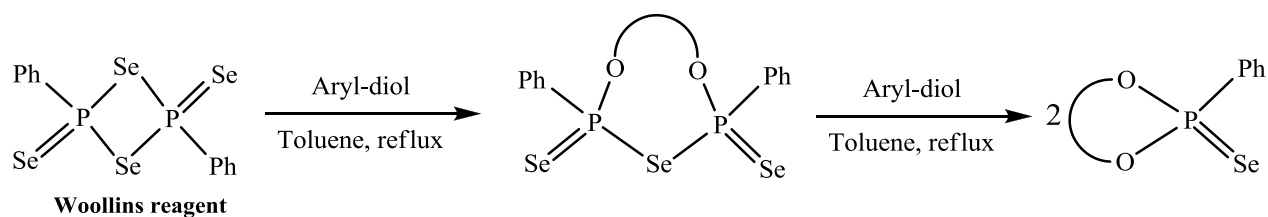


Novel Five- to Ten-Membered Organoselenium Heterocycles from the Selenation of Aromatic Diols

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

A series of new five- to ten-membered organoselenium heterocycles can be readily prepared by the selenation of aromatic diols to give large ring diphosphorus species which undergo ring contraction and elimination of H₂Se to give the corresponding small ring monophosphorus species by reaction with a second equivalent of aromatic diol.



(C = C₆H₄-1,2-isomer; Naphthacyl-2,3; 1,1'-Methylenebis(naphthalen-2); 2,2'-methylenebis(4-chlorobenzen-1)

Novel Five- to Ten-Membered Organoselenium Heterocycles from the Selenation of Aromatic Diols

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

School of Chemistry, University of St Andrews, Fife, KY16 9ST, UK

*Corresponding author. Tel.: (+44)-1334-463384; email: jdw3@st-and.ac.uk

Reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [$\{\text{PhP}(\text{Se})(\mu\text{-Se})\}_2$], *Woollins' Reagent*, **WR**, with aromatic diols in refluxing toluene afforded a series of novel five- to ten-membered phosphorus-selenium heterocycles **1 - 10** with an O-P(Se)-O or O-P(Se)-Se-P(Se)-O or O-P(Se)-O-P(Se)-O linkage in 12 - 74% isolated yields. It was found that the diphosphorus species O-P(Se)-Se-P(Se)-O rings could be readily reduced into the monophosphorus species O-P(Se)-O rings in almost quantitative yields *via* further reaction with another equivalent of corresponding aromatic diol. All new compounds have been characterized by IR, ^1H NMR, ^{13}C NMR, ^{31}P NMR, ^{77}Se NMR, mass spectrometry and elemental analysis or accurate mass measurement. Seven representative X-ray structures are reported.

Key words: Woollins' reagent; Aromatic diol; Phosphorus-selenium heterocycle; Organoselenium compound; X-ray structure.

Introduction

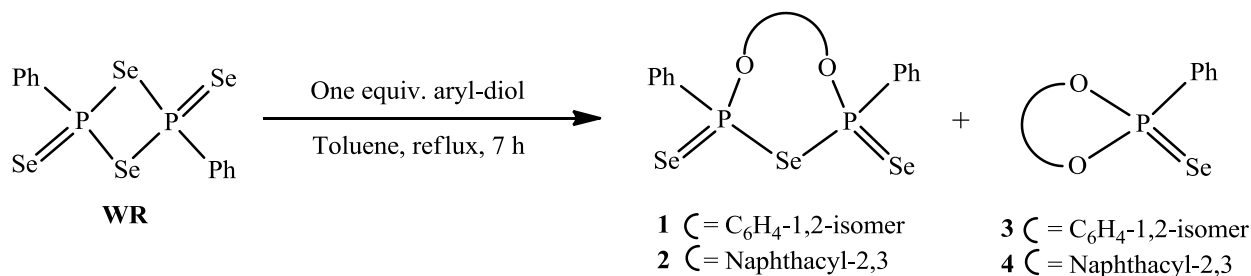
Organoselenium heterocyclic compounds have attracted considerable interest in the past several decades due to their unique properties¹ and applications as potential pharmaceuticals,² new materials³ as well as reagents and catalysts.⁴ However, the synthesis of selenium-containing organic heterocycles is not always easy due to the inconvenience of typical selenium reagents such as H_2Se , NaHSe , $(\text{Me}_3\text{Si})_2\text{Se}$, potassium selenocyanate and tetraethylammonium tetraselenotungstate $[\text{Et}_4\text{N}]_2\text{WSe}_4$, each exhibiting its own problems including toxicity, solubility, difficulty in handling and poor reactivity. 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [$\{\text{PhP}(\text{Se})(\mu\text{-Se})\}_2$], *Woollins' Reagent*, **WR**, has less unpleasant chemical properties and can be prepared readily and handled easily.⁵ In recent years, **WR** has been becoming a very useful selenium source or selenation reagent in synthetic chemistry.^{6,7}

As part of our studies aimed into the reactivity of **WR** towards different organic substrates, herein, we report the preparation of a series of novel five- to ten-membered phosphorus-selenium heterocycles from the selenation of aromatic diols by **WR** and seven X-ray crystal structures of the new heterocycles.

Results and Discussion

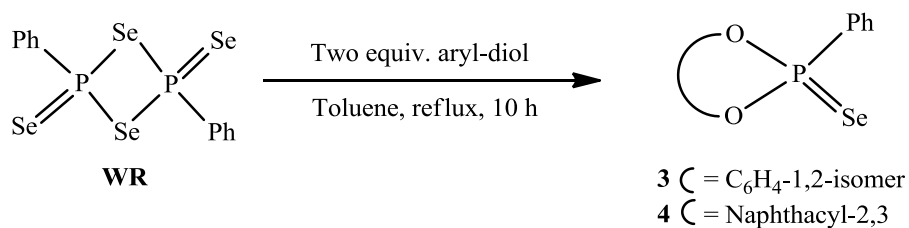
Heterocycles 1 - 4 from the selenation of catechol or 2,3-dihydroxynaphthalene

Refluxing a toluene suspension of **WR** with one equivalent of catechol or 2,3-dihydroxynaphthalene for 7 h gave rise to seven-membered diphosphorus species $\text{PhP}(\text{Se})\text{Se}(\text{Se})\text{PPh}(\text{OC}_6\text{H}_4\text{O-1,2})$ (**1**) and $\text{PhP}(\text{Se})\text{Se}(\text{Se})\text{PPh}(\text{OC}_{10}\text{H}_6\text{O-2,3})$ (**2**) in 39% and 29% yield, along with five-membered monophosphorus species $\text{PhP}(\text{Se})(\text{OC}_6\text{H}_4\text{O-1,2})$ (**3**) and $\text{PhP}(\text{Se})(\text{OC}_{10}\text{H}_6\text{O-2,3})$ (**4**) in 42% and 53% yield (Scheme 1).



