Synthesis and X-ray structures of new phosphorus–selenium heterocycles with an E–P(Se)–E′ (E, E′ = N, S, Se) linkage†‡§

Guoxiong Hua, Amy L. Fuller, Yang Li, Alexandra M. Z. Slawin and J. Derek Woollins*

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Refluxing a toluene solution of Woollins' reagent, **WR**, with difunctional aromatic substrates (aryldiamines and aryldithiols) leads to a series of novel five- to seven-membered heterocycles **2a–e**, **4a**, **4b** and **6a–c** with an E–P(Se)–E′ (E, E′ = N, S, Se) linkage in 7–98% isolated yields. This method offers a new approach to the library of phosphorus–selenium heterocyclic compounds. All new compounds have been characterized by IR, ^{1}H, ^{13}C, ^{31}P, ^{77}Se NMR, mass spectrometry and elemental analysis or accurate mass measurement. Four representative X-ray structures are reported.

Introduction

Following the discovery of seleno-enzymes, selenium-containing compounds have been studied extensively because of their interesting reactivity profile[1] and potential pharmaceutical significance.[2] For example, there has been considerable interest in organoselenium compounds as reagents or intermediates in synthetic chemistry,[3] as heavy atom versions of oligonucleotides and proteins for crystallographic studies,[4–6] as human metabolites,[7] as cancer-preventative agents[8,9] and as substrates for biomimetic studies.[10–12] Typical selenium reagents used for the preparation of organoselenium systems include SeO_2, $PhSeO_2H$, PhSeCl, $PhSe^-$,[1b,13,14] selenoethers and phosphine selenides.[15] However, the synthesis of selenium-containing organic heterocycles can be problematic due to the use of these toxic selenium reagents which are often difficult to handle. In recent years, 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$, which has been known as Woollins' reagent, **WR**, has received increasing attention due to its less unpleasant chemical properties and relatively easy preparation, as well as ease of handling.[16] Now it is becoming a very useful selenium source in synthetic chemistry.[17]

As part of our studies into the reactivity of **WR** towards different organic substrates, we have recently reported the facile synthesis of eight- to ten-membered macrocyclic diselenides bearing a P–Se–Se–P linkage.[18] Herein, we described the preparation of a series of novel five- to seven-membered phosphorus–selenium heterocycles *via* the selenation of a variety of difunctional nucleophilic substrates (aryldiamines, aryldithiol, aminoarylthiol) and their derivates by **WR**. Four representative X-ray crystal structures are reported.

School of Chemistry, University of St Andrews, Fife, UK KY16 9ST. E-mail: jdw3@st-and.ac.uk; Tel: +44 (0)1334-463384
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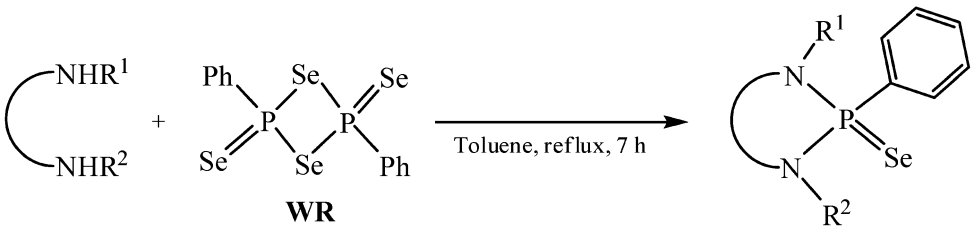
Results and discussion

Synthesis of monophosphorus–selenium heterocycles of 2a–e, 4a, 4b and 6a–c

The reaction between **WR** and two molar equivalents of **1a** or **1b** proceeded with the rupture of the $P_2(\mu\text{-}Se)_2$ ring to give the five-membered monophosphorus species $C_6H_5P(Se)(NR^1C_6H_4NR^2\text{-}1,2)$ **2a** (R^1 = C_6H_5; R^2 = H) and **2b** (R^1 = R^2 = $C_6H_5CH_2$) in 51% and 65% yield, respectively (Scheme 1). The difference in yields of diazaphosphepines suggests that the more substituted the amine, the easier is the completion of its cyclization with **WR**. This cannot be simply explained by the nucleophilic property of the nitrogen, as the $C_6H_5CH_2$ group makes the nitrogen atom of the amine more nucleophilic, but the C_6H_5 group has the opposite effect.

Refluxing a toluene solution of **WR** with two molar equivalents of 1,8-diaminonaphthalene (**1c**), 1-(2-aminophenyl)naphthalene-2-amine (**1d**), or 1,1′-binaphthyl-2,2′-diamine (**1e**) led to the corresponding six-/seven-membered monophosphorus species **2c**, **2d** and **2e** in good yields (68% for **2c**, 96% for **2d**, and 98% for **2e**) (Scheme 1). In addition to the increasing hyperconjugation effect of the aromatic rings, the reduced strain in the six- or seven-membered ring may contribute to the stability and therefore the yield of the product.

