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Synthesis of Novel Vinylic P–Se Heterocycles from Selenation of Alkynes by $[PhP(Se)(\mu\text{-}Se)]_2$

Guoxiong Hua,[a] Yang Li,[a] Alexandra M. Z. Slawin,[a] and J. Derek Woollins*[a]

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Eleven novel five-membered PSe_2C_2 heterocycles have been synthesised from $[PhP(Se)(\mu\text{-}Se)]_2$ (Woollins' reagent) and alkynes (one or two C≡C triple bonds) by insertion of a Ph(Se)-PSe_2 fragment into alkyne triple bonds. An unusual diselenide formed by an intramolecular cycloaddition/rearrangement is also reported. All compounds have been characterised spectroscopically and four demonstrative X-ray crystal structures are reported.

Introduction

Organoselenenium chemistry has attracted increasing attention in recent years. The interest in selenium-containing compound lies not only in their chemo-, regio-, and stereoselective reactions but also their useful biological activity.[1–7] However, the synthesis of selenium-containing organic heterocycles can be problematic involving use of toxic selenium reagents which are often difficult to handle. 2,4-Bis(phenyl)-1,3-diselenadiphosphetane 2,4-diselenide $[\{PhP(Se)(\mu\text{-}Se)\}_2]$ [**1**, Woollins' reagent (WR)], a selenium analogue of the well-known Lawesson's reagent, $[\{(p\text{-}MeOC_6H_4)P(S)(\mu\text{-}S)\}_2]$ has less unpleasant chemical properties than many systems and can be easily prepared and safely handled.[8,9]

WR has been shown to act as an efficient selenium transfer reagent for the synthesis of a range of selenoamides and selenoaldehydes by, for example, simple O/Se exchange reactions or reaction with ArCN followed by hydrolysis.[10–13] We have also reported the use of $FcP(S)S_2P(S)Fc$ (Fc = ferrocenyl) and WR in the preparation of novel metal complexes, C–P–S and C–P–Se heterocycles by reaction with a variety of reactive organic substrates/functionalities including CS_2, C=O, C=C double bond and C≡N triple bonds.[8,14–19]

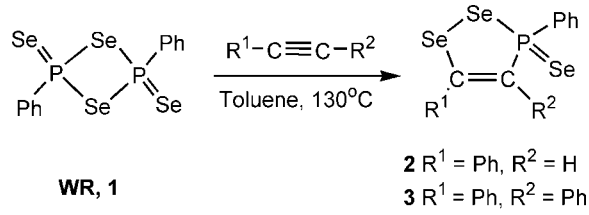
To date, no general method for the synthesis of vinylic selenium-containing heterocycles has been established. We have focused our attention on the preparation of a series of novel vinylic heterocycles by reaction of WR with alkynes and here describe a series of new heterocycles. Four X-ray crystal structures have been determined.

[a] School of Chemistry, University of St Andrews, Fife, KY16 9ST, UK
E-mail: jdw3@st-and.ac.uk

Results and Discussion

Reaction of WR with Alkynes Containing one C≡C Triple Bond

WR reacts with one molar equivalent of phenylacetylene or diphenylacetylene in toluene at 130 °C over 12 h to give brown, air-stable crystals of $PhP(Se)Se_2(PhC{=}CH)$ (**2**) or $PhP(Se)Se_2(PhC{=}CPh)$ (**3**), respectively, in high yields (91% and 94%, based on WR) after column chromatographic purification (silica gel, toluene as eluent) and recrystallisation from dichloromethane/*n*-hexane (Scheme 1).



Scheme 1. Synthesis of **2** and **3**.

Although **2** was described previously by us no crystal structure has been published. The data obtained here from microanalysis and spectroscopic analysis match the literature data from our previous study of **2**[15] except that the yield was much improved by lengthening the reaction time and increasing the reaction scale. The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of a sharp singlet at δ = 74.3 ppm, accompanied by a pattern of selenium satellites with ^{31}P-^{77}Se couplings of 357 and 779 Hz, respectively, similar to that observed in **2**. The $^{77}Se\{^1H\}$ NMR spectrum shows three distinct doublet signals at δ = 519.3 ppm [$^2J_{P,Se}$ 7 Hz], δ = 373.4 ppm [$^1J_{P,Se}$ 358 Hz] and δ = –28.6 ppm [$^1J_{P,Se}$ 777 Hz] assigned as C–Se, P–Se and P=Se, respectively. The ^1H

NMR spectrum of **3** shows that only aryl protons are present.

The molecular structures of **2** and **3** (Figure 1 and Figure 2, Table 1 and Table 3) are composed of approximately planar five-membered C_2PSe_2 rings generated by the addition of $Ph(Se)PSe_2$ fragments from WR to the C≡C bond of alkynes. For **2**, the mean deviation of the Se(1)–C(7)–P(1)–C(8)–Se(2) plane is 0.13 Å, while in **3** the value is 0.25 Å, the extra deviation from planarity in **3** is also evident in a contraction of the P(1)–Se(2)–Se(3) and C(8)–P(1)–Se(2) internal angles on going from **2** to **3** [92.18(3)° and 101.02(12)° for **2**, 89.56(5)° and 98.6(2)° for **3**] and both effects probably reflect the steric influence of the phenyl group in **3** compared to a hydrogen atom in **2**. The majority of the other geometric parameters in these two compounds are similar, thus the exocyclic P(1)–Se(1) bond lengths in **2** and **3** [2.1137(11) and 2.0965(18) Å, respectively] are in good agreement with each other and consistent with the related selenides containing P^V=Se bonds [2.08–2.12 Å].[9,15–18] The P(1)–Se(2) distances [2.2616(10) Å for **2** and 2.2511(17) Å for **3**] are in the range for reported values of heterocycles containing P^V–Se single bonds.[8,9,15–18,20] The C(7)–C(8) bond lengths in **2** and **3** are not significantly different [1.339(4) and 1.345(9) Å, respectively], however, the P(1)–C(8) bond length in **2** is shorter than that in **3** [1.783(3) vs. 1.822(7) Å] which may reflect the different electronic effect of a hydrogen atom compared to a phenyl group. Finally, we note that the structure of **3** is chiral in the solid state, i.e. the crystal examined was a single enantiomer.