Scheme 1. Reaction of **WR** with equiv-molar of aromatic diol

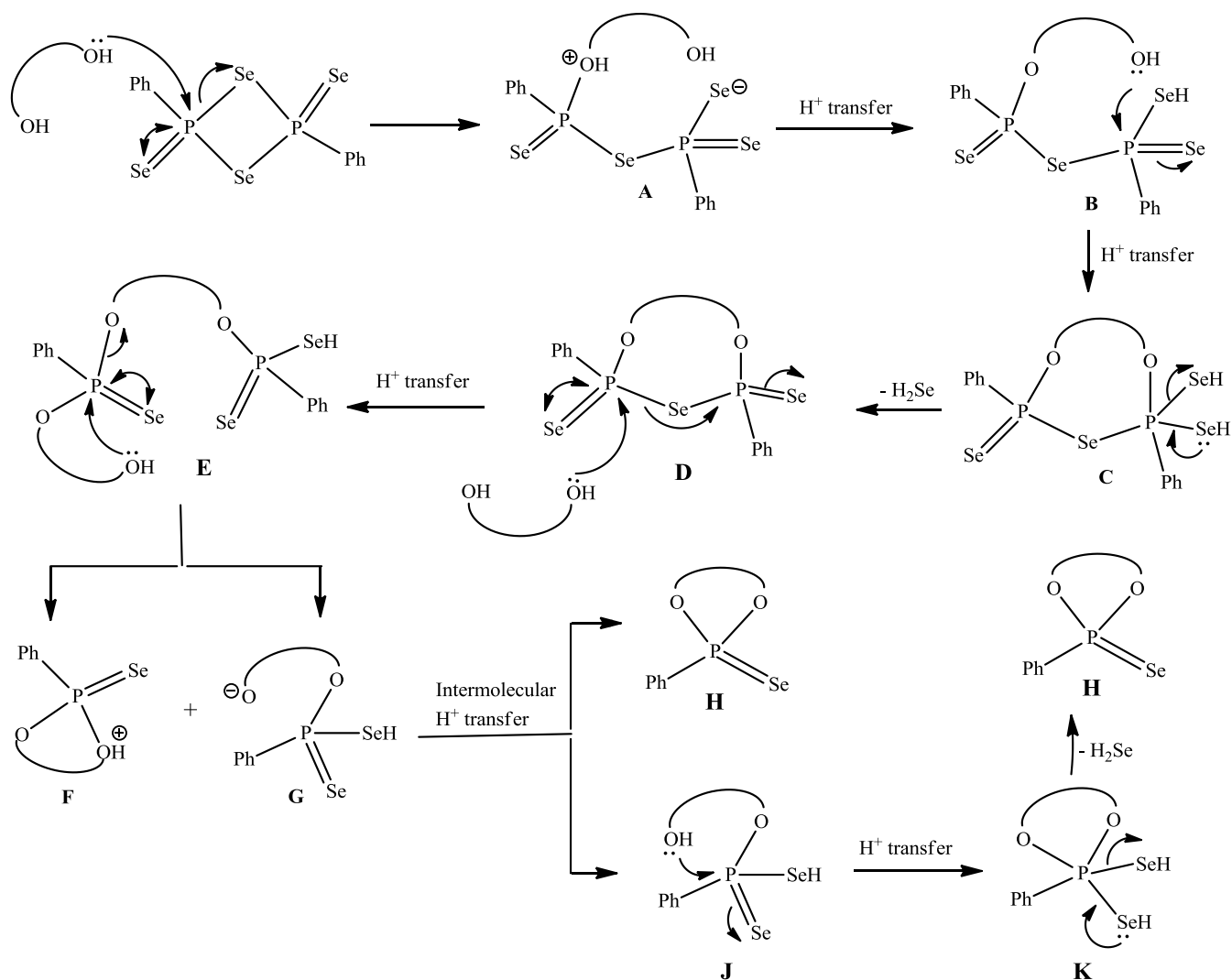
Compound **3** and **4** can be obtained as the only separated product in 85% and 88% yield by reaction of **WR** with two equivalents of aromatic diol in refluxing toluene for 10 h (Scheme 2). Compound **3** has been prepared previously in *ca.* 30% isolated yield by the reaction of **WR** with two equivalents of catechol in toluene at 130°C for 1 h.⁸ The reaction is apparently time dependant, prolonged reaction time here has improved the product yield considerably.



Scheme 2. Reaction of **WR** with two equivalents of aromatic diol

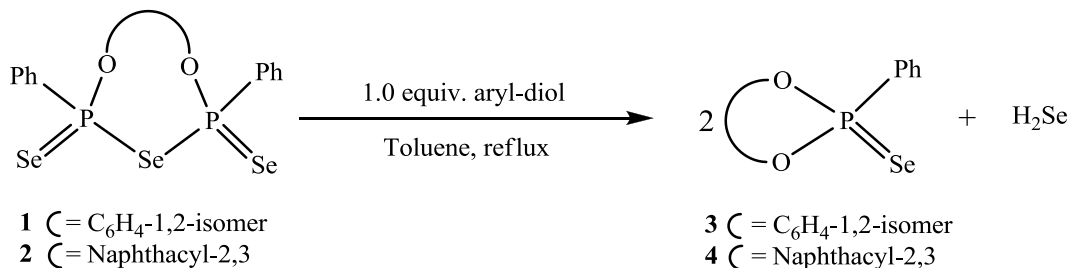
Mechanistically, we propose that the reaction proceeds through a step-wise nucleophilic substitution in which the selenium bridge in **WR** is broken once or twice and the P-Se bonds are replaced by P-O bonds step by step. The driving force of the reaction lies in that P-O bond is much stronger than P-Se bond, and five membered-ring is more stable than seven-membered ring. Scheme 3 illustrates the process through electron

push and proton transfer. First, one of the hydroxyl group of the diol attacks one of the phosphorus centres of **WR** to afford the unstable zwitterion **A**. Immediate intramolecular proton transfer from the O atom to the Se atom in **A** gives **B**. Cyclisation of **B** gives rise of **C** via a second nucleophilic addition of the other hydroxyl group of the diol to the second P=Se double bond within the molecule **C**. Loss of one molecule of hydrogen selenide from intermediate **C** results in the first product **D** (compound **1** or **2**). **D** reacts with another molecule of aromatic diol to generate two molecules of product **H** through intermediates **E**. Intermediate **E** collapses into two smaller fragments **F** and **G**. **F** passes on the proton to intermediate **G** to give stable product **H** (compound **3** or **4**) and intermediate **I**. Finally, **I** cyclises again by nucleophilic addition followed by rid of a hydrogen selenide to give a second molecule of product **H**. All the intermediates are not stable enough to survive the reflux in toluene and work up condition. But the products of **D** (compound **1** or **2**) and **H** (compound **3** or **4**) are quite stable. The attack of the hydroxyl group of the aromatic diol at the phosphorus centers lacks selectivity to **WR** or the diphosphorus species **1** or **2**. As a result, both diphosphorus (**1** and **2**) and monophosphorus species (**3** and **4**) form even though the reactants are in 1 : 1 molar ratio.



Scheme 3. Possible mechanism of the formation of heterocycles **1 - 4**

To confirm at least one aspect of the mechanism, the isolated diphosphorus species **1** and **2** were reacted with another equivalent of corresponding aromatic diol (Scheme 4). The monophosphorus species **3** or **4** formed in almost quantitative yields (98% and 99%) in this way.



Scheme 4. Ring contraction of diphosphorus species into monophosphorus species

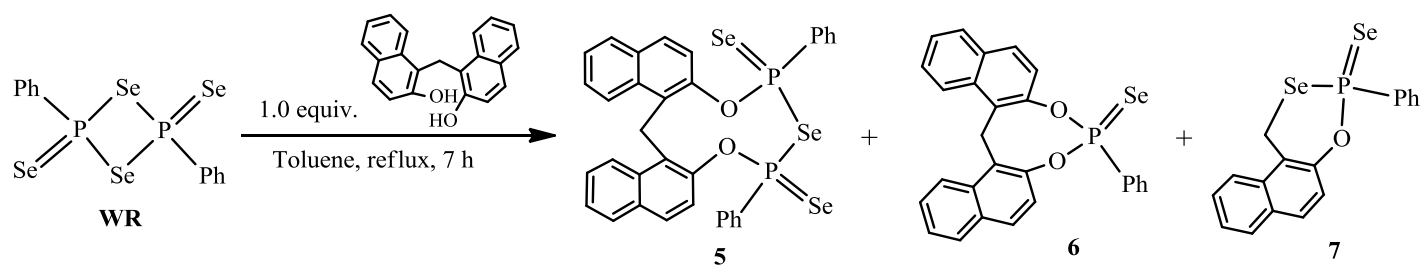
The release of H₂Se in the above reactions was observed in the bubbler (the formation of dark Se due to the decomposition of the H₂Se) which connects the N₂ line and the top of the condenser and could be trapped by sodium hydroxide as sodium selenate after the bubbler.

The characterisation of **3** has been reported previously.⁸ The proposed structures of **1**, **2** and **4** are based on their microanalysis, ¹H, ¹³C, ³¹P and ⁷⁷Se NMR, IR spectroscopic data and mass spectrometric data. The microanalyses of **1**, **2** and **4** were satisfactory, and all compounds showed the anticipated [M]⁺ or [MH]⁺ peak in their mass spectra. The ³¹P NMR spectra of **1** and **2** show sharp singlets at 77.7 and 79.7 ppm, respectively. There are two sets of selenium satellites associated with the equivalent phosphorus centres with *J*(P,Se) at 465 and 852 Hz for **1**, and 465 and 864 Hz for **2**. The lower magnitude couplings are attributed to the P-Se single bonded selenium atoms, and the higher magnitude values to the P=Se double bonded atoms. Detailed inspection of NMR spectra reveals the presence of a ²*J*(P,P) coupling of 9.4 Hz for **1** and 9.5 Hz for **2**. Meanwhile, the ³¹P NMR spectrum of **4** comprises a singlet at 115.9 ppm, flanked by ⁷⁷Se satellite *J*(P, Se_{exo}) 965 Hz, these values are similar to that in compound **3**,⁸ confirming the presence of only a phosphorus-selenium double bond, with a doublet at -188.3 ppm accompanied by a coupling constant of 965 Hz in the ⁷⁷Se NMR spectrum.

