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Symmetrical spiro-phosphoroheterocycles from the selenation of carbohydrazides

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ABSTRACT

2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (Woollins' reagent) reacts with benzoic hydrazides in refluxing toluene to give new symmetrical spiro heterocycles in 48–76% isolated yields. However, under identical conditions, treating Woollins' reagent with thiophene-2-carbohydrazide leads to an additional product, 1,3,4-selenadiazole (27% yield) together with the spiro phosphorus heterocycle in 44% yield. Three representative X-ray structures are reported.

Phosphorus-containing heterocycles continue to attract considerable attention, in part due to their large variety of interesting pharmacological and biological activities, such as herbicidal, insecticidal, antibacterial, antifungal and anticancer.[1–4] 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [{PhP(Se)(μ-Se)}$_2$, Woollins' reagent (WR)] has become a very useful selenium source or selenation reagent in synthetic chemistry[5–15] because of its ready preparation and ease of handling.[16] As part of our studies aimed at the reactivity of Woollins' reagent towards different organic substrates, herein, we report the preparation of a series of novel spiro organophosphorus heterocycles via the selenation of carbohydrazides with Woollins' reagent.

Woollins' reagent reacted with 2 equiv of benzohydrazides in refluxing toluene for 4 h. During this period the red suspension gradually disappeared and a pale yellow solution was formed with precipitation of small amounts of grey elemental selenium. Upon cooling to room temperature the solution was passed through a silica gel column. The fractions containing the product were combined and concentrated in vacuum to give the air- and moisture-stable compounds **1**–**4** in 48–76% isolated yields (Scheme 1).

Interestingly, treating Woollins' reagent with 2 equiv of thiophene-2-carbohydrazide under identical conditions led to 1,3,4-selenadiazole **5** in 27% yield along with spiro phosphorus heterocycle **6** in 44% yield after work-up in air (Scheme 2). We have previously noted that reaction of 1,2 diacylhydrazines with Woollins' reagent leads to 2,5-disubstituted 1,3,4-selenadiazoles[10] and so the formation of **5** is not surprising.

A possible reaction pathway for the formation of compounds **1**–**4** and **6** proceeds via two step-wise nucleophilic substitutions in which the selenium atoms in Woollins' reagent are replaced twice by nitrogen and oxygen atoms from the carbohydrazide. The lack of selenation of the carbonyl group suggests that the hydrazide attacks phosphorus through nitrogen first, rather than through the carbonyl oxygen. At elevated temperatures WR is believed to be in equilibrium with a diselenaphosphorane ($PhPSe_2$) intermediate **A**, which can be considered to be the reactive species in refluxing solution. First, the reaction of **A** with one molecule of carbohydrazide affords intermediate **B** via a nucleophilic substitution followed by an intramolecular proton transfer. Intermediate **C** (the tautomer of intermediate **B**) cyclizes and loses a molecule of H_2Se to afford **D**, which undergoes another nucleophilic substitution with a second molecule of carbohydrazide, followed by an intramolecular proton transfer to generate **E**. Intermediate **F** (the tautomer of intermediate **E**) cyclizes by eliminating a molecule of H_2Se to give stable compounds **1**–**4** or **6** (Scheme 3).

Reaction of Woollins' reagent with one equimolar equivalent of benzohydrazine was performed under identical conditions to investigate if intermediate **D** could be isolated or was stable. Unfortunately, the same compounds **1**–**4** and **6** were isolated as the only products with much lower yields (ca. 25–35%) rather than intermediate **D**.

The release of H_2Se in the above reactions was observed in the bubbler (the formation of dark Se due to the decomposition of the

