.32 (3.52). Selected IR (KBr, cm^{-1}): 2933 (vs), 2871 (m), 1588 (m), 1464 (m), 1435 (m), 1099 (m), 991 (s), 748 (m), 694 (s), 566 (s), 543 (s), 504 (m). ^1H NMR ($CDCl_3$, δ), 8.15 (m, 6H, NH_3^+), 7.83 (m, 4H, ArH), 7.44–7.35 (m, 6H, ArH), 3.74 (m, 4H, OCH_2), 2.82 (t, 4H, NCH_2), 1.84 (m, 4H, CH_2), 1.59 (m, 4H, CH_2), 1.35–1.22 (m, 8H, CH_2), 0.82 (m, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 142.0 (d, $^1J(P,C)=81$ Hz), 130.8 (d, $^4J(P,C)=3.1$ Hz), 130.1 (d, $^2J(P,C)=14.5$ Hz), 127.8 (d, $^3J(P,C)=12.5$ Hz), 66.1, 40.3, 31.2, 29.9, 25.6, 19.9, 13.7 ppm. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ), 79.33 (s, $^1J(P,Se)=657$ Hz) ppm. $^{77}Se-\{^1H\}$ NMR ($CDCl_3$, δ), 88.27 (d, $^1J(P,Se)=653$ Hz) ppm. MS (ES^-, *m*/*z*): 644 $[M-C_4H_{12}NSe]^+$, 385 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, *m*/*z*): 798 $[M]^+$, 719 $[M-SeH]^+$.

3.2.6. Dibutylammonium 1,8-dioxooctane-1,8-bis(phenyl-diselenophosphonate) (**6**)

Colourless paste (401 mg) in 97% yield. Found (calcd for $C_{28}H_{50}N_2O_2P_2Se_4$): C 41.22 (40.79), H 6.07 (6.11), N 3.51 (3.40). Selected IR (KBr, cm^{-1}): 2931(vs), 2860 (s), 1591 (w), 1464 (m), 1435 (m), 1024 (s), 748 (m), 694 (s), 565 (s), 544 (s), 504 (m). ^1H NMR ($CDCl_3$, δ), 8.13 (m, 6H, NH_3^+), 7.83 (m, 4H, ArH), 7.33 (m, 6H, ArH), 3.77 (dd, 4H, OCH_2), 2.71 (t, 4H, NCH_2), 1.57–1.40 (m, 8H, CH_2), 1.27–1.21 (m, 12H, CH_2), 0.82 (m, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 142.3 (d, $^1J(P,C)=83$ Hz), 131.7 (d, $^4J(P,C)=3.1$ Hz), 130.2 (d, $^2J(P,C)=14.5$ Hz), 127.7 (d, $^3J(P,C)=12.5$ Hz), 66.1, 40.5, 32.4, 29.9, 29.0, 25.7, 19.9, 13.8 ppm. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ), 78.93 (s, $^1J(P,Se)=657$ Hz) ppm. $^{77}Se-\{^1H\}$ NMR ($CDCl_3$, δ), 84.75 (d, $^1J(P,Se)=658$ Hz) ppm. MS (ES^-, *m*/*z*): 672 $[M-C_4H_{12}NSe]^+$, 413 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, *m*/*z*): 826 $[M]^+$, 747 $[M-SeH]^+$.

3.2.7. Dibutylammonium 1,10-dioxodecane-1,10-bis(phenyl-diselenophosphonate) (**7**)

Colourless paste (805 mg) in 95% yield. Found (calcd for $C_{30}H_{54}N_2O_2P_2Se_4$): C 41.98 (42.26), H 6.21 (6.38), N 3.50 (3.29). Selected IR (KBr, cm^{-1}): 2930 (vs), 2855 (m), 1590 (w), 1465 (m), 1435 (m), 1095 (m), 1025 (m), 748 (m), 694 (s), 566 (s), 543 (s), 504 (m). ^1H NMR ($CDCl_3$, δ), 8.13 (m, 6H, NH_3^+), 7.83 (m, 4H, ArH), 7.44–7.34 (m, 6H, ArH), 3.78 (dd, 4H, OCH_2), 2.80 (t, 4H, NCH_2), 1.58–1.47 (m, 8H, CH_2), 1.34–1.18 (m, 16H, CH_2), 0.86 (m, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, δ), 142.2 (d, $^1J(P,C)=82$ Hz), 131.7 (d, $^4J(P,C)=3.1$ Hz), 130.1 (d, $^2J(P,C)=14.5$ Hz), 127.7 (d, $^3J(P,C)=12.5$ Hz), 66.3, 40.2, 31.2, 30.1, 29.3, 29.1, 25.8, 20.0, 13.7 ppm. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ), 78.65 (s, $^1J(P,Se)=657$ Hz) ppm. $^{77}Se-\{^1H\}$ NMR ($CDCl_3$, δ), 87.81 (d, $^1J(P,Se)=658$ Hz) ppm. MS (ES^-, *m*/*z*): 700 $[M-C_4H_{12}NSe]^+$, 441 $[M-C_{14}H_{28}N_2PSe_2]^+$. MS (EI, *m*/*z*): 854 $[M]^+$, 775 $[M-SeH]^+$.