2a–e were obtained as white or off-white solids, which turned pink in air over several months due to slow decomposition in aerobic conditions. These compounds are soluble in both dichloromethane and chloroform. All compounds showed the anticipated $[M + H]^+$ or $[M + Na]^+$ peak in their mass spectra. The elemental microanalyses or accurate mass measurements for all of the compounds were satisfactory. In the ^{31}P NMR spectra of **2a–c** and **2e**, the coupling constants are in the region of 810–842 Hz ($J(P,Se_{exo})$), which are considerably lower than those in the non-substituted $PhP(Se)(NHC_6H_4NH\text{-}1,2)$ ($J(P,Se_{exo})$ = 895 Hz).[19] There is a progressive shift to low frequency in δ_P in the range of 84.7–40.5 ppm. The lowest case is **2c** due to the six-membered ring present. The ^{77}Se NMR spectra of **2a–c** and **2e** consist of a set of doublet (δ_{Se} = −115.7 ppm ($J(P,Se_{exo})$ = 842 Hz) for



1a = Phenyl-1,2-diyl, $R^1 = C_6H_5$, $R^2 = H$
1b = Phenyl-1,2-diyl, $R^1 = R^2 = C_6H_5CH_2$
1c = Naphthalene-1,8-diyl, $R^1 = R^2 = H$
1d = 1-Phenyl-1'-naphthyl-2,2'-diyl, $R^1 = R^2 = H$
1e = 1,1'-Dinaphthyl-2,2'-diyl, $R^1 = R^2 = H$

2a = Phenyl-1,2-diyl, $R^1 = C_6H_5$, $R^2 = H$, 51%
2b = Phenyl-1,2-diyl, $R^1 = R^2 = C_6H_5CH_2$, 65%
2c = Naphthalene-1,8-diyl, $R^1 = R^2 = H$, 68%
2d = 1-Phenyl-1'-naphthyl-2,2'-diyl, $R^1 = R^2 = H$, 96%
2e = 1,1'-Dinaphthyl-2,2'-diyl, $R^1 = R^2 = H$, 98%

Scheme 1 Synthesis of five- to seven-membered N–P(Se)–N heterocycles **2a–e**.

2a, −188.7 ppm ($J(P,Se_{exo})$ = 842 Hz) for **2b**, −182.1 ppm ($J(P,Se_{exo})$ = 820 Hz) for **2c** and −193.5 ppm ($J(P,Se_{exo})$ = 810 Hz for **2e**)). The NMR spectra of **2d** reveal a mixture of two diastereoisomers with similar ^{31}P and ^{77}Se NMR spectral patterns. In the IR spectra of **2** the ν(P=Se) vibration was observed in the region 607–562 cm^{-1}.

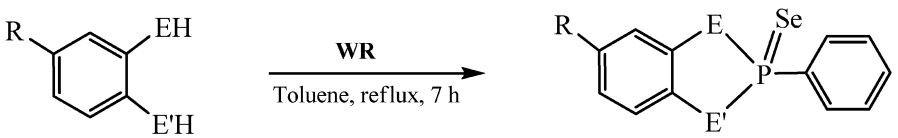
The two five-membered P–Se heterocyclic compounds **4a** and **4b** were prepared by the reaction of **WR** with one molar quantity of 4-methylbenzene-1,2-dithiol (**3a**) or 2-aminobenzenethiol (**3b**) in refluxing toluene (Scheme 2). **4a** was obtained as a white solid, while **4b**, a greenish paste. Both are air stable and soluble in dichloromethane and chloroform. The ^{31}P NMR spectra contain sharp singlets at δ = 74.4 and 71.3 ppm, with coupling constants $J(P,Se)$ = 840 and 836 Hz, respectively. The ^{1}H and ^{13}C NMR spectra confirm the presence of the aromatic substituents on the phosphorus centre, the benzyl groups being readily observed in the ^{1}H and ^{13}C NMR spectra. The IR spectra of **4a** and **4b** showed similar patterns except for the presence of the CH_3 absorption peak in **4b**. In all cases the expected M^+ ions are found in their mass spectra.

Reacting **WR** with two molar equivalents of naphtho[1,8-*cd*][1,2]dithiole (**5a**), naphtho[1,8-*cd*][1,2]thioselenole **5b** or naphtho[1,8-*cd*][1,2]selenole (**5c**) in refluxing toluene (Scheme 3) leads to the formation of **6a–c**. The isolated yields range from 7% for **6c** to 92% for **6a**, indicating that the reactive order with **WR** is naphtho[1,8-*cd*][1,2]dithiole (**5a**) > naphtho[1,8-*cd*][1,2]selenole (**5c**) ≫ naphtho[1,8-*cd*][1,2]-thioselenole (**5b**). **6a–c** were obtained as white or yellow or brown solids which turned pink in air over several months due to slow decomposition in aerobic conditions. All compounds showed the anticipated $[M]^+$ or $[M + H]^+$ peak in their EI or CI mass spectra. The elemental microanalyses or accurate mass measurements for all compounds were satisfactory. The ^{31}P NMR spectrum of **6a** comprises a singlet at 21.7 ppm, flanked by selenium satellite $J(P, Se_{exo})$ = 810 Hz; these values are similar to those in **2a–e**. However, the ^{31}P NMR spectra of **6b** and **6c** display sharp singlets at 3.7 and 76.6 ppm, respectively, accompanied by two sets of selenium satellites (798 and 390 Hz for **6b**, and 819 and 439 Hz for **6c**), indicating that there is a P–Se single bond and a P=Se double bond present in these two compounds. This is further substantiated by the ^{77}Se NMR spectrum, which shows two doublets at 502.6 and −50.9 ppm for **6b**, and 386.9 and −26.0 ppm for **6c** with coupling constants of $J(P,Se)$ 799 and 390 Hz for **6b**, and 820 and 441 Hz for **6c**.