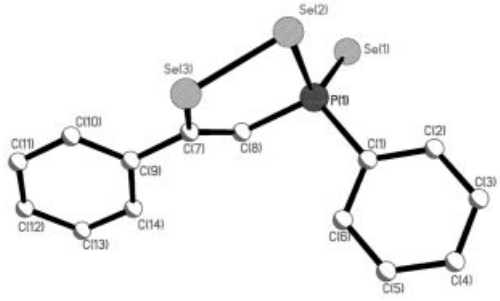


Figure 1. Molecular structure of **2** (C–H bonds omitted for clarity).

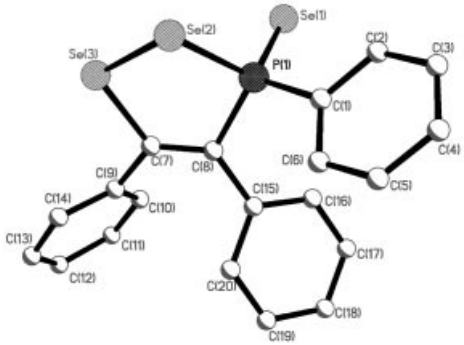


Figure 2. Molecular structure of **3** (C–H bonds omitted for clarity).

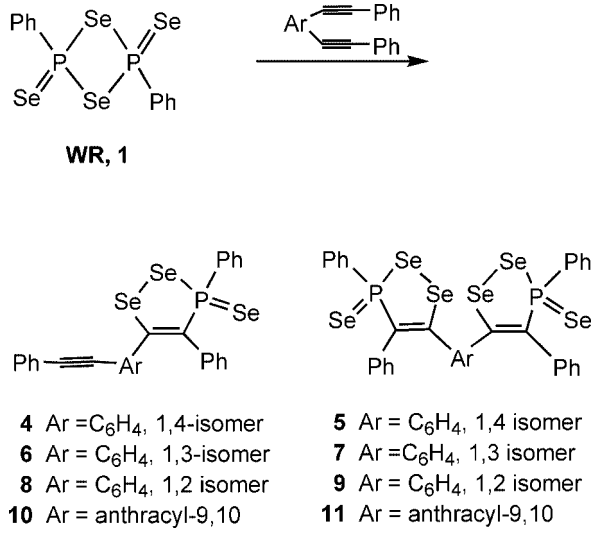
Table 1. Selected bond lengths [Å] and angles [°] for **2**, **3**, and **13**.

	2	**3**	**13**[a]
Se(1)–P(1)	2.1137(11)	2.0965(18)	2.1015(9) [2.1011(9)]
P(1)–Se(2)	2.2616(10)	2.2511(17)	2.2432(9) [2.2612(8)]
P(1)–C(1)	1.814(3)	1.814(7)	1.809(3) [1.812(3)]
P(1)–C(8)	1.783(3)	1.822(7)	1.826(3) [1.822(3)]
Se(2)–Se(3)	2.3735(7)	2.3417(9)	2.3484(5) [2.3473(5)]
Se(3)–C(7)	1.901(3)	1.927(6)	1.929(3) [1.921(3)]
C(7)–C(8)	1.339(4)	1.345(9)	1.334(4)
C(8)–P(1)–Se(2)	101.02(12)	98.6(2)	100.06(10) [99.71(9)]
Se(1)–P(1)–Se(2)	115.24(4)	116.66(8)	109.53(3) [117.80(3)]
P(1)–Se(2)–Se(3)	92.18(3)	89.56(5)	90.96(2) [87.62 (2)]
Se(3)–C(7)–C(8)	121.0(3)	122.5(5)	122.6(19) [120.9(2)]
Se(2)–Se(3)–C(7)	96.41(10)	94.3(2)	94.11(9) [95.43(9)]
C(7)–C(8)–P(1)	124.8(3)	116.9(5)	119.6(2) [118.8(2)]

[a] Dimensions for second independent molecule in square parentheses.

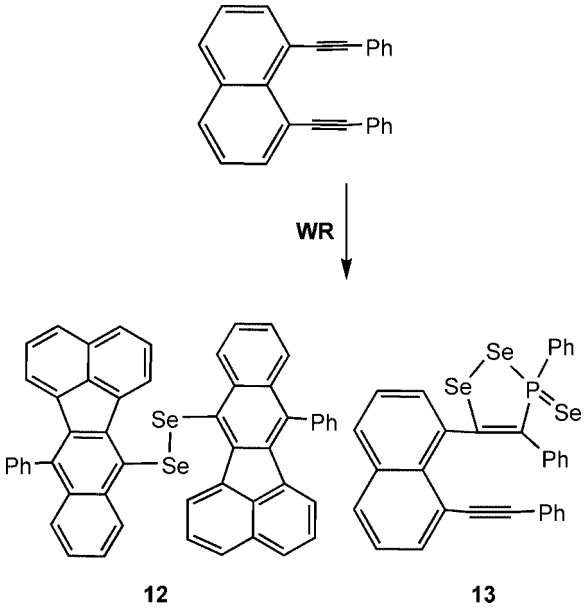
Reaction of WR with Alkynes Containing two C≡C Triple Bonds