3.3. General procedure for synthesis of bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester)

A tetrahydrofuran solution of dibutylammonium bisdiselenophosphonate (2.0 mmol) was cooled to 0 °C and CH_3I (0.60 g 0.26 ml, 4.2 mmol) was added dropwise to give a milky grey suspension. Continued stirring overnight at room temperature gave a pale green suspension. The resulting solution was concentrated in vacuo and the residue was dissolved in ethyl acetate and washed with 2% $Na_2S_2O_4$ aqueous solution, twice with water and brine, and dried over $MgSO_4$. Concentration in vacuo left the crude diester, which was purified on a silica gel column with dichloromethane as an eluent to give esters **8**–**14**.

3.3.1. 1,2-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**8**)

Pale yellow oil (537 mg) in 86% yield. Found (calcd for $C_{16}H_{20}O_2P_2Se_4$): C 30.55 (30.89), H 3.01 (3.24). Selected IR (KBr, cm^{-1}): 3054 (w), 2927 (m), 1436 (m), 1268 (w), 1105 (s), 1064 (m), 1021 (s), 942 (s), 775 (m), 745 (s), 712 (m), 688 (s), 550 (vs, P=Se). ^1H NMR ($CDCl_3$, δ), 7.98 and 7.91 (2×dd, $^3J(P,H)=13.1$ Hz, $^3J(H,H)=7.9$ Hz, 4H, ArH), 7.49–7.48 (2×m, 6H, ArH), 4.48 and 4.36 (2×m, 4H, OCH_2), 2.06 and 2.08 (2×d, $^3J(P,H)=6.4$ Hz, 6H, $SeCH_3$) ppm. ^{13}C NMR ($CDCl_3$, δ), 135.7 and 135.6 (2×d, $^1J(P,C)=99$ Hz), 132.4 and 132.3 (2×d, $^4J(P,C)=2$ Hz), 130.5 and 130.4 (2×d, $^3J(P,C)=13$ Hz), 128.6 (d, $^2J(P,C)=15$ Hz), 64.7 and 64.6 (2×d, $^2J(P,C)=10.5$ Hz, OCH_2), 11.1 and 11.2 (2×d, $^2J(P,C)=3.1$ Hz, $SeCH_3$) ppm. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ), 83.74 and 83.69 (2×s, $J(P,Se_{endo})=446$ Hz, $J(P,Se_{exo})=827$ Hz) ppm. $^{77}Se-\{^1H\}$ NMR ($CDCl_3$, δ), 250.34 and 260.31 (2×d, $J(P,Se_{endo})=446$ Hz), −100.25 and −103.3 (2×d, $J(P,Se_{exo})=827$ Hz) ppm. MS (EI, *m*/*z*): 624 $[M]^+$, 451 $[M-Se-SeCH_3]^+$, 205 $[M-C_{10}H_{12}OPSe_3]^+$. MS (CI^+, *m*/*z*): 625 $[M+H]^+$.