It is known that the S–S and S–Se bonds are fairly weak. It is not surprising that **WR** reacts with **5a–c** to give the E–P(Se)–E heterocycles **6a–c**. However, splitting the guanidine group, especially a cyclic guanidine, derived from diamine and cyanogen bromide in dry methanol in the presence of anhydrous sodium acetate, is rather difficult. We found that **WR** broke the ring of the cyclic guanidine 3*H*-dinaphtho-[2,1-*d*:1′,2′-*f*][1,3]diazepin-4-amine (**7**), and gave **2e** in excellent yield (90%) (Scheme 4). The result suggests that **WR** is a powerful phosphorus-selenation reagent.

X-Ray crystal structures of 2a, 2b, 4b and 6a

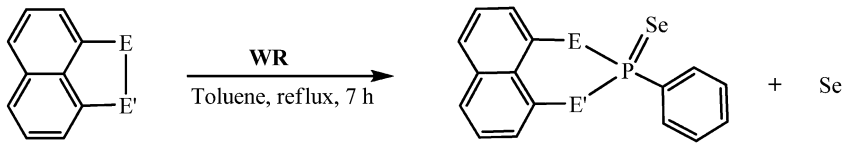
The molecular structures of **2a** and **2b** were established by X-ray diffraction and are depicted in Fig. 1 and 2. Their crystallographic data are reported in Table 1. The X-ray structure of **2a** reveals an intermolecular hydrogen bonding interaction between the exocyclic selenium atom and the H atom of the amine nitrogen leading to a dimer pair (Fig. 1). Within the hydrogen bonded dimers the Se(1)···H(5N) distance of 2.68(4) Å with N(5)–H(5N)···Se(1) angle of



3a R = H, E = NH, E' = S
3b R = CH_3, E = E' = S

4a R = H, E = NH, E' = S, 52%
4b R = CH_3, E = E' = S, 59%

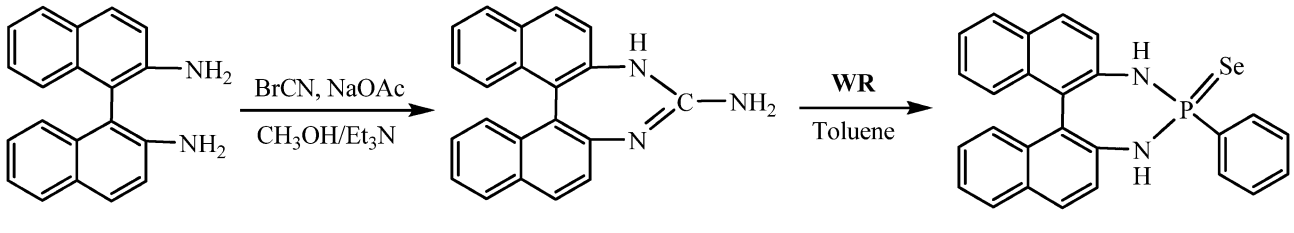
Scheme 2 Synthesis of five-membered S/NH–P(Se)–S heterocycles **4a** and **4b**.



5a E = E' = S
5b E = S, E' = Se
5c E = E' = Se

6a E = E' = S, 92%
6b E = S, E' = Se, 79%
6c E = E' = Se, 7%

Scheme 3 Synthesis of six-membered E–P(Se)–E (E, E′ = S, Se) heterocycles **6a–c**.



1e **7**, 81% **2e**, 90%

Scheme 4 Synthesis of **2e** *via* the reaction of 3*H*-dinaphtho[2,1-*d*:1′2′-*f*][1,3]diazepin-4-amine (**7**) with **WR**.

160(3)° is similar to that in the dimer pairs in the solid state structure of $NH(Ph_2PSe)_2$.[20] For compound **2b**, it can be seen from Fig. 2 that the molecule has approximate non-crystallographic mirror symmetry. For the structures of **2a** and **2b**, the five-membered rings (P–N–C–C–N) are essentially planar. The P═Se distances, 2.0927(10) Å for **2c**, 2.0804(16) Å for **2b**, are normal,[21–24] while the shortness of the P–N bond lengths (1.662(3), 1.690(3) Å for **2a**, 1.684(4), 1.678(5) Å for **2b**) suggests some multiple bond character. The X-ray structures of **2c** and **2e** whilst allowing confirmation of connectivity could not be refined well because of disorder issues and will not be discussed in detail.

The molecular structures of **4b** and **6a** (Fig. 3 and 4, Table 1) reveal a somewhat different structural motif. **4b** has a similar conformation to **2a** for the $P(Se)SNC_2$ heterocycle.

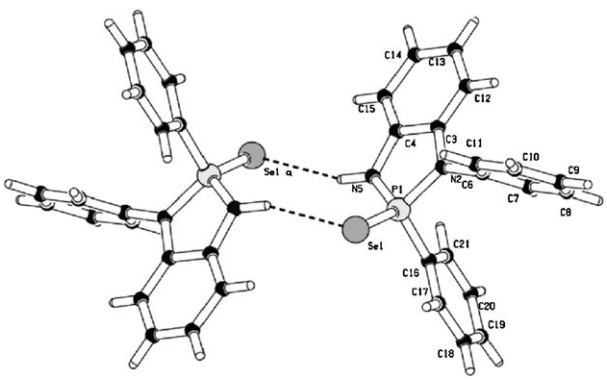


Fig. 1 The X-ray structure of **2a** illustrating the dimer pair H bonding. The additional "a" letter in the Se1a label indicates that this atom is at (1 − *x*,1 − *y*,2 − *z*). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.0927(10), P(1)–N(5) 1.662(3), P(1)–N(2) 1.690(3), P(1)–C(16) 1.801(4), N(2)–C(3) 1.400(4), N(5)–P(1)–N(2) 92.31(15), N(5)–P(1)–C(16) 107.79(16), N(2)–P(1)–C(16) 105.72(15), N(5)–P(1)–Se(1) 118.57(11), N(2)–P(1)–Se(1) 117.44(10), C(16)–P(1)–Se(1) 112.70(12), C(3)–N(2)–P(1) 112.2(2), C(4)–N(5)–P(1) 113.1(2).