The reaction between WR and bis(phenylethynyl)benzene or 9,10-bis(phenylethynyl)anthracene in refluxing toluene over 12 h gave two types of products, one involving cycloaddition at one C≡C triple bond (**4**, **6**, **8** and **10**) and the other involving cycloaddition at both C≡C triple bonds (**5**, **7**, **9** and **11**) (Scheme 2). In **4**–**11** the phosphorus atoms are potentially chiral but because there is no particular stereocontrol in the reaction we would expect to see racemic mixtures. Thus, **5, 7, 9** and **11** are diastereotopic with (*R*,*R*), (*R*,*S*), (*S*,*R*) and (*S*,*S*) isomers being possible. In the $^{31}P\{^1H\}$ NMR of **5** we observed two phosphorus signals with similar selenium satellites at δ_P = 73.3 and 73.0 ppm (intensity ratio 9:1) [$J_{P,Se}$ = 357/774 and 360/770 Hz, respectively] though we cannot assign them specifically to (*R*,*R*), (*S*,*S*) and (*R*,*S*), (*S*,*R*). Further purification of **5**, **7**, **9**, and **11** by recrystallisation from CH_2Cl_2/petroleum ether gave a single signal arising from one pair of enantiomers which are indistinguishable by NMR, [**5a** (11% yield), **7a** (18% yield), **9a** (15% yield) and **11a** (17% yield)].



Scheme 2. Synthesis of **4**–**11**.

The reaction between WR and 1,8-bis(phenylethynyl)-naphthalene gave the expected compound **13** and a surprising diselenide **12**, which arises from an intramolecular cycloaddition, but no product with cycloaddition at two triple bonds (Scheme 3). Compound **12** has an analogue in sulfur chemistry, which was synthesised by Blum et al. from the reaction of 1,8-bis(phenylethynyl)naphthalene with elemental sulfur.[21] However, we failed to obtain **12** by the reaction of 1,8-bis(phenylethynyl)naphthalene with elemental selenium under identical conditions. This suggests that **12** was formed from the reaction of WR and 1,8-bis(phenylethynyl)-naphthalene. The mechanism of this reaction must be rather complex and to test if **13** is involved we heated pure **13** at reflux in toluene for 5 h and obtained **12** in 18% isolated yield.



Scheme 3. Synthesis of **12** and **13**.

Heterocycles **4**–**13** are soluble in chlorinated solvents, toluene, methanol and diethyl ether, with lower solubility in hexane. They are air-stable in the solid state, however, their solutions are not stable at room temperature; red selenium crystals precipitated after a couple of days except for **12**. Characterisations of **4**–**13** were achieved by microanalysis, IR, ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR spectroscopy and mass spectrometry.

In the $^{31}P\{^{1}H\}$ NMR spectra for compounds **4**–**11** and **13** the magnitudes of $^{1}J_{P,Se}$ and $^{1}J_{P,Se}$ (348–380 Hz, 771–820 Hz, respectively) are normal.[15–18] For the products in which one C≡C triple bond has undergone P(Se)SeSe addition the $^{31}P\{^{1}H\}$ NMR spectra show singlets with similar patterns of ^{77}Se satellites. As mentioned above, in the crude products with two C_2PSe_2 rings the $^{31}P\{^{1}H\}$ NMR spectra are mixtures as a consequence of the chirality at phosphorus but after purification by crystallisation we were able to obtain spectrally pure samples which also display singlets with ^{77}Se satellites. Compounds **4**–**11** and **13** were further investigated by $^{77}Se\{^{1}H\}$ NMR which exhibit three signals, assigned as C–Se, P–Se and P=Se, respectively, indicating that in each compound there is one or more identical PhP(Se)–Se–Se fragment present and supporting the presence of both P–Se single and double bonds.[18]

The composition of **4**–**13** was confirmed by mass spectrometric data with a parent M^+, accompanied by major fragment ions. In their IR spectra the $\nu_{(P=Se)}$ vibration, observed in the range of 528–559 cm^{-1} for **4**–**11** and **13**, are consistent with the published P–Se five-membered heterocycles.[8,15]

The $^{77}Se\{^{1}H\}$ NMR spectrum of **12** shows a singlet at δ_{Se} = 279.7 ppm and its ^{1}H NMR spectrum displays only aromatic protons present in a wide range at δ_{H} = 6.08–9.64 ppm. Several of the ^{1}H NMR peaks are broad at room temp. which we attribute to lack of free rotation of the two phenyl rings. The broadening is particularly pronounced for the low field signals of the more hindered protons (see experimental section). We did carry out VT-^{1}H experiments and were able to sharpen the signals at 55 °C, whilst cooling to –61 °C gave considerable broadening, but no coalescence. The complexity of the overlapping peaks in the aromatic region precluded detailed analysis/extraction of activation barriers.