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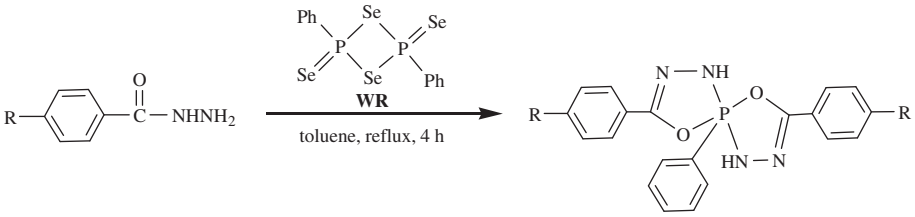
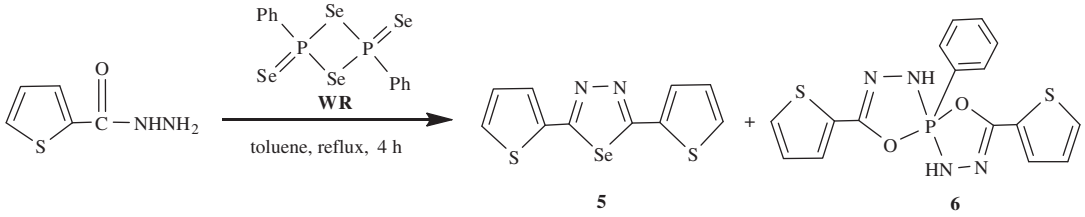
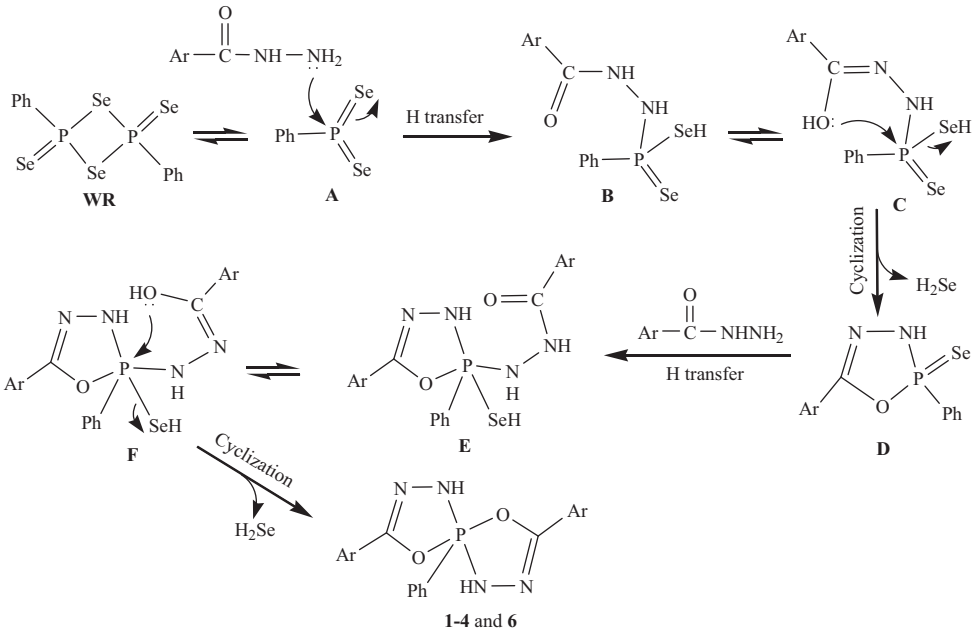


Scheme 1. Formation of spiro phosphorus heterocycles **1–4** from the selenation of benzohydrazines.



Scheme 2. Formation of compounds **5** and **6** from the selenation of thiophene-2-carbohydrazide.



Scheme 3. Possible reaction pathway for the formation of compounds **1–4** and **6**.

H_2Se) and could be trapped by sodium hydroxide as sodium selenate ($NaSeO_4$) after the bubbler.

The proposed structures of **1–6** are based on their spectral analysis and accurate mass measurement. Compounds **3**, **5** and **6** were further characterised by single crystal X-ray structure determination. Compounds **1–6** are stable to air and moisture for several months without any apparent visible decomposition. All compounds showed the anticipated $[M]^+$ or $[M+H]^+$ peak in their mass spectra. The IR spectra of compounds **1–4** and **6** displayed $\nu_{(C=N)}$ vibrations in the range of 1397–1485 cm^{-1}, with $\nu_{(P-O)}$ in the range of 1054–1097 cm^{-1} and $\nu_{(P-N)}$ in the range of 660–710 cm^{-1} being comparable with related heterocycles.[17,18] The absence of $\nu_{(C=O)}$ (1599–1637 cm^{-1}) and the presence of the typical ^{13}C NMR signals in the range of 142.2–164.6 ppm for the C=N double bond and the ^{31}P NMR spectra comprising only a singlet in the range of −37.1 to 35.0 ppm support the proposed formulation of these spiro heterocyclic systems. For **5**, the $\nu_{(C=N)}$ vibrations were observed at 1449 and 1406 cm^{-1}. The presence of the typical ^{13}C NMR signal at 164.1 ppm for the C=N double bond and ^{77}Se NMR signal at 689.6 ppm (similar to related structures[10]) confirmed the formation of the five-membered C–N–N–C–Se ring.