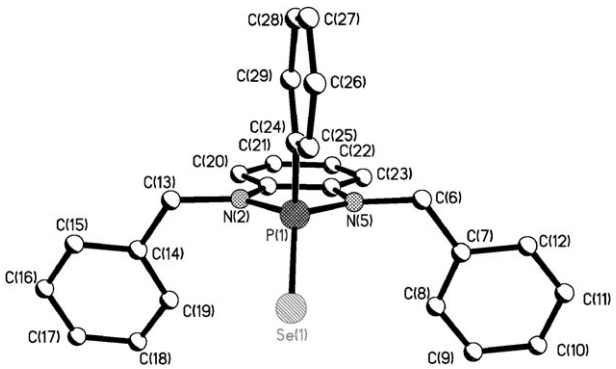


Fig. 2 The X-ray structure of **2b** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.0804(16), P(1)–N(5) 1.684(4), P(1)–N(2) 1.678(5), P(1)–C(24) 1.806(6), N(2)–C(3) 1.416(6), N(2)–P(1)–N(5) 91.2(2), N(2)–P(1)–C(24) 107.2(2), N(5)–P(1)–C(24) 106.2(2), N(2)–P(1)–Se(1) 118.20(16), N(5)–P(1)–Se(1) 117.75(16), C(24)–P(1)–Se(1) 113.65(18), C(3)–N(2)–P(1) 113.5(3), C(13)–N(2)–P(1) 123.1(3).

The six-membered $P(Se)S_2C_3$ ring in **6a** has a chair conformation. The exocyclic P(1)–Se(1) bond lengths in **4b** and **6a** [2.1021(6) and 2.0962(9) Å, respectively] are in good agreement with each other and are consistent with the related selenides containing P^V═Se bonds [2.08–2.12 Å].[19,21–24] The internal angle of S(1)–P(1)–S(2) being 102.28(5)° in **6a** shows significant distortion from ideal tetrahedral. We note that the internal angle of N(1)–P(1)–S(1) [94.23(7)°] in **4b** is slightly bigger than the value in the similar structure of **2a** [N(1)–P(1)–N(2) 92.31(15)°]. In **4b** adjacent molecules are linked by N–H···Se hydrogen bonds (NH(2)···Se(1)* 2.654(18), N···Se* 3.5368(19) Å N–H···Se* 163(2)°), where the * indicates that the Se atom is at 1 + *x*, *y*, *z* to form chain-like packing extending in the *a*-direction.

In conclusion, we have successfully applied Woollins' reagent, **WR**, to the synthesis of a series of novel five- to seven-membered heterocycles with an E–P(Se)–E′ (E, E′ = N,

Table 1 Details of the X-ray data collections and refinements for compounds **2a**, **2b**, **4b**, and **6a**

Compound	**2a**	**2b**	**4b**	**6a**
Formula	$C_{18}H_{15}N_2PSe$	$C_{26}H_{23}N_2PSe$	$C_{12}H_{10}NPSSe$	$C_{16}H_{11}PS_2Se$
M	369.25	473.39	310.20	377.32
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$
a/Å	9.108(2)	9.761(3)	5.3325(7)	8.5293(6)
b/Å	9.656(2)	10.318(3)	21.151(3)	9.9922(7)
c/Å	10.017(2)	12.940(4)	10.6495(15)	18.1201(12)
α	103.676(6)	112.187(10)	90	90
β	107.108(3)	95.998(13)	95.255(5)	94.3449(13)
γ	95.654(4)	109.128(14)	90	90
U/Å^3	804.6(3)	1100.6(6)	1196.1(3)	1539.87(18)
Z	2	2	4	4
μ/mm^{-1}	2.430	1.794	3.416	2.7992
Reflections collected	5691	6685	7419	15 498
Independent reflections	3086	3806	2150	3516
R_{int}	0.0397	0.0614	0.0224	0.0620
R_1; wR_2 [$I > 2\sigma(I)$]	0.0479; 0.0740	0.0642; 0.1219	0.0232; 0.0486	0.0465; 0.0888

S, Se) linkage from the selenation of difunctional aromatic substrates. Using ^{1}H, ^{31}P{1H}, ^{77}Se{1H} NMR spectroscopy and microanalysis or accurate mass measurements in conjunction with single-crystal X-ray crystallography, the structures of the novel heterocycles have been elucidated.

Experimental section

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 in $CDCl_3$ 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, and the University of St Andrews Mass Spectrometry Service.