Attempts to grow single crystals of **4**–**13** for X-ray analysis have, to date, been successful for only **12** and **13**. The X-ray structure of **12** shows some interesting features (Figure 3, Table 2 and Table 3). The two diselenide-bound benzo[*k*]fluoranthene moieties are not parallel planes with a dihedral angle of 162.4°, which is markedly different from sulfur analogue [157°].[21] The two terminal phenyl rings, which are connected to C8 and C38, respectively, are twisted, so that the dihedral angles between them and the two benzo[*k*]fluoranthene planes are 103° and 92.4° [corresponding angles in the sulfur analogue 106° and 103°].[21]

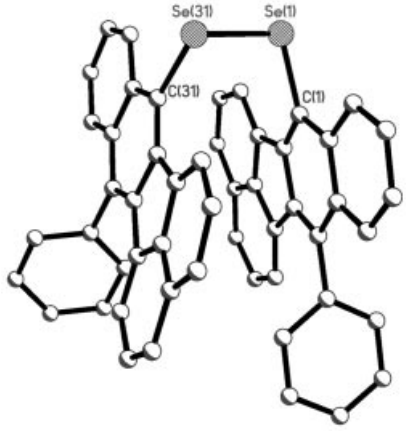


Figure 3. Molecular structure of **12** (C–H bonds omitted for clarity).

Table 2. Selected bond lengths [Å] and angles [°] for **12**.

Se(1)–C(1)	1.920(4)	C(31)–Se(31)–Se(1)	97.76(9)
Se(1)–Se(31)	2.3699(6)	C(2)–C(1)–Se(1)	120.8(2)
Se(31)–C(31)	1.921(3)	C(19)–C(1)–Se(1)	119.2(2)
		C(32)–C(31)–Se(31)	120.8(2)
C(1)–Se(1)–Se(31)	97.90(9)	C(49)–C(31)–Se(31)	120.1(2)

Table 3. Data collection and structural refinement parameters for **2**, **3**, **12** and **13**.

	2	**3**	**12**	**13**
Formula	$C_{14}H_{11}PSe_3$	$C_{20}H_{15}PSe_3$	$C_{59}H_{38}Se_2$	$C_{32}H_{21}PSe_3$
M	447.08	523.17	904.81	673.34
Crystal system	triclinic	orthorhombic	triclinic	triclinic
Space group	$P\bar{1}$	$P2(1)2(1)2(1)$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.681(3)	6.4664(5)	11.3721(8)	9.4900(17)
b [Å]	8.950(3)	11.6801(9)	12.5182(9)	14.217(2)
c [Å]	10.713(3)	24.8150(19)	16.2458(13)	19.639(4)
α	96.644(7)	90	74.019(14)	95.628(5)
β	94.434(7)	90	76.960(15)	93.245(3)
γ	104.116(10)	90	68.560(12)	99.543(5)
U/A^3	705.2(4)	1874.2(2)	2049.2(3)	2593.4(8)
Z	2	4	2	4
μ [mm^{-1}]	7.915	5.971	1.840	4.337
Reflections collected	4519	13355	14315	17831
Independent reflections (R_{int})	2444 (0.0243)	3309 (0.0430)	8163 (0.0343)	9908 (0.0196)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0281, 0.0656	0.0381, 0.0868	0.0457, 0.0779	0.0324, 0.0675

The structure of **13** contains two independent molecules within the unit cell (Figure 4, Table 1 and Table 3), the rotation of aryl ring C(27)–C(32) leads to some steric interactions in the second independent molecule, which account for the differences in metric parameters in the two molecules. Like **2** and **3**, and triselenapentalenes with carbon- and nitrogen-containing backbones,[22,23] **13** is approximately planar; the mean deviation of $P(Se)Se_2C_2$ is 0.22 Å [0.26 Å for molecule 2], while Se(3) lies 0.26 Å [0.30 Å for molecule 2] out of this plane. The Se(2)–Se(3) bond length of 2.3483(5) Å [2.3474(5) Å for molecule 2] is identical to that in $PhP(Se)Se_2$-containing five membered ring.[15,18]

In order to gain some mechanistic insight, we examined the $^{31}P\{^1H\}$ and ^{77}Se NMR of a crude reaction mixture during the reaction of phenylacetylene with WR. Apart from the major product **2** [δ = 67.1 ppm] there are several smaller doublets centred at δ = 76.2, 58.1, 40.1, 9.2, –15.7 ppm indicating different phosphorus environments present in the reaction mixture. None of these values corres-

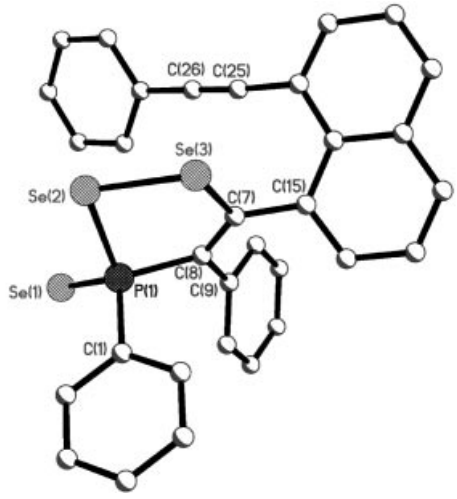
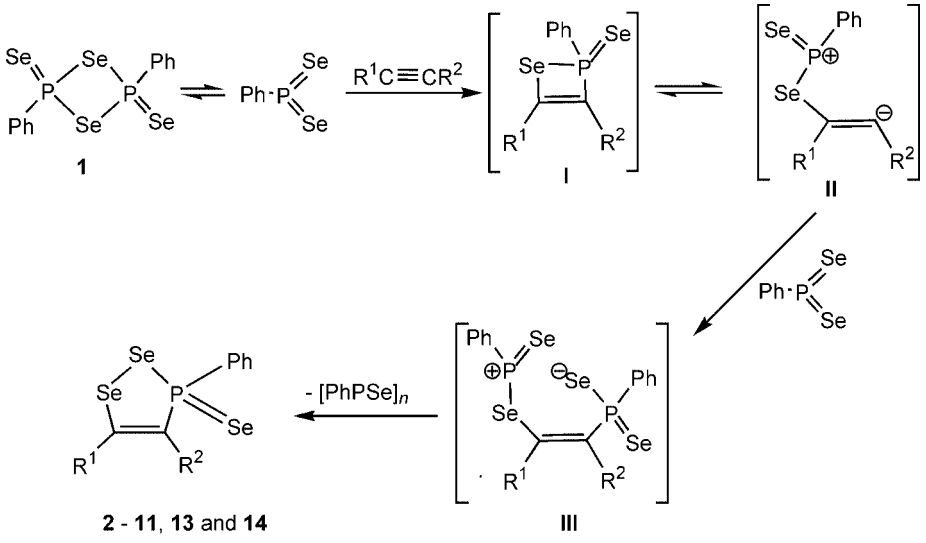