Compounds **3**, **5** and **6** were crystallized by slow diffusion of dichloromethane solutions into hexane to give colourless crystals of **3** and **6**, and brown crystals of **5**. The X-ray structures of **3** and **6** (Figs. 1 and 2) confirm the presence of the spiro heterocyclic rings, best described as existing in a 'T' stage conformation. The two newly formed phosphorus–nitrogen heterocycles in **3** or **6** have symmetrical (**6**) or near-symmetrical (**3**) configuration about the phosphorus–phenyl ring axis. Each phosphoroheterocycle is almost co-planar with the toluene ring or furan ring, the two rings

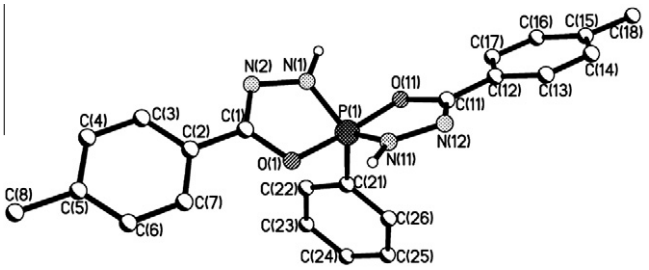


Figure 1. Single crystal X-ray structure of compound **3** (hydrogen atoms bound to carbon omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): P(1)–N(1) 1.652(4), P(1)–N(11) 1.650(4), P(1)–O(1) 1.739(2), P(1)–O(11) 1.720(2), O(1)–C(1) 1.355(5), O(11)–C(11) 1.356(5), C(1)–N(2) 1.309(5), C(11)–N(12) 1.288(5), N(1)–N(2) 1.398(4), N(11)–N(12) 1.403(4); N(1)–P(1)–N(11) 128.74(16), N(1)–P(1)–O(1) 86.51(15), N(11)–P(1)–O(11) 86.56(16), O(1)–P(1)–O(11) 172.05(11), C(1)–O(1)–P(1) 111.1(2), C(11)–O(11)–P(1) 111.9(2), N(12)–N(11)–P(1) 117.6(3), N(2)–N(1)–P(1) 118.3(3), N(2)–C(1)–O(1) 117.2(3), N(12)–C(11)–O(11) 116.6(3), C(1)–N(2)–N(1) 106.3(3), C(11)–N(12)–N(11) 107.3(3).

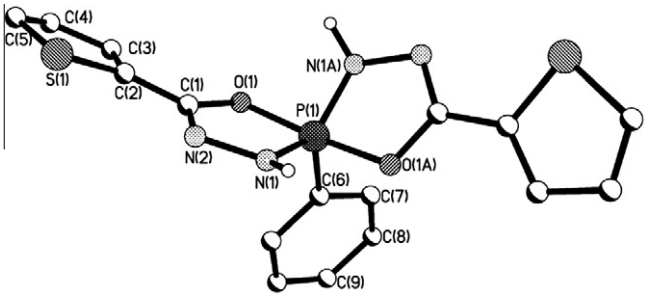


Figure 2. Single crystal X-ray structure of compound **6** (hydrogen atoms bound to carbon, and the minor occupancy form of the disordered thiophene ring omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): P(1)–N(1) 1.653(3), P(1)–O(1) 1.734(3), N(1)–N(2) 1.409(5), O(1)–C(1) 1.332(5), C(1)–N(2) 1.290(5); P(1)–N(1)–N(2) 117.7(3), N(1)–P(1)–N(1A) 128.6(3), N(1)–P(1)–O(1) 86.34(15), O(1)–P(1)–O(1A) 173.1(2), C(1)–O(1)–P(1) 111.2(2), N(2)–C(1)–O(1) 118.6(4), C(1)–N(2)–N(1) 105.8(3).