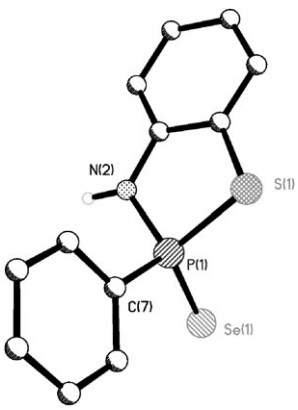


Fig. 3 The X-ray structure of **4b** (hydrogen atoms on phenyl rings omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.1021(6), S(1)–C(1) 1.772(2), S(1)–P(1) 2.1110(8), P(1)–N(2) 1.6671(19), P(1)–C(7) 1.803(2); C(1)–S(1)–P(1) 92.49(7), N(2)–P(1)–C(7) 105.77(10), N(2)–P(1)–Se(1) 117.15(7), C(7)–P(1)–Se(1) 113.71(7), N(2)–P(1)–S(1) 94.23(7), C(7)–P(1)–S(1) 107.81(7), Se(1)–P(1)–S(1) 116.09(3).

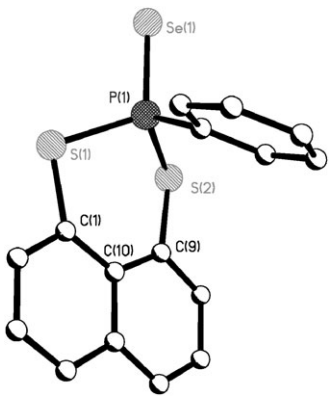


Fig. 4 The X-ray structure of **6a** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.0962(9), S(1)–P(1) 2.0750(12), S(1)–C(1) 1.793(3), S(2)–P(1) 2.0610(12), S(2)–C(9) 1.786(3), P(1)–C(11) 1.811(3), C(1)–C(10) 1.435(4), C(9)–C(10) 1.437(4); P(1)–S(1)–C(1) 101.04(11), P(1)–S(2)–C(9) 101.58(11), Se(1)–P(1)–S(1) 112.99(4), Se(1)–P(1)–S(2) 110.01(4), Se(1)–P(1)–C(11) 114.75(11), S(1)–P(1)–S(2) 102.28(5), S(1)–P(1)–C(11) 107.41(11), S(2)–P(1)–C(11) 108.60(11).

Syntheses

General procedure for the synthesis of 2a–e. A mixture of diamine (2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in 20 cm^{-3} of dry toluene was refluxed for 7 h. The red suspension disappeared and a grey solution formed along with a small amount of black elemental selenium. Upon cooling to room temperature and removing the solvent the residue was purified by column chromatography (silica gel, toluene as eluent) to give monophosphorus products **2a–e**.

2a. 190 mg as pale white solid in 51% yield. Mp 188–190 °C. Selected IR (KBr, cm^{-1}): 3259(m, NH), 1590(m), 1485(vs), 1377(m), 1297(m), 1249(s), 1183(m), 1100(s), 1024(m), 970(m), 897(m), 878(m), 738(s), 690(s), 568(s, P═Se). ^{1}H NMR ($CDCl_3$, δ), 7.99–7.90 (m, 2H, ArH), 7.45–7.32 (m, 3H, ArH), 7.30–7.22 (m, 2H, ArH), 7.22–7.18 (m, 2H, ArH),

6.85–6.77 (m, 4H, ArH), 6.50 (d, J(P,H) = 7 Hz, 2H, ArH), 5.29 (d, J(P,H) = 18 Hz, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, δ), 133.2, 132.7, 132.0 (d, ^3J(P,C) = 14 Hz), 129.7, 128.7, 128.3 (d, J(P,C) = 14 Hz), 127.8, 120.8 (d, ^3J(P,C) = 11 Hz), 111.2 (d, ^4J(P,C) = 8 Hz), 110.5 (d, ^4J(P,C) = 8 Hz) ppm. ^{31}P NMR ($CDCl_3$, δ), 75.5 (s, J(P,Se_{exo}) = 842 Hz) ppm. ^{77}Se NMR ($CDCl_3$, δ), −115.7 (d, J(P,Se_{exo}) = 842 Hz) ppm. MS (CI^+, m/z): 371 $[M + H]^+$. Accurate mass measurement (EIMS): 370.0133, calculated mass for $C_{18}H_{15}N_2PSe$: 370.0133.

2b. 306 mg as white solid in 65% yield. Mp 211–212 °C. Selected IR (KBr, cm^{-1}): 3056(w), 3017(w), 2892(w), 2843(w), 1595(m), 1492(vs), 1435(m), 1383(m), 1283(s), 1134(s), 1098(m), 1044(m), 911(m), 864(m), 735(s), 718(m), 688(m), 562(s, P═Se). ^{1}H NMR ($CDCl_3$, δ), 7.83 (dd, J(H,H) = 7.2 Hz, ^3J(P,H) = 15.3 Hz, 2H, ArH), 7.46 (m, J(H,H) = 7.2 Hz, 3H, ArH), 7.39–7.7.15 (m, 10H, ArH), 6.69 (dd, J(H,H) = 7.2 Hz, 2H, ArH), 6.54 (d, J(H,H) = 7.2 Hz, 2H, ArH), 4.68 (d, ^3J(P,H) = 15.8 Hz, 4H, NCH_2) ppm. ^{13}C NMR ($CDCl_3$, δ), 136.4 (J(P,C) = 3.1 Hz), 136.3 (d, J(P,C) = 106 Hz), 135.9, 135.7, 132.7, 132.0 (d, ^3J(P,C) = 14.5 Hz), 128.5, 128.4, 128.2, 127.4, 127.4, 120.1, 109.4 (d, J(P,C) = 6.2 Hz), 46.4 (d, ^3J(P,C) = 7.3 Hz) ppm. ^{31}P NMR ($CDCl_3$, δ), 84.7 (s, J(P,Se_{exo}) = 842 Hz) ppm. ^{77}Se NMR ($CDCl_3$, δ), −188.7 (d, J(P,Se_{exo}) = 842 Hz) ppm. MS (ES^+, m/z): 497 $[M + Na]^+$. Accurate mass measurement (EIMS): 470.0785, calculated mass for $C_{26}H_{23}N_2P^{76}Se$: 470.0786.