Figure 4. Molecular structure of one of the independent molecules in **13** (C–H bonds omitted for clarity).



Scheme 4. Suggested mechanism for the formation of **2**–**11** and **13**.

pond to known Ph–P–Se rings[9] or WR [δ_P (solid state) = 18.7 ppm] The ^{31}P-^{31}P coupling, typically ca. 270 Hz, along with ^{31}P-^{77}Se coupling constant of ca. 220 Hz, suggest P–P–Se or P–Se–P linkages but does not provide any discriminatory evidence. The ^{77}Se NMR showed >95% of the selenium present as the product **2** with only a very weak doublet at δ_{Se} = –308 ppm (J = 765 Hz) and a singlet at δ_{Se} = 317 ppm. We can only speculate on a mechanism. At elevated temperatures **1** is believed to be in equilibrium with a diselenaphosphorane $PhPSe_2$, which is the true reactive species in refluxing solution. The first step in the reaction is a [2 + 2] cycloaddition of a P=Se bond from $PhPSe_2$ across the C≡C bond, giving an intermediate **I**, which exists in equilibrium in solution in two forms: the 1,2-selenaphosphacyclobutene **I** and the dipolar species **II**. We speculate that the latter species **II** can react with $PhPSe_2$ to give a second dipolar intermediate **III**, which rapidly eliminates $[PhPSe]_n$ to cyclise to subsequently afford **2**–**11** and **13** (Scheme 4).

In conclusion, we have successfully used Woollins' reagent for the syntheses of a series of novel vinylic P–Se heterocycles from alkyl C≡C triple bond organic substrates. Using ^{1}H, ^{31}P{^{1}H} and ^{77}Se{^{1}H} NMR spectroscopy in conjunction with single-crystal X-ray crystallography we have elucidated the structures of the novel heterocycles.

Experimental Section

Unless otherwise stated, all reactions were carried out under oxygen-free nitrogenusing 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.[24] 1,4-Bis(phenylethynyl)benzene,[25] 1,2-bis(phenylethynyl)benzene,[26] 1,3-bis(phenylethynyl)-benzene,[27] and 1,8-bis(phenylethynyl)naphthalene[28] were synthesised according to the literature methods.

^{1}H (270 Hz), ^{13}C (67.9 Hz), ^{31}P{^{1}H} (109 Hz) and ^{77}Se{^{1}H} (51.4 Hz referenced to external Me_2Se) NMR spectra were recorded in $CDCl_3$ 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 **2**, **3**, **12** and **13** (Table 2 and Table 3) were collected at 93 K with a Rigaku MM007 High brilliance RA generator and Mercury CCD system. Intensities were corrected for Lorentz polarisation and for absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were obtained with full-matrix least squares based on F^2 by using the program SHELXTL.[29]

CCDC-6139164 to -613917 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3,5-Diphenyl-1,2,3-diselenaphosphole 3-Selenide (2): A mixture of phenylacetylene (0.10 g, 1 mmol) and WR (0.54 g, 1 mmol) in 10 cm^3 of dry toluene was refluxed over 12 h to give a brown solution. Upon cooling to room temperature the solution was column-chromatographed (silica gel, toluene as eluent) to give a brown fraction of **2**, which was crystallised from dichloromethane/hexane. Yield 401 mg, 91%. $C_{14}H_{11}PSe_3$ (447.09): calcd. C 37.6, H 2.5; found C 37.7, H 2.6. IR (KBr): $\tilde{\nu}$ = 523 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 8.29 (m, 2 H, Ph), 7.75 (m, 2 H, Ph), 7.65 (m, 3 H, Ph), 7.56 (m, 3 H, Ph), 7.26 (d, $^2J_{P,H}$ = 34 Hz, 1 H, =C–H) ppm. ^{13}C NMR: δ = 132.7, 131.9, 131.7, 131.0, 129.3, 128.8, 128.6, 127.9, 121.9, 120.7 ppm. ^{31}P NMR: δ = 67.1 (s, $^1J_{P,Se}$ = 350 Hz, $^1J_{P,Se}$ = 771 Hz) ppm. ^{77}Se NMR: δ = 559.9 (d, $^2J_{P,Se}$ = 7 Hz), 411.7 (d, $^1J_{P,Se}$ = 350 Hz), –15.4 (d, $^1J_{P,Se}$ = 774 Hz) ppm. MS (CI): m/z = 448 [M + H]$^+$.