being inclined by 16.1° in **3** and 4.9° and 3.0° in **6**, while the planes of the phosphoroheterocycles are inclined by 46.2° in **3** and 56.9° in **6**. The P–N bond distances [1.650(4) and 1.652(4) Å in **3**, 1.653(3) Å in **6**] are shorter than those observed in the aminophosphazenes, $N_4P_4(NMe_2)_8$ [1.69(1) Å][19] or $N_4P_4(NC_4H_8)_8$ [1.677(7) Å],[20] however, they are marginally longer than those in spiro cyclic phosphorus rings [mean: 1.626(12) Å].[21] The P–O bonds [1.720(2) and 1.739(2) Å in **3**, 1.734(3) Å in **6**] are significantly longer than those in the 1,3,2-dioxaphosphocine rings [mean: 1.567 Å][22] and those observed in the five-co-ordinate phosphorus compound (C_6H_{11}-NH)P{[O-4,6-(*t*-Bu)$_2$-C_6H_2]$_2$$CH_2$}(1,2-$O_2C_6H_4$)·0.5 Et_2O [mean: 1.632 Å], or in the three-co-ordinate derivative ($C_6H_{11}NH$)P{[O-4,6-(*t*-Bu)$_2$–C_6H_2]$_2$$CH_2$} [mean: 1.666 Å].[21] The geometry about the phosphorus atom in the plane defined by the phosphoroheterocycles [N(1)–P(1)–N(11) 128.74(16)° and O(1)–P(1)–O(11) 172.05(11)° in **3**, N(1)–P(1)–N(1A) 128.6(3)° and O(1)–P(1)–O(1A) 173.1(2)° in **6**] is intermediate between square pyramidal and trigonal bipyramidal, but tends towards the latter. Both **3** and **6** show the same general hydrogen-bonding motif, with a pair of hydrogen bonds between the protonated and nonprotonated nitrogen in adjacent molecules. This results in the formation of one-dimensional hydrogen-bonded chains, running along the *b*- (**3**) and *c*-axes (**6**). While this general motif is seen in both compounds, there are differences in the overall arrangement of the chains. In **3** the chains are nearly planar, and all the phenyl rings project from the same side of the chain, whereas in **6** the chain adopts a more zigzag form, and the orientation of the molecules is such that the phenyl rings alternate in the direction they project from the chain.

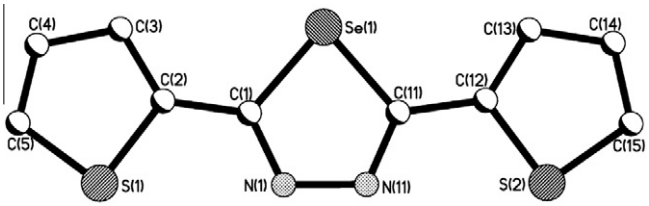


Figure 3. Single crystal X-ray structure of compound **5** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–C(1) 1.881(8), Se(1)–C(11) 1.876(8), C(1)–N(1) 1.314(10), C(11)–N(11) 1.300(10), N(1)–N(11) 1.372(9); C(1)–Se(1)–C(11) 81.9(4), Se(1)–C(1)–N(1) 113.6(6), Se(1)–C(11)–N(11) 115.2(7), C(1)–N(1)–N(11) 115.4(7), C(11)–N(11)–N(1) 113.9(7).

The X-ray structure of **5** (Fig. 3) shows the formation of a new five-membered ring compound, a bis-thiophene-substituted 1,3,4-selenadiazole. The C_2N_2Se ring is approximately co-planar with the two thiophene substituents, with angles between the ring-planes of 3.1° and 4.2°. The C–Se bond lengths [1.876(8) and 1.881(8) Å] are similar to those in the 2,5-diarylselenophenes (ca. 1.86–1.89 Å),[12] although they are slightly shorter than those observed in related structures containing single C–Se bonds (ca. 1.92–1.94 Å),[23,24] indicating a degree of delocalisation. However, the C–Se–C angle [81.9(4)°] is considerably smaller than those [ca. 87.7(7)–88.7(10)°] in 2,5-diarylselenophenes.[13]

In conclusion, the selenation of carbohydrazides to give a series of new symmetrical spiro-phosphoroheterocycles were effectively achieved using Woollins' reagent under mild conditions in moderate to high yields.[27]