Heterocycles **5 - 7**, **9** and **10** from the selenation of 1,1'-methylene-2-naphthol or 2,2'-methylenebis(4-chlorophenol)

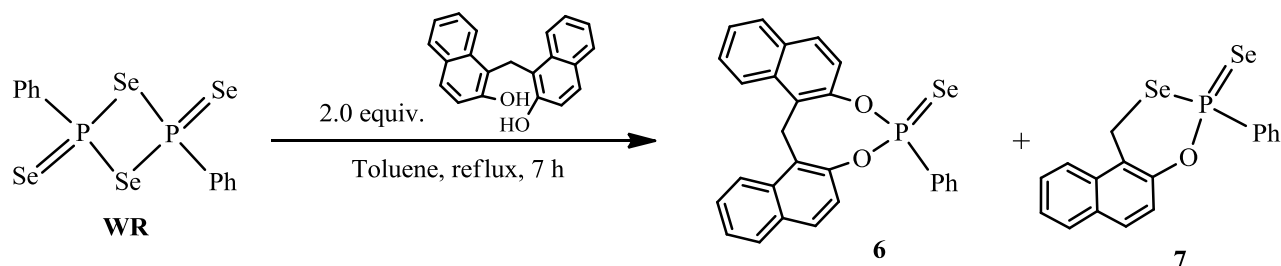
Reaction of **WR** with one molar equivalent of 1,1'-methylene-2-naphthol in the refluxing toluene gave the expected ten-membered diphosphorus species **5** (51% isolated yield) and eight-membered monophosphorus

species **6** (31% isolated yield), **but** surprisingly, another six-membered monophosphorus species **7** was isolated in 12% yield (Scheme 5).



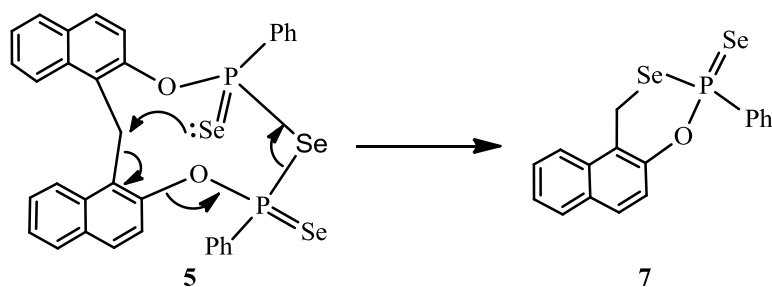
Scheme 5. Reaction of **WR** with one equivalent of 1,1'-methylene-2-naphthol

Treating **WR** with two equivalents of 1,1'-methylene-2-naphthol **in refluxing toluene** generated only two isolable products, eight-membered monophosphorus species **6** and six-membered monophosphorus species **7** in 62%, and 15% yield (Scheme 6).



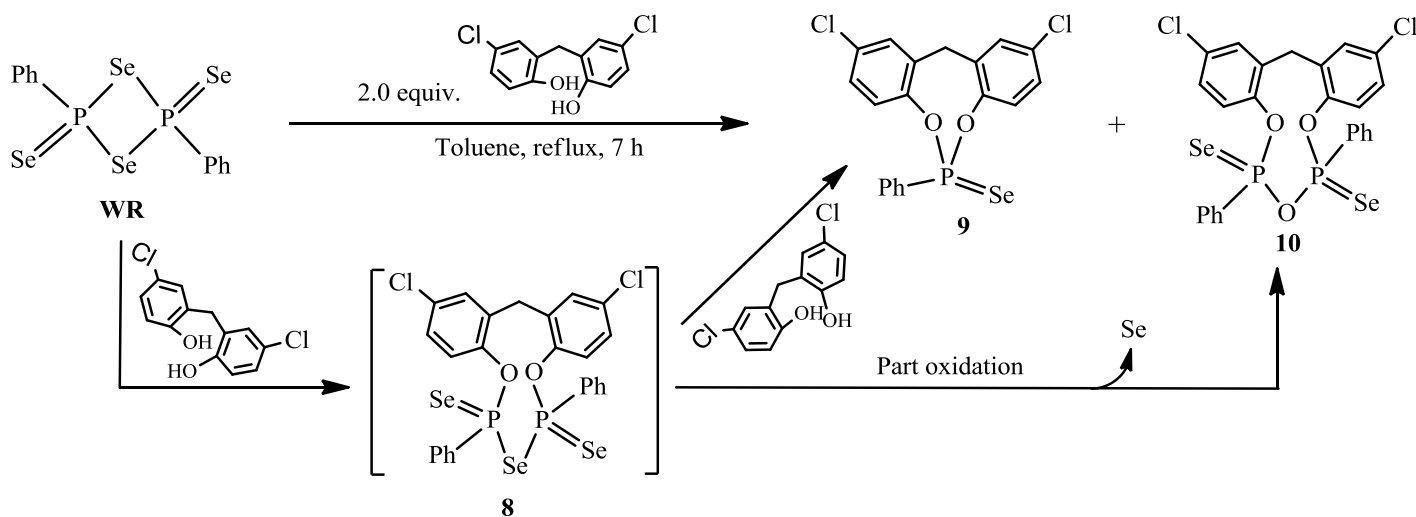
Scheme 6. Reaction of **WR** with two equivalents of 1,1'-methylene-2-naphthol

Apparently, compound **6** is the ring contraction product of compound **5**, following a similar mechanism to that described in Scheme 3. Due to the relative lability of the methylene between the two naphthalene groups and the large ring size of ten-membered diphosphorus species **5**, the six-membered monophosphorus species **7** might be formed by decomposition of diphosphorus species **5**, driven by the stability of the six-membered ring, although the extrusion of a **naphthalene** seems quite surprising (Scheme 7).



Scheme 7. Possible formation of monophosphorus species **5** from diphosphorus species **7**

The similar reaction of **WR** with two equivalents of 2,2'-methylenebis(4-chlorophenol) provided the expected eight-membered monophosphorus species **9** in 74% yield and the ten-membered diphosphorus species **10** with an O-P(Se)-O-P(Se)-O linkage in 24% yield. Obviously, the result is consistent with the mechanism in Scheme 3. We suppose that **WR** first reacts with one molecule of 2,2'-methylenebis(4-chlorophenol) leading to intermediate **8**, which is not thermodynamically stable but reacts with another molecule of 2,2'-methylenebis(4-chlorophenol) to afford compound **9**. The ten-membered diphosphorus species **10** could be the hydrolysis product of **8** during column chromatography, which was performed with no special exclusion of air and the silica was not dried (Scheme 8).



Scheme 8. Reaction of **WR** with two equivalents of 2,2'-methylenebis(4-chlorophenol)

Compounds **5 - 7**, **9** and **10** are soluble in common chlorinated solvents and air stable for several months as solids. Their formulations were ascertained by IR, MS (including accurate mass measurement), solution multi-nuclear NMR spectroscopy and in most cases additionally by single crystal X-ray structure determination. The ^{31}P NMR spectra of **5** and **7** exhibit sharp singlets at $\delta = 75.5$ and 85.3 ppm, respectively, which are flanked by two sets of satellites for the endocyclic and exocyclic selenium atoms ($J(\text{P},\text{Se}_{\text{endo}})$ and $J(\text{P},\text{Se}_{\text{exo}})$: 468 and 855 Hz for **5**, 434 and 857 Hz for **7**), thus indicating the presence of single P-Se bonds and double P=Se bonds in each compound. Meanwhile, the ^{31}P NMR spectra of **6**, **9** and **10** display sharp singlets at $\delta = 88.7$, 90.3 and 76.8 ppm, respectively, which are accompanied by single set of satellites for the exocyclic selenium atoms ($J(\text{P},\text{Se}_{\text{exo}})$: 923 Hz for **6**, 920 Hz for **9**, and 954 Hz for **10**), indicating only double P=Se bonds present in each compound. The ^{77}Se NMR spectra for **5** and **7** contain signals arising from exocyclic selenium atoms ($\delta = 57.8$ and 9.6 ppm; $J(\text{P},\text{Se}_{\text{exo}}) = 856$ and 856 Hz, respectively) and endocyclic selenium atoms ($\delta = 414.5$ and 367.5 ppm; $J(\text{P},\text{Se}_{\text{endo}}) = 468$ and 434 Hz, respectively). The ^{77}Se NMR spectra for **6**, **9** and **10** show doublets due to

the exocyclic selenium atoms ($\delta = -222.0, -251.5$ and -164.3 ppm; $J(\text{P}, \text{Se}_{\text{exo}}) = 923, 924$ and 954 Hz, respectively).