3.3.2. 1,3-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**9**)

Pale yellow oil (444 mg) in 70% isolated yield. Found (calcd for $C_{17}H_{22}O_2P_2Se_4$): C 31.65 (32.10), H 3.71 (3.49). Selected IR (KBr, cm^{-1}): 3053 (w), 2954 (m), 2919 (m), 1436 (m), 1269 (w), 1105 (s), 1034 (s), 960 (s), 747 (m), 713 (m), 689 (s), 551(vs, P=Se), 498(m). ^1H NMR (CD_2Cl_2, δ), 8.03–7.88 (3×m, 4H, ArH), 7.58–7.43 (3×m, 6H, ArH), 4.42 and 4.22 (3×m, 4H, OCH_2), 2.28–2.21 (3×m, 2H, CH_2), 2.13, 2.08 and 2.03 (3×d, 6H, $SeCH_3$) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.9, 135.9, 135.2, 132.4 (d, $^2J(P,C)=3.1$ Hz), 131.7, 130.8, 130.6, 130.4, 130.3, 128.7, 128.4, 128.3, 63.1, 63.0 and 62.8 (3×d, OCH_2), 33.6, 30.5 and 30.2 (CH_2), 13.5, 11.2 and 11.1 ($SeCH_3$) ppm. $^{31}P-\{^1H\}$

NMR (CD_2Cl_2, δ), three diastereoisomers (2.0:2.5:1.0), 81.95, 81.37 and 81.05 (3×s, $J(P,Se_{endo})$=441 Hz, $J(P,Se_{exo})$=826 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), three diastereoisomers, 257.81, 254.66 and 254.11 (3×d, $J(P,Se_{endo})$=439 Hz), −103.45, −104.39 and −104.86 (3×d, $J(P,Se_{exo})$=827 Hz) ppm. MS (EI, *m*/*z*): 638 $[M]^+$, 465 $[M-Se-SeCH_3]^+$, 205 $[M-C_{11}H_{14}OPSe_3]^+$. MS (CI^+, *m*/*z*): 639 $[M+H]^+$.

3.3.3. 1,4-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**10**)

Pale yellow oil (400 mg) in 62% yield. Found (calcd for $C_{18}H_{24}O_2P_2Se_4$): C 33.19 (33.25), H 4.01 (3.72). Selected IR (KBr, cm^{-1}): 3054 (w), 2952 (w), 2926 (w), 1436 (m), 1269 (w), 1105 (s), 945 (s), 747 (m), 712 (m), 689 (s), 550 (vs, P═Se), 499 (m). ^1H NMR (CD_2Cl_2, δ), 7.96–7.78 (3×m, 4H, ArH), 7.56–7.40 (3×m, 6H, ArH), 4.38–4.06 (3×m, 4H, OCH_2), 2.86–2.69 (3×m, 4H, CH_2), 2.09, 2.08 and 2.07 (3×d, 6H, $SeCH_3$) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.9, 136.2, 135.4, 132.4, 132.3, 131.7, 131.6, 130.7, 130.6, 130.4, 130.2, 128.6, 128.5, 128.4, 128.3, 68.1, 66.1 and 64.9 (3×d, $^2J(P,C)$=6.2 Hz, OCH_2), 26.8, 26.6, 26.4 (CH_2), 13.5, 11.1 and 11.0 ($SeCH_3$) ppm. ^{31}P–{^1H} NMR (CD_2Cl_2, δ), three diastereoisomers (1:1:0.5), 81.07, 81.03 and 80.84 (3×s, $J(P,Se_{endo})$=437 Hz, $J(P,Se_{exo})$=824 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), three diastereoisomers (1:1:0.5), 254.80, 254.71 and 254.52 (3×d, $J(P,Se_{endo})$=440 Hz), −103.03, −102.82 and −102.61 (3×d, $J(P,Se_{exo})$=825 Hz) ppm. MS (EI, *m*/*z*): 652 $[M]^+$, 479 $[M-Se-SeCH_3]^+$, 205 $[M-C_{12}H_{16}OPSe_3]^+$. MS (CI^+, *m*/*z*): 653 $[M+H]^+$.

3.3.4. 1,5-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**11**)