Acknowledgments

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27. *Compound* **1**: 0.090 g as a white solid in 48% yield. Mp 240–242 °C. Selected IR (KBr, cm^{-1}): 1608(w), 1547(m), 1485(s), 1446(m), 1333(m), 1069(s), 782(m), 710(s), 687(s). ^{1}H NMR (CD_2Cl_2, δ), 8.13–8.11 (m, 6H, ArH), 7.93 (d, 2H, NH, ^2J(P,H) = 43 Hz), 7.55–7.49 (m, 9H, ArH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 164.6 (d, J(P,C) = 11.4 Hz, C=N), 131.7, 131.1, 129.2, 128.7, 128.4, 126.9, 125.3, 124.1 ppm. ^{31}P NMR (CD_2Cl_2, δ), −37.1 ppm. MS (EI$^+$, m/z), 376 [M]$^+$. HRMS [CI$^+$, m/z]: 377.1161 [M+H]$^+$, calculated mass for $C_{20}H_{18}O_2N_4P$: 377.1162.
Compound **2**: 0.153 g as a white solid in 58% yield. Mp 254–256 °C. Selected IR (KBr, cm^{-1}): 1613(m), 1594(m), 1491(s), 1397(m), 1333(vs), 1130(m), 1101(m), 1071(s), 1035(s), 1012(m), 896(m), 828(m), 733(m), 719(m), 694(s), 660(s), 480(m). ^{1}H NMR (THF-d_8, δ), 8.22 (d, 2H, NH ^2J(P,H) = 46 Hz), 7.67–7.63 (m, 4H, ArH), 7.53–7.49 (m, 5H, ArH), 7.35 (m, 4H, ArH) ppm. ^{13}C NMR (THF-d_8, δ), 154.0 (d, J(P,C) = 11.3 Hz, C=N), 138.1, 131.3, 130.0, 128.8, 128.5, 128.3, 128.2, 128.1, 127.9, 126.8, 123.3 ppm. ^{31}P NMR (THF-d_8, δ), −35.6 ppm. MS (EI$^+$, m/z), 532 [M]$^+$, 534 [M]$^+$, 379 [M-PhBr]$^+$. HRMS [EI$^+$, m/z]: 531.99293 [M]$^+$, calculated mass for $C_{20}H_{15}O_2{}^{79}Br_2N_4P$: 531.9294.
Compound **3**: 0.055 g as a yellow solid in 54% yield. Mp 242–244 °C. Selected IR (KBr, cm^{-1}): 1656(m), 1421(s), 1389(m), 1233(m), 1233(m), 1097(s), 829(m), 690(s). ^{1}H NMR (CD_2Cl_2, δ), 8.01–7.81 (m, 5H, ArH), 7.49 (d, 2H, NH ^2J(P,H) = 44 Hz), 7.36–7.30 (m, 4H, ArH), 7.18–7.14 (m, 4H, ArH), 2.33 (s, 6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, δ), 142.4 (d, J(P,C) = 11.4 Hz, C=N), 129.8, 129.4, 129.1, 128.5, 127.5, 126.7, 125.3, 121.4 ppm. ^{31}P NMR (CD_2Cl_2, δ), −37.4 ppm. MS (EI$^+$, m/z), 404 [M]$^+$. HRMS [CI$^+$, m/z]: 405.1478 [M+H]$^+$, calculated mass for $C_{22}H_{22}O_2N_4P$: 405.1475.
Compound **4**: 0.175 g as a white solid in 76% yield. Mp 243–245 °C. Selected IR (KBr, cm^{-1}): 1613(m), 1594(m), 1490(m), 1397(s), 1333(vs), 1130(s), 1101(m), 1071(s), 1035(s), 1011(m), 894(m), 827(m), 732(m), 660(s), 479(m). ^{1}H NMR (DMSO-d_6, δ), 9.01 (d, 2H, NH ^2J(P,H) = 47 Hz), 7.82–7.58 (m, 9H, ArH), 7.53–7.37 (m, 4H, ArH) ppm. ^{13}C NMR (DMSO-d_6, δ), 154.1 (d, J(P,C) = 11.4 Hz, C=N), 141.3, 138.1, 132.2, 131.4, 130.9, 129.5, 129.2, 128.9, 128.8, 128.6, 127.4, 125.9, 123.7 ppm. ^{31}P NMR (DMSO-d_6, δ), −35.0 ppm. MS (EI$^+$, m/z), 466 [M]$^+$. HRMS [CI$^+$, m/z]: 467.0862 [M+H]$^+$, calculated mass for $C_{20}H_{16}O_6N_6P$: 467.0869.
Compound **5**: 0.080 g as a pale yellow solid in 27% yield. Mp 174–176 °C. Selected IR (KBr, cm^{-1}): 1536(m), 1449(s), 1406(s), 1236(m), 1078(m), 1048(m), 831(s), 691(vs). ^{1}H NMR (CD_2Cl_2, δ), 7.52 (d, J(H,H) = 6.3 Hz, 2H, Thioph-H), 7.35 (d, J(H,H) = 6.3 Hz, 2H, Thioph-H), 7.13 (dd, J(H,H) = 6.3 Hz, 2H, Thioph-H) ppm. ^{13}C NMR (CD_2Cl_2, δ), 164.1 (C=N), 129.7, 128.1, 127.6, 127.5 ppm. ^{77}Se NMR (CD_2Cl_2, δ), 689.6 ppm. MS (CI$^+$, m/z), 298 [M+H]$^+$. HRMS [CI$^+$, m/z]: 298.9220 [M+H]$^+$, calculated mass for $C_{10}H_7N_2S_2Se$: 298.9216.
Compound **6**: 0.171 g as a pale white solid in 44% yield. Mp 202–204 °C. Selected IR (KBr, cm^{-1}): 1610(m), 1527(m), 1439(s), 1360(s), 1349(m), 1323(m), 1054(s), 1027(m), 851(m), 697(s). ^{1}H NMR (CD_2Cl_2, δ), 7.81 (d, J(H,H) = 6.3 Hz, 2H, Thioph-H), 7.58 (d, J(H,H) = 6.3 Hz, 2H, Thioph-H), 7.42–7.35 (m, 5H, ArH), 7.19 (d, J(H,H) = 6.3 Hz, 2H, Thioph-H), 7.02 (d, 2H, NH ^2J(P,H) = 47 Hz) ppm. ^{13}C NMR (CD_2Cl_2, δ), 157.5 (d, ^2J(P,C) = 11.4 Hz, C=N), 131.2, 130.9, 130.3, 129.9, 128.8, 128.7, 128.3, 127.6, 127.5, 127.1, 125.0 ppm. ^{31}P NMR (CD_2Cl_2, δ), −37.1 ppm. MS (EI$^+$, m/z), 388 [M]$^+$, 111 [M-$C_{11}H_{11}N_4OS$]$^+$. HRMS [CI$^+$, m/z]: 389.0291 [M+H]$^+$, calculated mass for $C_{16}H_{14}O_2N_4PS_2$: 389.0290.