X-ray structures of **1**, **2**, **4**, **5**, **7**, **9** and **10**

Compounds **1**, **2** and **4** were crystallized from dichloromethane solutions with slow diffusion of hexane to give transparent, colorless, cubic crystals. The compounds are stable to air and moisture for several months. The X-ray structures of **1**, **2** and **4** (Figures 1 - 3) confirm the presence of the five-, and seven-membered rings. The structures of **1** and **2** are best described as boat conformation with two phosphorus atoms at the stern and prow positions, in **1** and **2** the P_2O_2 mean plane is inclined by $61.9(2)$ and $79.2(1)^\circ$, respectively with respect to the P_2C_2 plane. The two phenyl rings attached to phosphorus atoms are almost parallel and, in contrast to previous structures, in both **1** and **2** the exocyclic $\text{P}=\text{Se}$ groups are almost coplanar with the $\text{P}-\text{Se}-\text{P}$ backbone (the $\text{Se}=\text{P}\dots\text{P}=\text{Se}$ plane is inclined by only $22.96(3)$ and $21.99(1)^\circ$ with respect to the $\text{P}-\text{Se}-\text{P}$ plane in **1** and **2** respectively). The structure of **4** has a different motif compared to the above structures. The five-membered $\text{O}-\text{P}-\text{O}-\text{C}-\text{C}$ is co-planar with the naphthalene ring, whilst the phenyl ring and exocyclic selenium atoms lie on opposite sides of the heterocyclic ring. The internal $\text{P}-\text{Se}$ bond lengths (single bond, $2.2507(10), 2.2635(9)$ Å for **1**, and $2.2496(11), 2.2496(11)$ Å for **2**) and the exocyclic $\text{P}=\text{Se}$ double bond distances ($2.0820(9)$ and $2.0735(10)$ Å for **1**, $2.0771(11)$ and $2.0771(11)$ Å for **2**) are similar to those in other compounds which contain the $\text{P}(\text{Se})(\mu-\text{Se})$ unit.⁸⁻¹⁰ The geometry around the phosphorus atoms in **1** and **2** [$\text{Se}(1)-\text{P}(1)-\text{Se}(2)$ $108.42(3)^\circ$ and $\text{Se}(2)-\text{P}(3)-\text{Se}(3)$: $105.65(3)^\circ$ for **1**, $\text{Se}(1)-\text{P}(1)-\text{Se}(2)$ $106.52(5)^\circ$ and $\text{Se}(1\text{A})-\text{P}(1\text{A})-\text{Se}(2)$ $106.52(5)^\circ$ for **2**] are distorted from ideal tetrahedral geometry due to steric effects of the phenyl groups.⁸ The transannular $\text{P}\dots\text{P}$ bond distances are 3.54 and 3.52 Å for **1** and **2**, respectively, being marginally longer than those observed in the four-membered P_2Se_2 ring system (3.1 Å) and considerably shorter than those measured in a six-membered P_2Se_4 ring system (4.3 Å).¹¹ However, the exocyclic $\text{P}-\text{Se}_{\text{exo}}$ bond distance ($2.0547(10)$ Å) in **4** is shorter than that in the above structures. It is clear that **4** must be somewhat strained. The geometry around phosphorus atom [$\text{O}(1)-\text{P}(1)-\text{Se}(1)$ $114.51(10)^\circ$, $\text{O}(2)-\text{P}(1)-\text{Se}(1)$ $116.24(12)^\circ$] is highly distorted due to the five-membered ring strain.

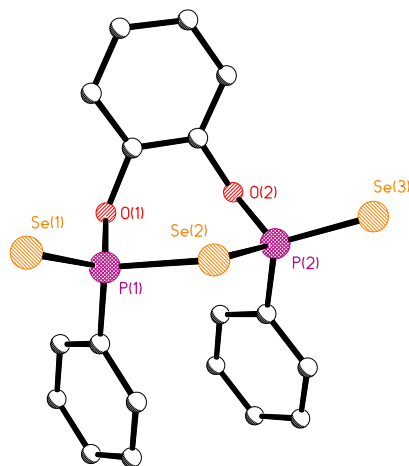


Figure 1. Single crystal X-ray structure of **1** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): P(1)-Se(1) 2.0820(9), P(1)-Se(2) 2.2507(10), P(2)-Se(2) 2.2635(9), P(2)-Se(3) 2.0735(10), P(1)-O(1) 1.621(2), P(2)-O(2) 1.606(2), P(1)-C(7) 1.798(2), P(2)-C(13) 1.793(2), O(1)-C(1) 1.406(2), O(2)-C(6) 1.411(3); P(1)-Se(2)-P(2) 103.33(3), Se(1)-P(1)-Se(2) 108.42(3), Se(1)-P(1)-O(1) 116.82(9), Se(1)-P(1)-C(7) 116.95(11), Se(2)-P(1)-O(1) 104.64(10), Se(2)-P(1)-C(7) 108.94(13), O(1)-P(1)-C(7) 100.14(11), Se(2)-P(2)-Se(3) 105.65(3), Se(2)-P(2)-O(2) 105.15(9), Se(2)-P(2)-C(13) 109.38(10), Se(3)-P(2)-O(2) 118.45(8), Se(3)-P(2)-C(13) 117.45(13), O(2)-P(2)-C(13) 100.03(13), P(1)-O(1)-C(1) 119.85(19), P(2)-O(2)-C(6) 123.05(19).

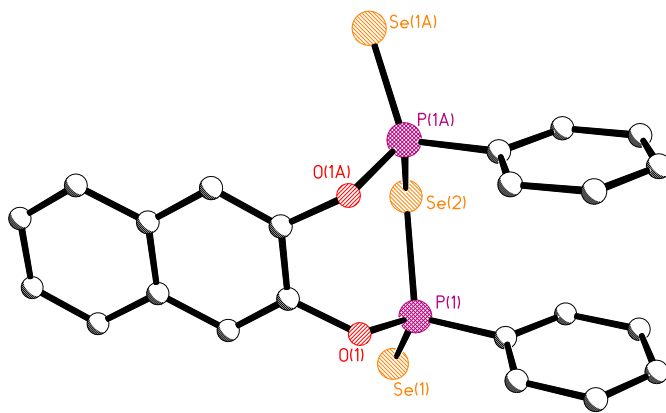


Figure 2. Single crystal X-ray structure of **2** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.0771(11), Se(2)-P(1) 2.2496(11), Se(2)-P(1) 2.2496(11), Se(1A)-P(1A) 2.0771(11), P(1)-O(1) 1.621(2), P(1)-C(6) 1.790(4), O(1)-C(1) 1.398(5); P(1A)-Se(2)-P(1) 102.74(6), O(1)-P(1)-C(6) 100.91(17), O(1)-P(1)-Se(1) 117.97(11), C(6)-P(1)-Se(1) 116.30(14), O(1)-P(1)-Se(2) 105.05(10), C(6)-P(1)-Se(2) 109.42(14), Se(1)-P(1)-Se(2) 106.52(5), C(1)-O(1)-P(1) 120.1(2).