Pale yellow oil (445 mg) in 67% yield. Found (calcd for $C_{19}H_{26}O_2P_2Se_4$): C 33.79 (34.30), H 4.09 (4.16). Selected IR (KBr, cm^{-1}): 3056 (w), 2949 (m), 2872 (w), 1436 (m), 1269 (w), 1105 (s), 974 (s), 747 (m), 713 (m), 689 (m), 552 (vs, P═Se), 499 (m). ^1H NMR (CD_2Cl_2, δ), 7.94–7.77 (3×m, 4H, ArH), 7.51–7.45 (3×m, 6H, ArH), 4.26–4.04 (3×m, 4H, OCH_2), 2.08, 2.06 and 2.05 (3×d, 6H, $SeCH_3$), 1.86–1.54 (3×m, 4H, CH_2), 1.41–1.17 (3×m, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 137.0, 135.5, 134.2, 132.3, 132.2, 131.6, 131.5, 130.7, 130.6, 130.4, 130.2, 128.6, 128.5, 128.4, 128.3, 66.4, 66.3 and 65.2 (3×d, OCH_2), 29.8, 29.5 and 29.4 (CH_2), 22.4, 22.3 and 19.8 (CH_2), 13.5, 10.9 and 10.8 ($SeCH_3$) ppm. ^{31}P–{^1H} NMR (CD_2Cl_2, δ), three diastereoisomers (1:1:0.5), 80.60, 80.56 and 80.49 (3×s, $J(P,Se_{endo})$= 439 Hz, $J(P,Se_{exo})$=826 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), three diastereoisomers, 253.81, 253.66 and 253.65 (3×d, $J(P,Se_{endo})$= 439 Hz), −102.38, −102.52 and −102.71 (3×d, $J(P,Se_{exo})$= 825 Hz) ppm. MS (EI, *m*/*z*): 666 $[M]^+$, 493 $[M-Se-SeCH_3]^+$, 205 $[M-C_{13}H_{18}OPSe_3]^+$. MS (CI^+, *m*/*z*): 667 $[M+H]^+$.

3.3.5. 1,6-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**12**)

Purification by silica gel (eluent by dichloromethane) gave two fractions. Compound **12a**: 160 mg of pale yellow oil in 24% yield. Found (calcd for $C_{20}H_{28}O_2P_2Se_4$): C 35.09 (35.42), H 3.91 (4.16). Selected IR (KBr, cm^{-1}): 3050 (w), 2929 (m), 2855 (w), 1436 (m), 1268 (w), 1105 (m), 987 (s), 746 (m), 713 (m), 689 (m), 552 (vs, P═Se), 499 (m). ^1H NMR (CD_2Cl_2, δ), 7.95–7.87 (m, 4H, ArH), 7.52–7.48 (m, 6H, ArH), 4.25–4.05 (m, 4H, OCH_2), 2.06 (d, 6H, $SeCH_3$), 1.82–1.77 (m, 4H, CH_2), 1.53–1.45 (m, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.3 (d, $^1J(P,C)$=99.7 Hz), 132.3 (d, $^4J(P,C)$=3.1 Hz), 130.3 (d, $^3J(P,C)$=12.5 Hz), 128.5 (d, $^2J(P,C)$=14.5 Hz), 66.3 (d, $^2J(P,C)$=6.2 Hz, OCH_2), 29.8 (CH_2), 25.5 (CH_2), 10.8 (d, $^2J(P,C)$=4.2 Hz, $SeCH_3$) ppm. ^{31}P–{^1H} NMR (CD_2Cl_2, δ), 80.43 (s, $J(P,Se_{endo})$=434 Hz, $J(P,Se_{exo})$=824 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), 253.62 (d, $J(P,Se_{endo})$=436 Hz), −102.38 (d, $J(P,Se_{exo})$=825 Hz) ppm. MS (EI, *m*/*z*): 680 $[M]^+$, 507 $[M-Se-SeCH_3]^+$, 205 $[M-C_{14}H_{20}OPSe_3]^+$. MS (CI^+, *m*/*z*): 681 $[M+H]^+$. Compounds **12b**,**c**: 207 mg of pale yellow oil in 31% yield. Found (calcd for $C_{20}H_{28}O_2P_2Se_4$): C 35.11 (35.42), H 4.04 (4.16). Selected IR (KBr, cm^{-1}): 3050 (w), 2930 (m), 2860 (w), 1437 (m), 1268 (w), 1106 (m), 989 (s), 747 (m), 713 (m), 690 (m), 552 (vs, P═Se), 499 (m). ^1H NMR (CD_2Cl_2, δ), a pair of diastereoisomers: 7.95–7.87 (2×m, 4H, ArH), 7.52–7.41 (2×m, 6H, ArH), 4.28–3.92 (2×m, 2×4H, OCH_2), 2.08 and 2.04 (2×d, 6H, $SeCH_3$), 1.79 and 1.75 (2×m, 4H, CH_2), 1.52 and 1.45 (2×m, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.3 and 135.5 (2×d, $^1J(P,C)$=99.7 Hz), 132.2 and 131.5 (2×d, $^4J(P,C)$=3.1 Hz), 130.6 and 130.3 (2×d, $^3J(P,C)$=11.4 Hz), 128.5 and 128.4 (2×d, $^2J(P,C)$=14.5 Hz), 66.6 and 65.4 (2×d, $^2J(P,C)$= 6.2 Hz, OCH_2), 30.0 and 29.8 (CH_2), 25.5 and 25.4 (CH_2), 10.8 and 10.7 (2×d, $^2J(P,C)$=4.2 Hz, $SeCH_3$) ppm. ^{31}P–{^1H} NMR (CD_2Cl_2, δ), two diastereoisomers (1:1): 80.41 and 80.36 (s, $J(P,Se_{endo})$=437 Hz, $J(P,Se_{exo})$=826 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), two diastereoisomers: 153.72 and 253.51 (2×d, $J(P,Se_{endo})$=436 Hz), −102.38 and −102.47 (2×d, $J(P,Se_{exo})$=825 Hz) ppm. MS (EI, *m*/*z*): 680 $[M]^+$, 507 $[M-Se-SeCH_3]^+$, 205 $[M-C_{14}H_{20}OPSe_3]^+$. MS (CI^+, *m*/*z*): 681 $[M+H]^+$.