2c. 250 mg as milky white solid in 67% yield. Mp 195–197 °C. Selected IR (KBr, cm^{-1}): 3248(vs, NH), 1589(vs), 1359(s), 1107(m), 1057(s), 908(s), 809(s), 748(s), 683(s), 607(m, P═Se). ^{1}H NMR ($CDCl_3$, δ), 8.12 (m, J(H,H) = 7 Hz, 2H, ArH), 7.65–7.53 (m, 11H, ArH), 7.01 (d, J(H,H) = 7 Hz, 2H, ArH), 6.28 (d, J(P,H) = 13 Hz, 2H, NH) ppm. ^{13}C NMR ($CDCl_3$, δ), 139.1 (d, ^1J(P,C) = 107 Hz), 136.2, 135.9 (d, ^2J(P,C) = 52 Hz), 132.1, 130.6 (d, ^3J(P,C) = 13 Hz), 128.8 (d, ^3J(P,C) = 15 Hz), 127.4, 121.5, 111.9 (d, ^4J(P,C) = 7 Hz) ppm, ^{31}P NMR ($CDCl_3$, δ), 40.5 (s, J(P,Se_{exo}) = 817 Hz) ppm. ^{77}Se NMR ($CDCl_3$, δ), −182.1 (d, J(P,Se_{exo}) = 820 Hz) ppm. MS (CI^+, m/z): 373 $[M + H]^+$. Anal. calcd for $C_{18}H_{17}N_2PSe$ (372.03): C, 58.1; H, 4.6; N, 7.5%. Found: C, 58.4; H, 4.7; N, 7.3%.

2d. 402 mg as white solid in 96% yield. Mp 201–203 °C. The NMR spectra of ^{31}P and ^{77}Se showed that the product is a mixture of two diastereoisomers. Selected IR (KBr, cm^{-1}): 3168(s, NH), 1493(m), 1434(s), 1365(s), 1285(m), 1229(m), 1102(s), 753(s), 690(m), 584(m, P═Se). ^{1}H NMR (CD_2Cl_2, δ), 8.00–7.73 (2× m, 10H, ArH), 7.56–7.17 (2× m, 20H, ArH), 6.89 (2× d, J(P,H) = 8.6 Hz, 4H, NH) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C, δ), 136.2, 133.0, 132.5, 132.1, 131.9, 131.7, 129.5, 129.3, 129.0, 128.7, 128.3, 128.1, 127.9, 127.0, 126.7, 126.5, 126.1, 125.8, 125.5, 125.2, 124.9, 124.5, 124.4 ppm. ^{31}P NMR (CD_2Cl_2, δ), 83.5 (s, J(P,Se) = 805 Hz) ppm; 84.5 (s, J(P,Se) = 805 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −207.0 (d, J(P,Se_{exo}) = 805 Hz) ppm; −209.8 (d, J(P,Se_{exo}) = 805 Hz) ppm. Mass spectrum (EI^+): m/z 420 $[M + H]^+$, 217 $[M - C_6H_6NPSe]^+$. Anal. calcd for $C_{22}H_{17}N_2PSe$: C, 63.0; H, 4.1; N, 6.7%. Found: C, 63.3; H, 3.8; N, 6.6%.

2e. 460 mg as slightly pink white solid in 98% yield. Mp 198–199 °C. Selected IR (KBr, cm^{-1}): 3168 (vs, NH), 1617(m), 1599(m), 1505(s), 1433(s), 1362(s), 1220(m), 1102(m), 956(m), 815(s), 748(vs), 694(m), 574(m, P═Se). ^{1}H NMR (acetone-d_6, δ), 8.09–690 (m, 12H, ArH), 2.05 (s, 2H, NH) ppm. ^{13}C NMR (acetone-d_6, δ), 144.1, 134.2, 136.1, 129.1, 128.4, 127.8, 127.6, 127.2, 126.6, 126.2, 125.3, 124.7, 123.7, 118.5 ppm. ^{31}P NMR (acetone-d_6, δ), 82.5 (s, J(P,Se_{exo}) = 810 Hz) ppm. ^{77}Se NMR (acetone-d_6, δ), −193.5 (d, J(P,Se_{exo}) = 810 Hz). MS (CI^+, m/z): 470 $[M + H]^+$. Anal. calcd for $C_{26}H_{19}N_2PSe$ (469.38): C, 66.5; H, 4.1; N, 6.0%. Found: C, 66.1; H, 4.4; N, 6.3%.