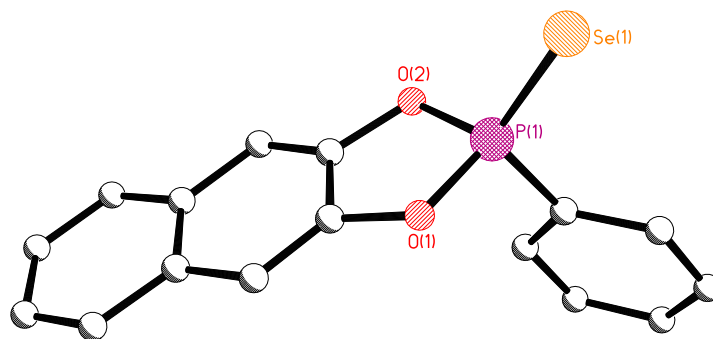


Figure 3. Single crystal X-ray structure of **4** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.0547(10), P(1)-O(1) 1.630(3), P(1)-O(2) 1.630(3), P(1)-C(11) 1.789(4), O(1)-C(1) 1.402(4); O(1)-P(1)-O(2) 95.99(12), O(1)-P(1)-C(11) 105.72(15), O(2)-P(1)-C(11) 104.53(15), O(1)-P(1)-Se(1) 114.51(10), O(2)-P(1)-Se(1) 116.24(12), C(1)-O(1)-P(1) 110.5(2).

The structures of **5** (which co-crystallised with one molecule of dichloromethane) **7** and **9** and **10** (which crystallised with two crystallographically independent molecules and a half of molecule of dichloromethane in the asymmetric unit) are illustrated in Figures 4-7. Compounds **7** and **9** contain the same monophosphorus unit PhP=Se derived from the cleavage of **WR** ring. Meanwhile, the structures of **5** and **10** reveal very similar conformations of their ten-membered rings even though they have different bridging atoms (selenium or oxygen atoms) between two PhP=Se groups in the new rings. **Interestingly** the P=Se groups in **5** are rotated onto opposite sides of the P-Se-P group whereas the P=Se groups **in 10** are approximately on the same side of the P-O-P unit. The structure of **7** is best described as a boat conformation consisting of a highly puckered six-membered C₃OPSe ring with the naphthalene ring and phenyl ring being in opposite positions and being inclined by 74.1°. **In the crystal 5** adopts a less symmetric conformation with a highly puckered C₅O₂P₂Se ring, leading to two naphthalene rings being in nearly vertical position (89.7°) and an angle of 53.0° for two phenyl rings. The C₅O₂P ring in **9** is also highly puckered but has approximate molecular C₂ symmetry, resulting in two phenyl rings being bent towards the same face of the molecule with an inter-ring angle of 58.7° and an overall appearance which is reminiscent of a Klingon ‘Bird of Prey’ warship. The structure of **10** is similar to **5** with a less symmetric conformation along with a highly puckered C₅O₂P₂O ring, three phenyl rings being towards the same side above the new ring. The exocyclic P=Se double bond distances [2.0781(14) Å for **7**, 2.0836(12) and 2.0705(12) Å for **5** and 2.0670(17) Å for **9**] are similar to those in other compounds which contain the P(Se)(μ-Se) unit.⁸⁻¹⁰ However, the P=Se lengths in **10** [2.0453(3) [2.046(3)] and 2.064(2) [2.062(2)] Å] are similar to that [2.0547(10) Å] in **4**, but slightly shorter than those in other compounds which contain the P(Se)(μ-Se) unit.^{7,8,12,13} and those in compounds **1** and **2**. The geometry around P [Se(1)-P(1)-O(1): 102.21(12)° for **7**, Se(3)-P(1)-O(1): 106.95(11)° and Se(3)-P(2)-O(2): 98.85(11)° for **5**,

O(1)-P(1)-O(2): 104.9(2)° for **9** and O(3)-P(1)-O(1): 96.5(3)° [95.8(3)°] and O(3)-P(2)-O(2): 104.8(3)° [105.9(2)° for **10**] is highly distorted.

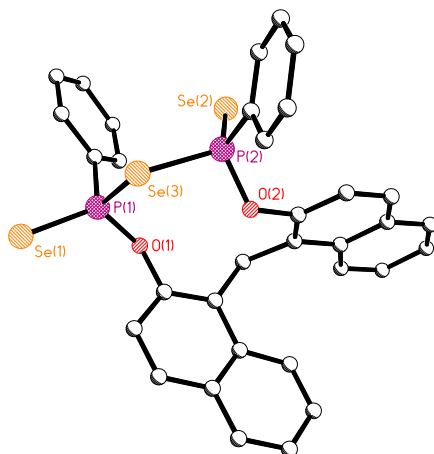


Figure 4. Single crystal X-ray structure of **5** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.0836(12), Se(2)-P(2) 2.0705(12), Se(3)-P(1) 2.2439(11), Se(3)-P(2) 2.2660(12), P(1)-O(1) 1.605(3), P(2)-O(2) 1.628(3), P(1)-C(22) 1.795(4), P(2)-C(28) 1.817(4), O(1)-C(1) 1.417(4), O(2)-C(13) 1.421(5); P(1)-Se(3)-P(2) 103.62(4), Se(1)-P(1)-Se(3) 105.99(5), Se(1)-P(1)-O(1) 120.39(11), Se(1)-P(1)-C(22) 113.34(15), Se(3)-P(1)-O(1) 106.95(11), Se(3)-P(1)-C(22) 109.27(13), O(1)-P(1)-C(22) 100.48(19), Se(2)-P(2)-Se(3) 120.22(5), Se(2)-P(2)-O(2) 114.35(12), Se(2)-P(2)-C(28) 115.06(15), Se(3)-P(2)-O(2) 98.85(11), Se(3)-P(2)-C(28) 98.51(15), O(2)-P(2)-C(28) 107.52(17), P(1)-O(1)-C(1) 128.0(2).

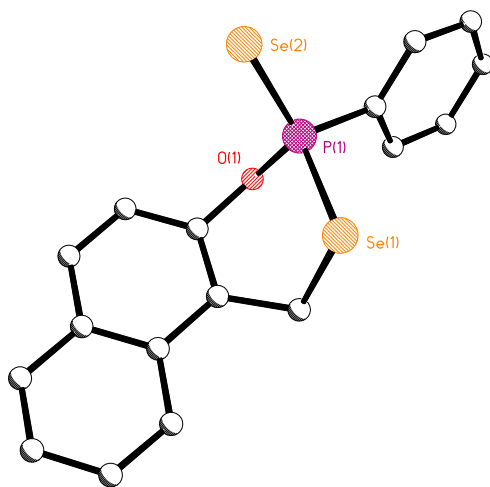


Figure 5. Single crystal X-ray structure of **7** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.2346(11), Se(2)-P(1) 2.0781(14), P(1)-C(12) 1.795(4), Se(1)-C(11) 1.989(5), P(1)-O(1) 1.624(3), O(1)-C(1) 1.403(5); P(1)-Se(1)-C(11) 93.10(14), Se(1)-P(1)-O(1) 102.21(12), Se(2)-P(1)-O(1) 117.55(14), O(1)-P(1)-C(12) 99.5(2), O(1)-C(1)-C(2) 117.9(4), Se(1)-P(1)-Se(2) 113.46(5), Se(1)-P(1)-C(12) 108.75(16), Se(2)-P(1)-C(12) 113.90(17), P(1)-O(1)-C(1) 118.9(2).