3.3.6. 1,8-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**13**)

Yellow oil (334 mg) in 50% yield. Found (calcd for $C_{22}H_{32}O_2P_2Se_4$): C 36.97 (37.41), H 4.39 (4.47). Selected IR (KBr, cm^{-1}): 3050 (w), 2928 (m), 2854 (w), 1436 (m), 1269 (w), 1105 (s), 990 (s), 746 (m), 713 (m), 689 (m), 552 (vs, P═Se), 499 (m). ^1H NMR (CD_2Cl_2, δ), 7.94–7.76 (m, 4H, ArH), 7.51 (m, 6H, ArH), 4.22–4.01 (m, 4H, OCH_2), 2.06 (d, 6H, $SeCH_3$), 1.74 (m, 4H, CH_2), 1.39 (m, 4H, CH_2), 1.25 (m, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.3 (d, $^1J(P,C)$=100.0 Hz), 132.3 (d, $^4J(P,C)$=3.1 Hz), 130.3 (d, $^3J(P,C)$=12.4 Hz), 128.5 (d, $^2J(P,C)$=13.5 Hz), 66.8, 29.9, 25.8, 20.1, 10.8 ($SeCH_3$) ppm. ^{31}P–{^1H} NMR (CD_2Cl_2, δ), 81.17 (s, $J(P,Se_{endo})$=439 Hz, $J(P,Se_{exo})$=834 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), 253.41 (d, $J(P,Se_{endo})$=434 Hz), −103.03 (d, $J(P,Se_{exo})$= 823 Hz) ppm. MS (EI, *m*/*z*): 708 $[M]^+$, 535 $[M-Se-SeCH_3]^+$, 205 $[M-C_{16}H_{24}OPSe_3]^+$. MS (CI^+, *m*/*z*): 709 $[M+H]^+$.

3.3.7. 1,10-Dioxoethane-1,2-bis(phenyl-diselenophosphonic acid Se,Se-dimethyl ester) (**14**)

Yellow oil (392 mg) in 53% yield. Found (calcd for $C_{24}H_{36}O_2P_2Se_4$): C 38.96 (39.25), H 5.01 (4.94). Selected IR (KBr, cm^{-1}): 3050 (w), 2925 (m), 2853 (w), 1436 (m), 1269 (w), 1105 (s), 983 (s), 746 (m), 713 (m), 689 (s), 553 (vs, P═Se), 499 (m). ^1H NMR (CD_2Cl_2, δ), 7.92 (m, 4H, ArH), 7.50 (m, 6H, ArH), 4.20 (m, 4H, OCH_2), 2.08 (d, 6H, $SeCH_3$), 1.76 (m, 4H, CH_2), 1.53 (m, 4H, CH_2), 1.41–1.25 (m, 8H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.3 (d, $^1J(P,C)$=99.7 Hz), 132.3 (d, $^4J(P,C)$=3.1 Hz), 130.3 (d, $^3J(P,C)$=11.4 Hz), 128.5 (d, $^2J(P,C)$=14.5 Hz), 66.8, 29.9, 25.9, 19.8, 13.5, 10.8 ($SeCH_3$) ppm. ^{31}P–{^1H} NMR (CD_2Cl_2, δ), 80.04 (s, $J(P,Se_{endo})$= 437 Hz, $J(P,Se_{exo})$=824 Hz) ppm. ^{77}Se–{^1H} NMR (CD_2Cl_2, δ), 253.34 (d, $J(P,Se_{endo})$=436 Hz), −102.06 (d, $J(P,Se_{exo})$=825 Hz) ppm. MS (EI, *m*/*z*): 736 $[M]^+$, 563 $[M-Se-SeCH_3]^+$, 205 $[M-C_{18}H_{28}OPSe_3]^+$. MS (CI^+, *m*/*z*): 737 $[M+H]^+$.