3,4,5-Triphenyl-3*H*-1,2,3-diselenaphosphole 3-Selenide (3): A refluxing mixture of diphenylacetylene (0.18 g, 1 mmol) and WR (0.54 g, 1 mmol) in toluene was heated at 130 °C over 12 h to give a brown solution. Upon cooling to room temperature the solution was column-chromatographed (silica gel, toluene as eluent) to give an orange crystal of **3**, which was crystallised from dichloromethane/hexane. Yield 495 mg, 94 %. $C_{20}H_{15}PSe_3$ (523.19): calcd. C 45.9, H 2.9; found C 45.8, H 3.1. IR (KBr): $\tilde{\nu}$ = 539 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 8.13 (m, 2 H, Ph), 7.45 (m, 3 H, Ph), 7.24 (m, 5 H, Ph), 7.01 (m, 5 H, Ph) ppm. ^{1}H NMR: δ = 132.6, 132.4, 132.2, 130.7, 130.6, 129.8, 128.7, 128.6, 128.4, 128.2, 127.8 ppm. ^{31}P NMR: δ = 74.3 (s, $^1J_{P,Se}$ = 357 Hz, $^1J_{P,Se}$ = 779 Hz) ppm. ^{77}Se NMR: δ = 519.3 (d, $^2J_{P,Se}$ = 7 Hz), 373.4 (d, $^1J_{P,Se}$ = 358 Hz), –28.6 (d, $^1J_{P,Se}$ = 777 Hz) ppm. MS (ES$^+$): m/z (%) = 546 [M + Na]$^+$.

3,4-Diphenyl-5-[4-(phenylethynyl)phenyl]-3*H*-1,2,3-diselenaphosphole 3-Selenide (4) and 5,5′-(1,4-Phenylene)bis(3,4-diphenyl-3*H*-1,2,3-diselenaphosphole) 3,3′-Diselenide (5): A solution of WR (1.08 g, 2 mmol) and 1,4-bis(phenylethynyl)benzene (0.28 g, 1 mmol) in toluene (10 cm^3) in a sealed tube was refluxed for 12 h, giving a yellow solution. Upon cooling to room temperature, the toluene solution was purified by column chromatography (silica gel, toluene as eluent) to afford a yellow fraction of **4** followed by another orange band, which was proved to be a mixture of conformational isomers by ^{31}P NMR spectroscopy. Layering a dichloromethane solution of the mixture with hexane gave a major orange powder of **5a**.

Compound 4: Yield 180 mg, 29%. $C_{28}H_{19}PSe_3$ (623.30): calcd. C 54.0, H 3.1; found C 53.4, H 3.7. IR (KBr): $\tilde{\nu}$ = 539 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 7.29–8.15 (m, 19 H, Ph) ppm. ^{1}H NMR: δ = 140.6, 139.6, 134.8, 134.0, 133.0, 132.8, 132.6, 132.4, 132.2, 131.9, 129.8, 128.7, 128.6, 128.5, 128. 3, 125.4, 121.8, 121.4, 104.1, 83.6, 83.2, 81.7, 74.0 ppm. ^{31}P NMR: δ = 73.9 (s, $^1J_{P,Se}$ = 357 Hz, $^1J_{P,Se}$ = 779 Hz) ppm. ^{77}Se NMR: δ = 519.8 (d, $^2J_{P,Se}$ = 7 Hz), 382.3 (d, $^1J_{P,Se}$ = 355 Hz), –16.4 (d, $^1J_{P,Se}$ = 779 Hz) ppm. MS (EI): m/z = 623 [M]$^+$, 278 [M – $PhPSe_3$]$^+$.

Compound 5a: Yield 105 mg, 11%. $C_{34}H_{24}P_2Se_6$ (968.26): calcd. C 42.2, H 2.5; found C 42.7, H 2.5. IR (KBr): $\tilde{\nu}$ = 559 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 6.94–8.09 (m, 24 H, Ph) ppm. ^{1}H NMR: δ = 132.4, 132.3, 132.2, 132.0, 130.5, 130.2, 130.1, 129.9, 129.6, 128.7, 128.5, 128.4, 128.2, 128.0, 127.6 ppm. ^{31}P NMR: δ = 73.3 (s, $^1J_{P,Se}$ = 357 Hz, $^1J_{P,Se}$ = 774 Hz) ppm. ^{77}Se NMR: δ = 522.9 (d, $^2J_{P,Se}$ = 7 Hz), 384.7 (d, $^1J_{P,Se}$ = 355 Hz), –16.3 (d, $^1J_{P,Se}$ = 773 Hz) ppm. MS (EI): m/z = 968 [M]$^+$, 278 [M – 2$PhPSe_3$]$^+$.

3,4-Diphenyl-5-[3-(phenylethynyl)phenyl]-3*H*-1,2,3-diselenaphosphole 3-Selenide (6) and 5,5′-(1,3-Phenylene)bis(3,4-diphenyl-3*H*-1,2,3-diselenaphosphole) 3,3′-Diselenide (7): WR (1.08 g, 2 mmol) and 1,3-bisphenylethynylbenzene (0.28 g, 1 mmol) were stirred in 10 cm^3 of dry toluene at 130 °C in a sealed tube for 12 h, producing a dark yellow solution plus a tiny amount of black solid (selenium, resulted from the decomposition of WR). Column chromatography

(silica gel, toluene as eluent) produced a yellow fraction of **6** and subsequent another yellow band whose $^{31}P\{^{1}H\}$ NMR spectrum revealed a mixture of conformational isomers. Layering a dichloromethane solution of the mixture with hexane gave a yellow powder of **7a**.