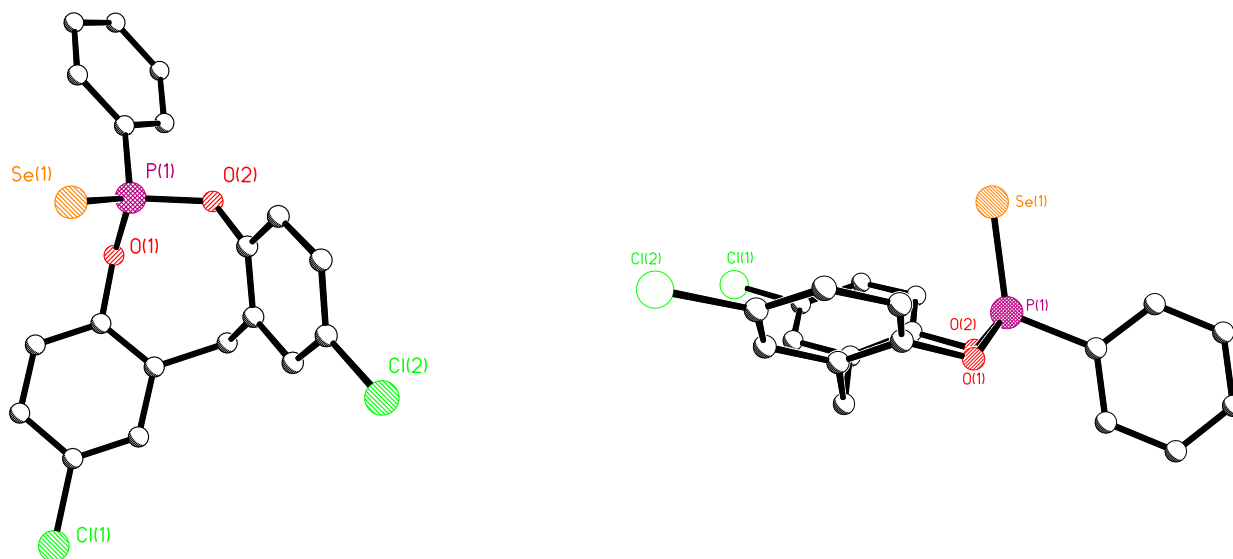


Figure 6. Single crystal X-ray structure of **9** (Hydrogen atoms omitted for clarity). The right hand picture illustrates the ‘Klingon bird of prey’ like shape of the molecule. Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.0670(17), P(1)-O(1) 1.611(4), P(1)-O(2) 1.606(4), O(1)-C(1) 1.408(6), O(2)-C(9) 1.414(5), P(1)-C(14) 1.784(5); Se(1)-P(1)-O(1) 115.37(17), Se(1)-P(1)-C(14) 119.5(2), O(1)-P(1)-C(14) 99.8(2), P(1)-O(1)-C(1) 124.4(3), Se(1)-P(1)-O(2) 114.87(16), O(1)-P(1)-O(2) 104.9(2), O(2)-P(1)-C(14) 100.0(2), P(1)-O(2)-C(9) 122.4(3).

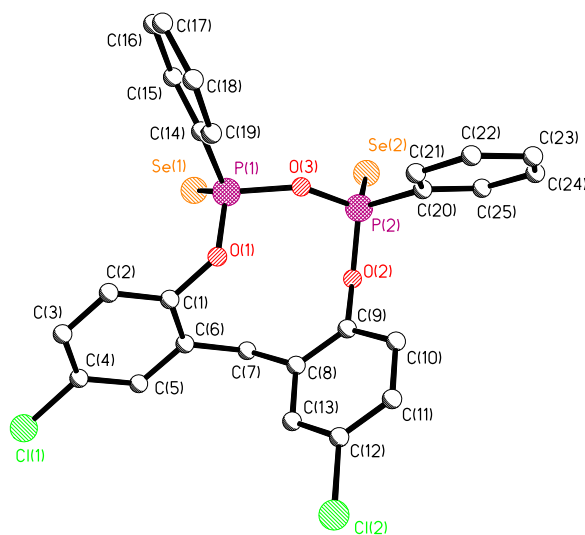


Figure 7. Single crystal X-ray structure of **10** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses) (dimensions for second independent molecule in square parentheses): Se(1)-P(1) 2.0453(3) [2.046(3)], Se(2)-P(2) 2.064(2) [2.062(2)], P(1)-O(1) 1.593(6) [1.597(5)], P(1)-O(3) 1.627(6) [1.622(7)], P(1)-C(14) 1.759(9) [1.789(9)], P(2)-O(2) 1.581(5) [1.597(5)], P(2)-O(3) 1.602(7) [1.622(7)], P(2)-C(20) 1.804(9) [1.801(11)], O(1)-C(1) 1.411(8) [1.419(10)], O(2)-C(9) 1.428(11) [1.419(10)]; P(1)-O(3)-P(2) 136.8(4) [136.4(4)], Se(1)-P(1)-O(3) 118.7(2) [118.4(2)], Se(1)-P(1)-O(1) 116.1(2) [117.0(2)], Se(1)-P(1)-C(14) 117.3(4) [117.9(3)], O(3)-P(1)-O(1) 96.5(3) [95.8(3)], O(3)-P(1)-C(14) 99.4(3) [100.4(4)], O(1)-P(1)-C(14) 105.6(4) [103.7(3)], Se(2)-P(2)-O(3)

117.3(3) [118.3(2)], Se(2)-P(2)-O(2) 109.2(2) [107.9(2)], Se(2)-P(2)-C(20) 115.1(3) [116.2(3)], O(3)-P(2)-O(2) 104.8(3) [105.9(2)], O(3)-P(2)-C(20) 99.49(4) [99.4(4)], O(2)-P(2)-C(20) 109.4(4) [108.3(3)], P(1)-O(1)-C(1) 123.0(6) [122.7(6)], P(2)-O(2)-C(9) 132.5(5) [131.9(5)].

Table 1. Details of the x-ray data collections and refinements for **1**, **2** and **4**

Compound	1	2	4
Formula	C ₁₈ H ₁₄ O ₂ P ₂ Se ₃	C ₂₂ H ₁₆ O ₂ P ₂ Se ₃	C ₁₆ H ₁₁ O ₂ PSe
<i>M</i>	561.13	611.17	345.18
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	Cmc2(1)	P2(1)/c
<i>a</i> /Å	8.3203(4)	14.040(3)	14.462(3)
<i>b</i> /Å	9.6324(4)	9.6720(17)	7.7917(15)
<i>c</i> /Å	13.5237(6)	16.270(3)	13.186(3)
<i>α</i>	103.2960(14)	90	90
<i>β</i>	91.4965(15)	90	114.195(4)
<i>γ</i>	115.0917(13)	90	90
<i>U</i> /Å ³	945.81(7)	2209.4(7)	1355.4(5)
<i>Z</i>	2	4	4
<i>μ</i> /mm ⁻¹	6.0130	5.156	2.885
Reflections collected	10009	7054	8383
Independent reflections	4343	2012	2485
<i>R</i> _{int}	0.0210	0.0376	0.0434
<i>RI</i> ; <i>wR2</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0256; 0.0694	0.0317; 0.0614	0.0446; 0.1072

Table 2. Details of the x-ray data collections and refinements for **5**, **7**, **9** and **10**

Compound	5	7	9	10
Formula	C ₃₄ H ₂₆ O ₂ P ₂ Se ₃ Cl ₂	C ₁₇ H ₁₃ OPSe ₂	C ₁₉ H ₁₃ O ₂ PSeCl ₂	C _{25.25} H _{18.5} O ₃ P ₂ SeCl _{2.5}
<i>M</i>	836.31	422.18	454.15	678.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	P-1
<i>a</i> /Å	9.6007(16)	9.1244(15)	11.868(3)	12.990(5)
<i>b</i> /Å	11.5387(18)	8.6606(13)	7.585(2)	13.829(5)
<i>c</i> /Å	29.679(5)	20.178(3)	21.097(6)	16.436(5)
<i>α</i>	90	90	90	94.306(3)
<i>β</i>	94.742(4)	102.065(4)	104.045(6)	107.147(6)
<i>γ</i>	90	90	90	108.060(9)
<i>U</i> /Å ³	3276.6(9)	1559.3(4)	1842.3(9)	2636(17)
<i>Z</i>	4	4	4	4
<i>μ</i> /mm ⁻¹	1.695	1.798	1.637	1.709
Reflections collected	19447	9508	10247	27400
Independent reflections	5756	2704	3214	9120
<i>R</i> _{int}	0.0500	0.0390	0.0530	0.0770
<i>RI</i> ; <i>wR2</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0402; 0.1404	0.0382; 0.1370	0.0637; 0.1640	0.1021; 0.2457

In summary, a series of novel five- to ten-membered phosphorus-selenium heterocycles with an O-P(Se)-O or O-P(Se)-Se-P(Se)-O or O-P(Se)-O-P(Se)-O linkage have been successfully prepared from the selenation of aromatic diols by **WR**. The large diphosphorus species O-P(Se)-Se-P(Se)-O rings could be readily reduced into the small monophosphorus species O-P(Se)-O rings *via* further treatment with one equivalent of aromatic diol. The method offers a new approach to the library of phosphorus-selenium heterocyclic compounds. The structures of the novel heterocycles have been elucidated by using ¹H, ³¹P, ⁷⁷Se NMR spectroscopy and microanalysis or accurate mass measurements in conjunction with single-crystal X-ray crystallography.