3.3.8. 2,4-Bisphenyl-2,4-diseleno-1,5-dioxa-3-seleno-2,4-diphosphetane (**15**) and 1,3,2-dioxaphosphorinane-2-phenyl-2-selenide (**16**)

A mixture of ethylene glycol (0.06 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in toluene (10 ml) was heated at reflux for 2 h. The red suspension disappeared and a green mixture was formed. Upon cooling to room temperature the mixture was purified by silica gel (toluene as eluent) to give 370 mg of **15** as greenish yellow oil and 30 mg of **16** as green oil.

*3.3.8.1. Compound (**15**).* Yield 72%. Found (calcd for $C_{14}H_{14}O_2P_2Se_3$): C 32.49 (32.77), H 2.80 (2.75). Selected IR (KBr, cm^{-1}): 3058 (w), 2933 (w), 1436 (s), 1103 (s), 1054 (s), 1024 (m), 930 (m), 744 (m), 713 (s), 685 (s), 542 (s), 493 (m), 421 (m). ^1H NMR (CD_2Cl_2, δ), 8.21–8.12 (m, 4H, ArH), 7.55–7.53 (m, 6H, ArH), 4.35 (m,

4H, OCH_2). ^{13}C NMR (CD_2Cl_2, δ), 135.4 (d, $^1J(P,C)$=104 Hz), 133.2, 133.0, 131.4, 131.3, 131.2, 130.4 (d, $^3J(P,C)$=12.5 Hz), 129.0, 128.6, 128.5, 128.4, 128.3, 67.0 ppm. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, 25 °C, δ), 75.02 (s, $^1J(P,Se_{endo})$=397 Hz, $^1J(P,Se_{exo})$=852 Hz, $^2J(P,P)$=14.1 Hz) ppm. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), 696.24 (t, $^1J(P,Se_{endo})$=396 Hz), 5.37 (dd, $^1J(P,Se_{exo})$=851 Hz, $^3J(P,Se_{exo})$=9.8 Hz) ppm. MS (CI^+): m/z 515 $[M+H]^+$.

*3.3.8.2. Compound (**16**).* Yield 12%. Found (calcd for $C_8H_9O_2PSe$): C 38.31 (38.89), H 3.61 (3.67). Selected IR (KBr, cm^{-1}): 2928 (w), 1437 (m), 1114 (s), 1021 (vs), 918 (s), 823 (m), 790 (m), 747 (m), 718 (m), 689 (m), 633 (m), 527 (m). ^1H NMR (CD_2Cl_2, δ), 7.89–7.80 (m, 2H, ArH), 7.57–7.45 (m, 3H, ArH), 4.53 (m, 4H, OCH_2). ^{13}C NMR (CD_2Cl_2, δ), 134.4 (d, $^1J(P,C)$=101 Hz), 133.0, 130.8 (d, $^3J(P,C)$=13.5 Hz), 128.5 (d, $^3J(P,C)$=14.5 Hz), 67.3 ppm. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, 25 °C, δ), 111.60 (s, $^1J(P,Se_{exo})$=911 Hz) ppm. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), −203.95 (d, $^1J(P,Se_{exo})$=911 Hz) ppm. MS (CI^+): m/z 249 $[M+H]^+$.

*3.3.9. 2,5-Diphenyl-(1,6,3,4,2,5)-dioxadiselenadiphosphocane-2,5-diselenide (**17**) and 1,3,2-dioxaphosphorinane-2-phenyl-2-selenide (**18**)*

A mixture of 1,3-propanediol (0.08 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in toluene (10 ml) was heated at reflux for 2 h. The red suspension disappeared and a green mixture was formed. Upon cooling to room temperature the mixture was purified by silica gel (toluene as eluent) to give 160 mg of **17** as yellow powder and 134 mg of **18** as green solid.