Compound 6: Yield 360 mg, 58%. $C_{34}H_{24}P_2Se_6$ (968.26): calcd. C 54.0, H 3.1; found C 53.7, H 3.2. IR (KBr): $\tilde{\nu}$ = 532 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 6.95–8.18 (m, 19 H, Ph) ppm. ^{1}H NMR: δ = 135.5, 135.3, 134.6, 134.3, 133.5, 133.5, 132.7, 132.5, 132.2, 131.7, 131.6, 131.1, 130.7, 130.6, 130.0, 129.7, 129.3, 128.8, 128.4, 128.3, 122.8 ppm. ^{31}P NMR: δ = 74.3 (s, $^{1}J_{P,Se}$ = 356 Hz, $^{1}J_{P,Se}$ = 778 Hz) ppm. ^{77}Se NMR: δ = 520.7 (d, $^{2}J_{P,Se}$ = 7 Hz), 379.4 (d, $^{1}J_{P,Se}$ = 358 Hz), –25.3 (d, $^{1}J_{P,Se}$ = 777 Hz) ppm. MS (EI): *m*/*z* = 623 $[M]^+$, 278 $[M - PhPSe_3]^+$.

Compound 7a: Yield 175 mg, 18%. $C_{34}H_{24}P_2Se_6$ (968.26): calcd. C 42.2, H 2.5; found C 42.8, H 2.2. IR (KBr): $\tilde{\nu}$ = 538 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 7.13–8.06 (m, 24 H, Ph) ppm. ^{1}H NMR: δ = 132.0, 129.9, 129.7, 128.8, 128.7, 128.6, 128.5, 128.4 ppm. ^{31}P NMR: δ = 74.28 (s, $^{1}J_{P,Se}$ = 352 Hz, $^{1}J_{P,Se}$ = 771 Hz) ppm. ^{77}Se NMR: δ = 525.0 (d, $^{2}J_{P,Se}$ = 7 Hz), 381.9 (d, $^{1}J_{P,Se}$ = 354 Hz), –14.6 (d, $^{1}J_{P,Se}$ = 771 Hz) ppm. MS (EI): *m*/*z* = 968 $[M]^+$, 546 [M – Ph or Se – $PhPSe_3]^+$, 278 $[M - 2PhPSe_3]^+$.

3,4-Diphenyl-5-[2-(phenylethynyl)phenyl]-3*H*-1,2,3-diselenaphosphole 3-Selenide (8) and 5,5′-(1,2-Phenylene)bis(3,4-diphenyl-3*H*-1,2,3-diselenaphosphole) 3,3′-Diselenide (9): 1,2-Bis(phenylethynyl)-benzene (0.28 g, 1 mmol) and WR (1.08 g, 2 mmol) in toluene (10 cm^3) were refluxed for 12 h, giving a brownish yellow solution. Column chromatography (silica gel, toluene) gave a yellow fraction of **8** followed by a yellow band whose $^{31}P\{^{1}H\}$ NMR spectrum revealed a mixture of conformational isomers once again. Layering a dichloromethane solution of the mixture with hexane afforded a yellow powder of **9a**.

Compound 8: Yield 437 mg, 70%. $C_{34}H_{24}P_2Se_6$ (968.26): calcd. C 54.0, H 3.1; found C 54.2, H 3.8. IR (KBr): $\tilde{\nu}$ = 539 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 6.98–7.67 (m, 19 H, Ph) ppm. ^{1}H NMR: δ = 133.6, 133.3, 132.5, 132.3, 132.1, 132.0, 131.9, 131.4, 130.5, 129.7, 129.2, 129.0, 128.7, 128.5, 128.1, 128.0, 127.7 ppm. ^{31}P NMR: δ = 73.8 (s, $^{1}J_{P,Se}$ = 343 Hz, $^{1}J_{P,Se}$ = 779 Hz) ppm. ^{77}Se NMR: δ = 528.6 (d, $^{2}J_{P,Se}$ = 7 Hz), 409.8 (d, $^{1}J_{P,Se}$ = 346 Hz), –22.2 (d, $^{1}J_{P,Se}$ = 778 Hz) ppm. MS (EI): *m*/*z* = 623 $[M]^+$, 278 $[M - PhPSe_3]^+$.

Compound 9a: Yield 144 mg, 15%. $C_{34}H_{24}P_2Se_6$ (968.26): calcd. C 42.2, H 2.5; found C 42.7, H 2.6. IR (KBr): $\tilde{\nu}$ = 528 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 7.00–7.41 (m, 24 H, Ph) ppm. ^{1}H NMR: δ = 133.6, 133.4, 132.5, 132.3, 132.1, 131.9, 131.4, 130.6, 129.7, 129.2, 128.7, 128.5, 128.2, 128.1, 127.7 ppm. ^{31}P NMR: δ = 77.5 (s, $^{1}J_{P,Se}$ = 364 Hz, $^{1}J_{P,Se}$ = 822 Hz) ppm. ^{77}Se NMR: δ = 528.4 (d, $^{2}J_{P,Se}$ = 8 Hz), 409.8 (d, $^{1}J_{P,Se}$ = 365 Hz), –21.9 (d, $^{1}J_{P,Se}$ = 820 Hz) ppm. MS (EI): *m*/*z* = 968 $[M]^+$, 624 $[M - PhPSe_3]^+$, 278 $[M - 2PhPSe_3]^+$.

3,4-Diphenyl-5-[10-(phenylethnyl)anthracen-9-yl]-3*H*-1,2,3-diselenaphosphole 3-Selenide (10) and 5,5′-Anthracene-9,10-diylbis(3,4-diphenyl-3*H*-1,2,3-diselenaphosphole) 3,3′-Diselenide (11): A solution of WR (1.08 g, 2 mmol) and bis(phenylethynyl)anthracene (0.38 g, 1 mmol) in toluene (10 cm^3) in a sealed tube was refluxed for 12 h, giving a yellow solution. After cooling to room temperature the toluene solution was purified by column chromatography (SiO_2, toluene as eluent) to afford a yellow fraction of **10** followed by another orange band of the mixture. Layering a dichloromethane solution of the mixture with hexane gave orange powder of **11a**.