4a. A toluene (10 cm^{-3}) refluxing mixture of 2-amino-benzenethiol (0.12 g, 1.0 mmol) and **WR** (0.54 g, 1.0 mmol) was carried out for 7 h. The red suspension disappeared and a black red suspension was formed. The mixture was dried *in vacuo* to remove toluene and the residue was dissolved in dichloromethane. The unique compound **7a** (160 mg, white solid) was obtained after fresh chromatographic purification (silica gel, dichloromethane as eluent) and crystallization from dichloromethane–hexane in 52% yield. Mp: 160–162 °C. Selected IR (KBr, cm^{-1}): 3211(s), 1579(m), 1470(s), 1454(m), 1438(m), 1368(s), 1293(m), 1260(m), 1096(s), 892(s), 743(vs), 687(m), 555(s), 489(m). ^{1}H NMR (CD_2Cl_2, δ), 8.08–7.98 (m, 2H, ArH), 7.57–7.43 (m, 3H, ArH), 7.23–7.20 (m, J(H,H) = 8.2 Hz, 1H, ArH), 7.13–7.06 (m, J(H,H) = 8.2 Hz, 1H, ArH), 6.93–6.87 (m, J(H,H) = 8.2 Hz, 2H, ArH), 5.68 (d, ^2J(P,H) = 13.5 Hz, 1H, NH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 138.7 (d, ^1J(P,C) = 93.4 Hz), 132.7 (d, ^4J(P,C) = 3.1 Hz), 131.2 (d, ^2J(P,C) = 14.5 Hz), 128.4 (d, ^2J(P,C) = 15.6 Hz), 126.7, 124.2 (d, ^3J(P,C) = 6.2 Hz), 121.8, 113.0, 112.9 ppm. ^{31}P NMR (CD_2Cl_2, δ), 74.4 (s, J(P,Se_{exo}) = 840 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −32.5 (d, J(P,Se_{exo}) = 842 Hz) ppm. Mass spectrum (EI^+): m/z 311 $[M]^+$, 231 $[M - Se]^+$, 154 $[M - C_6H_5Se]^+$. Anal. calcd for $C_{12}H_{10}NPSSe$: C, 46.5; H, 3.3; N, 4.5%. Found: C, 46.7; H, 3.1; N, 4.7%.

4b. A mixture of 4-methyl-1,2-benzenedithiol (66.0 mg, 0.5 mmol) and **WR** (270 mg, 0.5 mmol) in toluene (20 cm^{-3}) was refluxed for 7 h. The red suspension disappeared and a reddish yellow solution was formed. Upon cooling to RT, the mixture was dried *in vacuo*. The residue was dissolved in dichloromethane and was purified by column chromatography (silica gel, dichloromethane as eluent) to afford compound **7b** (100 mg) as greenish yellow paste in 59% yield. Mp: 150–151 °C. Selected IR (KBr, cm^{-1}): 3215(m), 2935(m), 1576(m), 1472(s), 1439(m), 1366(s), 1294(m), 1096(s), 895(s), 742(vs), 685(m), 554(s), 490(m). ^{1}H NMR (CD_2Cl_2, δ), 8.20–8.10 (m, 2H, ArH), 7.54–7.43 (m, 3H, ArH), 7.27–7.20 (m, 2H, AeH), 7.02–6.99 (m, 1H, ArH), 2.29 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, δ), 138.2, 136.7, 135.8, 135.6, 133.0, 132.9, 131.0 (d, ^2J(P,C) = 13.5 Hz), 128.7, 128.6, 128.5, 126.2 (d, ^3J(P,C) = 8.3 Hz), 125.4 (d, ^3J(P,C) = 8.3 Hz), 20.9 ppm. ^{31}P NMR (CD_2Cl_2, δ), 71.3 (s, J(P,Se_{exo}) = 836 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −34.6 (d, J(P,Se_{exo}) = 835 Hz) ppm. Mass spectrum (EI^+): m/z 342 $[M]^+$, 294 $[M - Se]^+$.

Anal. calcd for $C_{13}H_{11}PS_2Se$: C, 45.8; H, 3.3%. Found: C, 46.0; H, 3.5%.

General procedure for the synthesis of 6a–c. A mixture of naphtho[1,8-*cd*][1,2]dithiole, naphtho[1,8-*cd*][1,2]selenole, or naphtho[1,8-*cd*][1,2]thioselenole (2.0 mmol) and **WR** (0.54 g, 1.0 mmol) in 20 cm^{-3} of dry toluene was stirred at room temperature for 7 h, the red suspension stayed unchanged. Then the mixture was refluxed for 7 h. The red suspension disappeared and a solution with some black selenium precipitate formed. Upon cooling to room temperature and removing the solvent, the residue was purified by column chromatography (silica gel, toluene as eluent) to give compounds **6a–c**.

6a. 348 mg as white solid in 92% yield. Mp: 154–155 °C. Selected IR (KBr, cm^{-1}): 1545(m), 1477(w), 1432(m), 1330(w), 1198(w), 1154(w), 1093(s), 813(s), 749(s), 576(s), 566(s, P═Se). ^{1}H NMR (CD_2Cl_2, δ), 7.88 (dd, J(P,H) = 16.5 Hz, J(H,H) = 7.4 Hz, 2H, ArH), 7.70 (d, J(H,H) = 7.4 Hz, 1H, ArH), 7.60 (dd, J(H,H) = 7.4 Hz, 2H, ArH), 7.43 (d, J(H,H) = 8.0 Hz, 2H, ArH), 7.32 (m, 2H, ArH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 135.9, 134.9 (d, J(P,C) = 73 Hz), 132.5 (d, J(P,C) = 3.1 Hz), 131.0 (d, J(P,C) = 7.3 Hz), 130.6, 130.5, 13.4, 128.9 (d, J(P,C) = 14.5 Hz), 126.3 ppm. ^{31}P NMR (CD_2Cl_2, δ), 21.7 (s, J(P,Se_{exo}) = 810 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −81.2 (d, J(P,Se_{exo}) = 810 Hz) ppm. Mass spectrum (EI^+): m/z 378 $[M]^+$, 298 $[M - Se]^+$, 190 $[M - C_6H_5PSe]^+$. Mass spectrum (CI^+): 379 $[M + H]^+$. Anal. calcd for $C_{16}H_{11}PS_2Se$: C, 50.9; H, 2.9%. Found: C, 50.4; H, 2.8%.