*3.3.9.1. Compound (**17**).* Yield 30%. Mp 162–163 °C. Found (calcd for $C_{15}H_{16}O_2P_2Se_4$): C 29.52 (29.73), H 2.54 (2.66). Selected IR (KBr, cm^{-1}): 1433 (m), 1262 (m), 1103 (s), 987 (s), 804 (m), 740 (m), 684 (m), 538 (s, P═Se). ^1H NMR (CD_2Cl_2, δ), 8.00–7.56 (m, 10H, ArH), 4.66 (m, J=12 Hz, 2H, CH_2), 4.30 (t, J=12 Hz, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 135.1 (d, $^1J(P,C)$=103 Hz), 133.2 (d, $^4J(P,C)$=3 Hz), 130.7 (d, $^3J(P,C)$=12 Hz), 128.6 (d, $^2J(P,C)$=15 Hz), 62.4 (d, $^2J(P,C)$=15 Hz, CH_2), 28.4 (t, $^3J(P,C)$=10 Hz, CH_2) ppm. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, δ), 67.21 ppm, singlet with ^{77}Se satellites ($^1J(P,Se_{exo})$=812 Hz, $^1J(P,Se_{endo})$=465 Hz, $^3J(P,P)$=4.2 Hz), lines for $^2J(P,Se_{endo})$ were hidden under intensive central line, prohibiting calculation of its coupling constant. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), 441.17 (dd, $^1J(P,Se_{endo})$=465 Hz, $^2J(P,Se_{endo})$=21.5 Hz), −61.15 (dd, $^1J(P,Se_{exo})$=810 Hz) ppm. Accurate mass measurement (EI, m/z): 609.7284, calculated mass for $C_{15}H_{16}O_2P_2Se_4$: 609.7281.

*3.3.9.2. Compound (**18**).* Yield 51%. Found (calcd for $C_9H_{11}O_2PSe$): C 41.05 (41.40), H 4.07 (4.25). Selected IR (KBr, cm^{-1}): 3053 (w), 2956 (w), 2886 (w), 1438 (s), 1119 (m), 1106 (m), 1031 (vs), 921 (m), 737 (m), 687 (m), 538 (s), 471 (m). ^1H NMR (CD_2Cl_2, δ), 8.00–7.92 (m, 2H, ArH), 7.59–7.47 (m, 3H, ArH), 4.78 (m, 4H, OCH_2), 4.26 (m, 2H, CH_2). ^{13}C NMR (CD_2Cl_2, δ), 133.9 (d, $^1J(P,C)$=102 Hz), 133.2, 132.2, 131.2 (d, $^3J(P,C)$=13.5 Hz), 128.5 (d, $^3J(P,C)$=14.5 Hz), 65.9, 27.6 ppm. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, δ), 93.27 (s, $^1J(P,Se_{exo})$=876 Hz) ppm. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), −247.17 (d, $^1J(P,Se_{exo})$=877 Hz) ppm. MS (CI^+): m/z 263 $[M+H]^+$.

*3.3.10. 2,5-Diphenyl-(1,6,3,4,2,5)-dioxadiselenadiphosphocane-2,5-diselenide (**19**) and 1,3,2-dioxaphosphorinane-2-phenyl-2-selenide (**20**)*

A solution of 1,4-butanediol (0.07 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in toluene (10 ml) was heated at reflux for 2 h. The red suspension disappeared and a pale green solution was formed. Upon cooling to room temperature the mixture was passed through a flash chromatography column (silica gel, eluting with toluene and 1:9 ethyl acetate/toluene) leading to 80 mg of **19** as pale yellow solid (eluting with toluene only) and 240 mg of **20** as yellow oil (eluting with 1:9 ethyl acetate/toluene).