Experimental Section

Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, **while** subsequent chromatographic and work up procedures were performed in air. ¹H (270 MHz), ¹³C (67.9 MHz), ³¹P-¹H (109 MHz) and ⁷⁷Se-¹H (51.4 MHz) referenced to external Me₂Se) NMR spectra were recorded in CDCl₃ 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.

X-ray crystal data for compounds **2** and **4** were collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Data for **1**, **5**, **7**, **9** and **10** were collected using the St Andrews Robotic diffractometer (Saturn724 CCD) at 125 K with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).^{14,15} 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 SHELXL.¹⁶ Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. CCDC 761969 – 761975 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Reaction of WR with equimolar aromatic diol (A): A suspension of **WR** (0.54 g, 1.0 mmol) with aromatic diol (1.0 mmol) in 20 mL of toluene was refluxed for 7 h, during which time the dark red suspension became a yellow solution with some grey precipitate of elemental selenium. Upon cooling to room temperature the solvent was removed in vacuo, the crude residue extracted into dichloromethane (5 mL) and purified by column chromatography (1:9 ethyl acetate/toluene as eluent) to give compounds **1** and **2**, and compounds **3** and **4**.

Reaction of WR with two molar equivalents of aromatic diol (B): A solution of **WR** (0.54 g, 1.0 mmol) with aromatic diol (2.0 mmol) in 20 mL of toluene was refluxed for 10 h, during which time the dark red suspension became a yellow solution with some grey precipitate of elemental selenium. Upon cooling to room temperature the solvent was removed in vacuo, the crude residue extracted into dichloromethane (5 mL) and purified by column chromatography (1:9 ethyl acetate/toluene as eluent) to give compounds **3** and **4**.

Reaction of 1 or 2 with equi-molar of the corresponding aromatic diol (C): A mixture of **1** or **2** (1.0 mmol) with aromatic diol (1.0 mmol) in 20 mL of toluene was refluxed for 7 h. Upon cooling to room

temperature the solvent was removed in vacuo, the crude residue extracted into dichloromethane (5 mL) and purified by column chromatography (1:9 ethyl acetate/toluene as eluent) to give compounds **3** and **4**.

Compound 1. Greenish yellow crystals (220 mg) in 39% yield. Selected IR (KBr, cm^{-1}): 1485(s), 1434(m), 1233(s), 1099(m), 915(m), 885(s), 762(m), 737(m), 715(m), 682(m), 546(s, P=Se). ^1H NMR (CDCl_3 , δ), 7.72-7.56 (m, 4H, ArH), 7.44-7.31 (m, 6H, ArH), 7.22-7.15 (m, 4H, ArH) ppm. ^{13}C NMR (CDCl_3 , δ), 133.7, 132.7, 130.2, 130.1, 130.0, 128.5, 128.3, 127.8, 124.3 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 77.7 (s, $J(\text{P},\text{Se}_{\text{endo}}) = 465$ Hz, $J(\text{P},\text{Se}_{\text{exo}}) = 852$ Hz) ppm. ^{77}Se NMR (CDCl_3 , δ), 434.7 (d, $J(\text{P},\text{Se}_{\text{endo}}) = 465$ Hz), 77.3 (d, $J(\text{P},\text{Se}_{\text{exo}}) = 852$ Hz) ppm. Mass spectrum (EI^+ , m/z): 562 $[\text{M}]^+$. Elemental analysis: Found: C, 38.9; H, 2.8; $\text{C}_{18}\text{H}_{14}\text{O}_2\text{PSe}$ requires C, 38.5; H, 2.5.

Compound 2. A white solid (178 mg) in 29% yield. Selected IR (KBr, cm^{-1}): 1503(w), 1461(m), 1434(m), 1241(m), 1103(m), 1079(m), 904(s), 720(m), 683(m), 533(s, P=Se). ^1H NMR (CD_2Cl_2 , δ), 8.01 (m, 2H, ArH), 7.96 (m, $J(\text{H},\text{H}) = 7.2$ Hz, 2H, ArH), 7.74-7.60 (m, 6H, ArH), 7.38 (m, $J(\text{H},\text{H}) = 7.2$ Hz, 2H, ArH), 7.22 (m, 4H, ArH) ppm. ^{13}C NMR (CD_2Cl_2 , 25°C , δ), 154.5, 144.3, 132.9, 130.0, 129.9, 128.5, 127.9, 127.2, 121.9 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 79.7 (s, $J(\text{P},\text{Se}_{\text{endo}}) = 465$ Hz, $J(\text{P},\text{Se}_{\text{exo}}) = 864$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 352.8 (d, $J(\text{P},\text{Se}_{\text{endo}}) = 465$ Hz), 67.08 (d, $J(\text{P},\text{Se}_{\text{exo}}) = 864$ Hz). Mass spectrum (EI^+ , m/z): 612 $[\text{M}]^+$. Elemental analysis: Found: C, 43.5; H, 2.7; $\text{C}_{22}\text{H}_{16}\text{O}_2\text{P}_2\text{Se}_3$ requires C, 43.2; H, 2.6.

Compound 4. A colorless solid (182 mg in 53% yield from method **A**; 304 mg in 88% yield from method **B** and 342 mg in 99% from method **C**). Selected IR (KBr, cm^{-1}): 1454(m), 1233(m), 1154(m), 1111(m), 882(s), 858(s), 784(m), 750(m), 720(m), 640(m), 532(s, P=Se). ^1H NMR (CD_2Cl_2 , δ), 7.93-7.78 (m, 4H, ArH), 7.62 (d, $J(\text{H},\text{H}) = 7.2$ Hz, 2H), 7.51-7.44 (m, 6H, ArH) ppm. ^{13}C NMR (CDCl_3 , δ), 145.1 (d, $J(\text{P},\text{C}) = 117$ Hz), 134.3 (d, $J(\text{P},\text{C}) = 3.1$ Hz), 131.1 (d, $J(\text{P},\text{C}) = 13.5$ Hz), 130.5, 128.8 (d, $J(\text{P},\text{C}) = 15.6$ Hz), 127.6, 125.9, 109.9, 108.9. ^{31}P NMR (CDCl_3 , δ), 115.9 (s, $J(\text{P},\text{Se}_{\text{exo}}) = 965$ Hz). ^{77}Se NMR (CDCl_3 , δ), -188.3 (d, $J(\text{P},\text{Se}_{\text{exo}}) = 965$ Hz). Mass spectrum (EI^+ , m/z): 346 $[\text{M}]^+$, 266 $[\text{M}-\text{Se}]^+$. Elemental analysis: Found: C, 55.4; H, 3.4; $\text{C}_{16}\text{H}_{11}\text{O}_2\text{PSe}$ requires C, 55.7; H, 3.2.

Synthesis of 5 - 7. A mixture of 1,1'-methylenedi-2-naphthol (1.0 or 2.0 mmol) and **WR** (0.54g, 1.0 mmol) in 20 mL of toluene was refluxed for 7 h. The red suspension disappeared and a pale green solution was formed. Upon cooling to room temperature and removing solvent in vacuum, the residue was purified by silica gel chromatography column (eluent by 50/50 hexane/dichloromethane) to give compounds **5**, **6** and **7**. Only compounds **6** and **7** were obtained in the case of the ratio of **WR** : diol = 1 : 2.

Compound 5. An orange solid (381 mg in 51% yield). Selected IR (KBr, cm^{-1}): 3051(w), 2923(w), 1628(m), 1599(m), 1513(m), 1462(m), 1266(m), 1216(vs), 995(m), 959(m), 845(m), 809(s), 742(s). ^1H NMR (CD_2Cl_2 , δ), 8.24-7.04 (m, 29H, ArH), 4.74 (s, 4H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 153.8, 148.6 (d, $J(\text{P},\text{C}) = 10.5$ Hz), 134.8, 133.8, 132.8, 132.0, 131.6, 131.4, 129.8, 129.4, 128.9, 128.7, 128.5, 127.8, 127.6, 126.7, 126.5, 126.4, 125.6, 124.7, 124.4, 123.6, 123.2, 123.0, 121.2, 120.2, 118.5, 118.1, 117.9, 117.7, 109.4, 21.5 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 75.5 (s, $J(\text{P},\text{Se}_{\text{endo}}) = 468$ Hz, $J(\text{P},\text{Se}_{\text{exo}}) = 855$ Hz) ppm. ^{77}Se NMR (CDCl_3 , δ), 414.5 (d, $J(\text{P},\text{Se}_{\text{endo}}) = 468$ Hz), 57.8 (d, $J(\text{P},\text{Se}_{\text{exo}}) = 856$ Hz) ppm. Mass spectrum (EI^+ , m/z): 754 $[\text{M}]^+$. Accurate mass measurement (EIMS): 753.8745, calculated mass for $\text{C}_{33}\text{H}_{24}\text{O}_2\text{PSe}_3$: 753.8747.