6b. 335 mg as pale brown solid in 79% yield. Mp: 130–131 °C. Selected IR (KBr, cm^{-1}): 1543(w), 1431(w), 1151(w), 1090(m), 811(m), 748(s), 686(m), 568(vs, P═Se), 548(P-Se). ^{1}H NMR (CD_2Cl_2, δ), 7.94–7.60 (m, 6H, ArH), 7.41–7.33 (m, 5H, ArH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.1 (d, J(P,C) = 63.4 Hz), 132.5, 132.4, 132.3, 131.9 (d, J(P,C) = 7.3 Hz), 131.4, 130.8, 130.7, 130.5128.8 (d, J(P,C) = 14.5 Hz), 126.4, 126.1 ppm. ^{31}P NMR (CD_2Cl_2, δ), 3.7 (s, J(P,Se_{exo}) = 798 Hz, J(P,Se_{endo}) = 390 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 502.6 (d, J(P,Se_{endo}) = 390 Hz), −50.9 (d, J(P,Se_{exo}) = 799 Hz) ppm. Mass spectrum (EI^+): m/z 424 $[M]^+$, 237 $[M - C_6H_5PSe]^+$. Anal. calcd. for $C_{16}H_{11}PSSe_2$: C, 45.3; H, 2.6%. Found: C, 45.4; H, 2.9%.

6c. 33 mg as yellow solid in 7% yield. Mp: 90–91 °C. ^{1}H NMR (CD_2Cl_2, δ), 8.01–7.92 (m, 5H, ArH), 7.51–7.47 (m. 4H, ArH), 7.25–7.10 (m, 2H, ArH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 138.0, 132.2, 131.3, 130.3, 130.1, 129.9, 128.6, 128.4 ppm. ^{31}P NMR (CD_2Cl_2, δ), 76.6 (s, J(P,Se_{exo}) = 819 Hz), J(P,Se_{endo}) = 439 Hz ppm. ^{77}Se NMR (CD_2Cl_2, δ), 386.9 (d, J(P,Se_{endo}) = 441 Hz), −26.0 (d, J(P,Se_{exo}) = 820 Hz) ppm. Mass spectrum (EI^+): m/z 472 $[M]^+$, 286 $[M - C_6H_5PSe]^+$. Anal. calcd for $C_{16}H_{11}PSe_3$: C, 40.8; H, 2.4%. Found: C, 41.1; H, 2.5%.

Preparation of 3*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3]diazepin-4-amine (7). To a solution of 1,1′-binaphthyl-2,2′-diamine **1e** (1.00 g, 3.5 mmol) and 2.40 g of NaOAc in 50 cm^{-3} of dry methanol and 20 cm^{-3} of Et_3N was added 3.4 cm^{-3} of BrCN (3 M in dichloromethane, 10 mmol). The reaction mixture was stirred for 2 h at 0 °C, and then at room temperature for 70 h to give a white suspension. The solvent was removed under vacuum, and the residue was extracted by dichloromethane–H_2O (300 cm^{-3}, 1 : 1 ratio) to give two layers of liquid, an organic layer and an aqueous solution. The organic layer was dried over $MgSO_4$, filtered and rotary evaporated to give crude product (a white solid). The crude product was purified on silica gel (1 : 9 = ethyl acetate–dichloromethane as eluent) to afford 1.06 g as a grey green solid. Re-crystallization from dichloromethane–hexane gave **7** as grey green needles. Yield: 98%. Selected IR (KBr, cm^{-1}): 3048(w), 1619(vs, C═N), 1508(m), 1430(m), 1380(m), 1348(m), 1280(m), 1210(m), 1145(m), 1092(m), 1022(m), 922(w), 816(s), 748(s). ^{1}H NMR ($CDCl_3$, δ), 7.82–7.78 (m, 2H, ArH), 7.22–7.02 (m, 11H, ArH), 5.28(s, 1H, NH), 3.67 (br s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, δ), 142.8, 133.8, 129.6, 128.6, 128.3, 126.9, 124.1, 122.5, 118.4, 112.7, 45.9 ppm. MS (CI^+, m/z): 310 $[M + H]^+$. Anal. calcd for $C_{21}H_{15}N_3$ (309.36): C, 81.53; H, 4.89; N, 13.58%. Found: C, 81.45; H, 4.92; N, 13.67%.

Reaction of compound 7 with WR. A mixture of 3*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3]diazepin-4-amine **7** (0.31 g, 1.0 mmol) and **WR** (0.27 g, 0.5 mmol) in 20 cm^{-3} of dry toluene was heated to reflux for 30 min. The red suspension turned orange. Upon cooling to room temperature and removal of the solvent, the residue was extracted by ethyl acetate and purified by silica gel (1 : 1 ethyl acetate–dichloromethane as eluent) to give **2e** as a pinkish white solid (190 mg) in 81% yield based on **WR**.

X-Ray structure determinations. X-Ray crystal data for compounds **2a**, **2b** and **4b** were collected at 93 K using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Data for **6a** were collected using the St Andrews Robotic diffractometer (Saturn724 CCD) at 125 K with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å).[25,26] 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.[27] Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

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