*3.3.10.1. Compound (**19**).* Yield 13%. Mp 108 °C. Found (calcd for $C_{16}H_{18}O_2P_2Se_4$): C 30.77 (30.99), H 3.01 (2.93). Selected IR (KBr, cm^{-1}): 3039 (w), 2944 (m), 2910 (w), 1435 (m), 1103 (m), 1079 (m), 991 (s), 917 (m), 744 (s), 712 (s), 686 (s), 540 (s), 485 (m), 425 (m). ^1H NMR (CD_2Cl_2, δ), 8.04 (m, 4H, ArH), 7.56 (m, 6H, ArH), 4.39 (m, $^3J(P,H)$=40 Hz, $^3J(H,H)$=8.9 Hz, 4H, CH_2), 2.04 (m, $^3J(H,H)$=8.9 Hz, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 137.5 (d, $^1J(P,C)$=98 Hz), 132.3 (d, $^4J(P,C)$=3 Hz), 129.6 (d, $^3J(P,C)$=13 Hz), 128.4 (d, $^2J(P,C)$=15 Hz), 65.9 ($^2J(P,C)$=32 Hz, CH_2), 25.1 ($^3J(P,C)$=8 Hz, CH_2) ppm. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, δ), 68.28 (s, $^1J(P,Se_{endo})$=460 Hz, $^1J(P,Se_{exo})$=808 Hz, $^3J(P,P)$=4.7 Hz) ppm. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), 474.21 (d, $^1J(P,Se_{endo})$=463 Hz, $^2J(P,Se_{endo})$=21.5 Hz), −80.17 (d, $^1J(P,Se_{exo})$=806 Hz) ppm. Accurate mass measurement (EIMS): 621.7450, calculated mass for $C_{16}H_{18}O_2P_2Se_4$: 621.7445.

*3.3.10.2. Compound (**20**).* Yield 86%. Found (calcd for $C_{10}H_{13}O_2PSe$): C 43.29 (43.65), H 4.28 (4.76). Selected IR (KBr, cm^{-1}): 3055 (w), 2950 (m), 2890 (m), 1467 (m), 1437 (m), 1118 (m), 1080 (m), 1003 (vs), 992 (vs), 940 (s), 905 (m), 852 (m), 775 (m), 744 (m), 715 (s), 691 (m), 579 (s), 532 (m). ^1H NMR (CD_2Cl_2, δ), 7.91–7.85 (m, 2H, ArH), 7.54–7.48(m, 3H, ArH), 4.21 (dd, J(H,H)=7.9 Hz, $^3J(P,H)$=16.0 Hz, 4H, OCH_2), 2.02 (d, J(H,H)=7.9 Hz, $^4J(P,H)$=2.7 Hz, 4H, CH_2). ^{13}C NMR (CD_2Cl_2, δ), 136.4 (d, $^1J(P,C)$=137 Hz), 132.3 (d, $^4J(P,C)$=3.1 Hz), 130.4, 130.2, 128.4 (d, $^3J(P,C)$=14.5 Hz), 68.1, 29.4. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, δ), 93.09 (s, $^1J(P,Se_{exo})$=878 Hz) ppm. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), −212.44 (d, $^1J(P,Se_{exo})$=880 Hz). MS (ESI^+): m/z 298 $[M+Na]^+$.

*3.3.11. 1,3,2-Dioxaphosphorinane-2-phenyl-2-selenides (**21**)*

A mixture of pinacol (0.11 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in toluene (10 ml) was stirred for 18 h at room temperature, the colour of the mixture remained unchanged. ^{31}P NMR spectroscopy of the mixture showed that no reaction had occurred. The mixture was heated at reflux for 2 h, the red suspension disappeared and a brown suspension was formed. Upon cooling to room temperature the mixture was purified by silica gel (toluene as eluent) to afford 210 mg of **21** as pale yellow solid in 69% yield. Mp 87 °C. Found (calcd for $C_{12}H_{17}O_2PSe$): C 47.19 (47.54), H 5.51 (5.65). Selected IR (KBr, cm^{-1}): 2980 (w), 2923 (w), 1478 (w), 1435 (m), 1374 (m), 1137 (m), 1118 (m), 956 (m), 912 (s), 861 (m), 715 (m), 690 (m), 625 (m), 535 (s, P═Se). ^1H NMR (CD_2Cl_2, δ), 7.82–7.73 (m, 2H, ArH), 7.48–7.40 (m, 3H, ArH), 1.58 (s, 6H, CH_3), 1.27 (s, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 139.4 (d, J(P,C)=120 Hz), 131.8 (d, J(P,C)=14.5 Hz), 129.2, 129.0, 128.3 (d, J(P,C)=3.1 Hz), 90.6, 24.8, 24.2 ppm. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, δ), 99.19 (s, $J(P,Se_{exo})$=885 Hz, J(P,C)=120 Hz) ppm. $^{77}Se-\{^1H\}$ NMR (CD_2Cl_2, δ), −81.14 (d, $J(P,Se_{exo})$=885 Hz) ppm. MS (EI, m/z): 304 $[M]^+$, 224 $[M-Se]^+$, 220 $[M-C(CH_3)_2C(CH_3)_2]^+$.

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