Compound 10: Yield 410 mg, 57%. $C_{36}H_{23}P_2Se_6$ (991.28): calcd. C 59.8, H 3.2; found C 59.9, H 3.4. IR (KBr): $\tilde{\nu}$ = 533 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 6.66–8.56 (m, 23 H, Ph) ppm. ^{1}H NMR: δ = 134.5, 134.3, 133.2, 133.0, 132.4, 132.1, 131.5, 130.1, 129.1, 128.8, 128.5, 128.2, 128.0, 127.1, 127.0, 126.7, 126.3, 126.0, 123.2, 119.8 ppm. ^{31}P NMR: δ = 73.3 (s, $^{1}J_{P,Se}$ = 352 Hz, $^{1}J_{P,Se}$ = 794 Hz) ppm. ^{77}Se NMR: δ = 529.3 (d, $^{2}J_{P,Se}$ = 7 Hz), 414.4 (d, $^{1}J_{P,Se}$ = 353 Hz), –19.6 (d, $^{1}J_{P,Se}$ = 792 Hz) ppm. MS (CI): *m*/*z* = 727 $[M + H]^+$, 378 $[M - PhPSe_3]^+$.

Compound 11a: Yield 183 mg, 17%. $C_{34}H_{24}P_2Se_6$ (968.26): calcd. C 47.2, H 2.6; found C 46.7, H 2.7. IR (KBr): $\tilde{\nu}$ = 533 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 6.63–8.26 (m, 28 H, Ph) ppm. ^{1}H NMR: δ = 133.2, 132.9, 132.8, 132.2, 132.0, 131.7, 129.9, 129.1, 128.7, 128.5, 127.9, 127.4, 127.0, 126.0 ppm. ^{31}P NMR: δ = 73.3 (s, $^{1}J_{P,Se}$ = 352 Hz, $^{1}J_{P,Se}$ = 779 Hz) ppm. ^{77}Se NMR: δ = 535.2 (d, $^{2}J_{P,Se}$ = 7 Hz), 404.0 (d, $^{1}J_{P,Se}$ = 355 Hz), –16.8 (d, $^{1}J_{P,Se}$ = 780 Hz) ppm. MS (CI): *m*/*z* = 1069 $[M + H]^+$, 726 $[M - PhPSe_3]^+$, 565 [M – $PhPSe_3$ – 2Se or 2Ph]$^+$, 378 $[M - 2PhPSe_3]^+$.

Synthesis of Diselane 12 and 3,4-Diphenyl-5-[8-(phenylethynyl)-1-naphthyl]-3*H*-1,2,3-diselenaphosphole 3-Selenide (13): A mixture of Woollins' reagent (1.08 g, 2 mmol) and 1,8-bis(phenylethynyl)naphthalene (0.45 g, 1 mmol) in toluene (20 cm^3) was heated at reflux for 12 h resulting in red solution. After cooling to room temperature, the solution was subjected to column chromatography (SiO_2, toluene as eluent) and afforded successively red **12** followed a pale yellow **13**.

Compound 12: Yield 57 mg, 14%. $C_{52}H_{30}Se_2$ (812.71): calcd. C 76.8, H 3.7; found C 76.1, H 3.9. IR (KBr): $\tilde{\nu}$ = 825 (w), 759 (m), 701 (w), 448 (w) cm^{-1}. ^{1}H NMR: δ = 6.08 (br., d, 1 H, Ph), 6.56–8.67 (br., m, 28 H, Ph), 9.64 (br., d, 1 H, Ph) ppm. ^{1}H NMR: δ = 135.7, 135.0, 134.2, 132.1, 131.7, 130.0, 129.9, 129.7, 129.3, 128.9, 128.0, 127.9, 125.7, 124.9, 124.8, 123.9, 122.3, 121.7, 120.9, 119.9, 119.1, 118.8 ppm. ^{77}Se NMR: δ = 279.7 (s, 2Se) ppm. MS (CI): *m*/*z* = 831 $[M + NH_4]^+$.

Compound 13: Yield 147 mg, 22%. $C_{32}H_{21}PSe_3$ (673.36): calcd. C 57.1, H 3.1; found C 57.7, H 3.3. IR (KBr): $\tilde{\nu}$ = 546 (s, $\nu_{P=Se}$) cm^{-1}. ^{1}H NMR: δ = 6.81–8.70 (m, 21 H, Ph) ppm. ^{1}H NMR: δ = 135.6, 134.0, 133.0, 132.4, 131.4, 131.0, 130.9, 130.0, 129.5, 129.4, 128.9, 128.7, 128.5, 127.3, 126.1, 125.8 ppm. ^{31}P NMR: δ = 66.5 (s, $^{1}J_{P,Se}$ = 380 Hz, $^{1}J_{P,Se}$ = 803 Hz) ppm. ^{77}Se NMR: δ = 564.9 (d, $^{2}J_{P,Se}$ = 11 Hz), 461.5 (d, $^{1}J_{P,Se}$ = 383 Hz), –14.7 (d, $^{1}J_{P,Se}$ = 802 Hz) ppm. MS (CI^+): *m*/*z* = 674 $[M + H]^+$, 436 [M – 3Se or 3Ph]$^+$, 328 $[M - PhPSe_3]^+$.

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