X-ray crystal data for compounds **3**, **5** and **6** were collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All the 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 (SHELXTL[25]or Superflip[26]) and refined by full-matrix least-squares against F^2 using the programme SHELXTL.[25] Hydrogen atoms bound to carbon were assigned riding isotropic displacement parameters and constrained to idealized geometries, whereas those bound to nitrogen were located from the difference Fourier map and refined isotropically subject to a distance restraint. The thiophene in **6** was found to be disordered, with occupancies of 0.7:0.3, the lower occupancy component was refined anisotropically. Both components were subject to distance restraints. CCDC-818632–818634 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://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.

Crystal data for compound **3**: $C_{22}H_{21}N_4O_2P$, M = 404.40, monoclinic, space group $P2_1$, a = 11.457(4) Å, b = 6.074(2) Å, c = 15.495(6) Å, β = 107.218(9)°, U = 1029.9(7) Å^3, Z = 2, μ = 0.16 mm^{-1}, 7292 reflections collected, 3544 independent reflections, R_{int} = 0.099, final R indices [$I > 2\sigma(I)$] R_1 = 0.058, wR_2 (all data) = 0.133. CCDC 818632.

Crystal data for compound **5**: $C_{10}H_6N_2S_2Se$, M = 297.25, monoclinic, space group $P2_1/c$, a = 6.227(3) Å, b = 9.516(4) Å, c = 18.225(7) Å, β = 95.951(11)°, U = 1074.1(7) Å^3, Z = 4, μ = 3.85 mm^{-1}, 6238 reflections collected, 2216 independent reflections, R_{int} = 0.097, final R indices [$I > 2\sigma(I)$] R_1 = 0.072, wR_2 (all data) = 0.182. CCDC 818633.

Crystal data for compound **6**: $C_{16}H_{13}N_4O_2PS_2$, M = 388.39, monoclinic, space group C2/c, a = 18.561(6) Å, b = 8.563(3) Å, c = 11.118(4) Å, β = 91.951(15)°, U = 1766.1(10) Å^3, Z = 4, μ = 0.41 mm^{-1}, 5000 reflections collected, 1755 independent reflections, R_{int} = 0.058, final R indices [$I > 2\sigma(I)$] R_1 = 0.091, wR_2 (all data) = 0.207. CCDC 818634.