Compound 6. A white solid (200 mg in 31% yield from the ratio of **WR** : diol = 1 : 1 and 399 mg in 62% yield the ratio of **WR** : diol = 1 : 2). Selected IR (KBr, cm^{-1}): 3057(w), 2923(w), 1621(m), 1593(s), 1514(m), 1460(m), 1434(m), 1405(m), 1244(vs), 1212(m), 959(m), 804(s), 730(m), 733(m). ^1H NMR (CD_2Cl_2 , δ), 8.36 (d, $J(\text{H},\text{H}) = 8.5$ Hz, 2H, ArH), 8.05 (m, 2H, ArH), 7.87 (m, 2H, ArH), 7.77 (m, 2H, ArH), 7.63 (m, 3H, ArH), 7.49 (m, 2H, ArH), 7.31 (m, 2H, ArH), 7.06 (m, 2H, ArH), 4.59 (s, 3H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 148.9 (d, $J(\text{P},\text{C}) = 12.5$ Hz), 150.0 (d, $J(\text{P},\text{C}) = 12.5$ Hz), 132.9, 132.3, 132.0, 130.6, 130.4, 129.0, 128.9, 128.4, 127.3, 126.9, 125.5, 124.4, 123.7, 122.4, 121.3, 121.2, 117.8, 111.2, 22.4 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 88.7 (s, $J(\text{P},\text{Se}_{\text{exo}}) = 923$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), -222.0 (d, $J(\text{P},\text{Se}_{\text{exo}}) = 923$ Hz) ppm. Mass spectrum (CI^+ , m/z): 647 $[\text{M}+\text{H}]^+$. Accurate mass measurement (EIMS): 645.8614, calculated mass for $\text{C}_{27}\text{H}_{19}\text{O}_2\text{PSe}$: 645.8618.

Compound 7. A reddish white solid (52 mg in 12% yield from the ratio of **WR** : diol = 1 : 1 and 64 mg in 15% yield from the ratio of **WR** : diol = 1 : 2). Selected IR (KBr, cm^{-1}): 3050(w), 2920(w), 1592(m), 1510(m), 1460(m), 1435(m), 1215(vs), 1055(s), 997(m), 953(m), 890(s), 816(s), 690(m), 554(m). ^1H NMR (CD_2Cl_2 , δ), 8.20-7.06 (m, 22H, ArH), 4.96 (d, $J(\text{P},\text{H}) = 15.6$ Hz, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 148.9 (d, $J(\text{P},\text{C}) = 12.5$ Hz), 133.0, 132.9, 132.1, 130.9, 130.7, 130.6, 130.5, 129.6, 129.0, 128.8, 127.4, 125.5, 123.7, 122.7, 121.3, 25.3 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 85.3 (s, $J(\text{P},\text{Se}_{\text{endo}}) = 434$ Hz, $J(\text{P},\text{Se}_{\text{exo}}) = 857$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 367.5 (d, $J(\text{P},\text{Se}_{\text{endo}}) = 434$ Hz); 9.6 (d, $J(\text{P},\text{Se}_{\text{exo}}) = 856$ Hz) ppm. Mass spectrum (CI^+ , m/z): 425 $[\text{M}+\text{H}]^+$. Accurate mass measurement (EIMS): 423.9031, calculated mass for $\text{C}_{17}\text{H}_{13}\text{OPSe}_2$: 423.9034.

Synthesis of 9 and 10. A mixture of 2,2'-methylenebis(4-chlorophenol) (0.54g, 2.0 mmol) and **WR** (0.54g, 1.0 mmol) in 20 mL of toluene was refluxed for 7 h. The red suspension disappeared and a pale green solution was formed. Upon cooling to room temperature and removing solvent the residue was purified by silica gel to give compounds **9** (eluent by 50:50 hexane/dichloromethane) and **10** (eluent by dichloromethane).

Compound 9. A pale yellow solid (346 mg in 74% yield). Selected IR (KBr, cm^{-1}): 3076(w), 2930(w), 1479(s), 1438(m), 1400(m), 1225(s), 1167(s), 1111(s), 932(s), 873(m), 854(s), 816(s), 731(s), 646(s), 537(m). ^1H NMR (CD_2Cl_2 , δ), 8.22 (m, 2H, ArH), 7.64 (m, 3H, ArH), 7.39 (m, 2H, ArH), 7.21 (m, 2H, ArH), 6.99 (m, 2H, ArH), 4.46 (s, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 147.1 (d, $J(\text{P,C}) = 10.4$ Hz), 135.0 (d, $J(\text{P,C}) = 3.1$ Hz), 133.5 (d, $J(\text{P,C}) = 3.1$ Hz), 131.4, 130.6 (d, $J(\text{P,C}) = 12.5$ Hz), 130.2, 128.8, 128.6, 128.4, 125.7, 125.6, 33.1 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 90.3 (s, $J(\text{P,Se}_{\text{exo}}) = 920$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), -251.5 (d, $J(\text{P,Se}_{\text{exo}}) = 924$ Hz) ppm. Mass spectrum (CI^+ , m/z): 455 $[\text{M}+\text{H}]^+$. Accurate mass measurement (EIMS): 453.9190, calculated mass for $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{O}_2\text{PSe}$: 453.9195.

Compound 10. A pale yellow solid (160 mg in 24% yield). Selected IR (KBr, cm^{-1}): 3052(w), 2948(w), 2921(w), 1481(s), 1438(m), 1401(m), 1216(m), 1167(s), 1112(s), 943(s), 899(s), 815(s), 725(s), 688(m), 643(m), 543(m). ^1H NMR (CD_2Cl_2 , δ), 7.96-7.16 (m, 16H, ArH), 4.36 (s, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 148.5, 133.5, 131.1, 131.0, 130.7, 130.6, 130.5, 128.9, 128.8, 128.7, 127.9, 122.7, 30.6 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 76.8 (s, $J(\text{P,Se}_{\text{exo}}) = 954$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), -164.3 (d, $J(\text{P,Se}_{\text{exo}}) = 954$ Hz) ppm. Mass spectrum (CI^+ , m/z): 659 $[\text{M}+\text{H}]^+$. Accurate mass measurement (EIMS): 657.8436, calculated mass for $\text{C}_{25}\text{H}_{18}\text{Cl}_2\text{O}_3\text{P}_2\text{Se}_2$: 657.8439.

Acknowledgements

We are grateful to the University of St Andrews and the Engineering and Physical Science Research Council (EPSRC, U.K.) for financial support.

References

1. J. Nakayama, I. Akiyama, Y. Sugihara, T. Nishio, *J. Am. Chem. Soc.* **1998**, *120*, 10027-10031; H. Fujihara, T. Nakahodo, N. Furukawa, *Tetrahedron Lett.* **1995**, *36*, 6275-6278; W. Nakanishi, Y. Ikeda, H. Iwamura, *J. Org. Chem.* **1982**, *47*, 2275-2278; W. Ando, Y. Kumamoto, N. Tokitoh, *J. Phys. Org. Chem.* **1988**, 317-332.
2. T. Schewe, *Gen. Pharmac.* **1995**, *26*, 1153-1169; M. J. Parnham, E. Graf, *Prog. Drug Res.* **1991**, *36*, 9-47; G. Mugesh, K. B. Singh, *Chem. Soc. Rev.* **2000**, *29*, 347-357; G. Mugesh, W. -W. du Mont, H. Sies, *Chem. Rev.* **2001**, *101*, 2125-2180; S. Garcia, *Curr. Med. Chem.* **2004**, *11*, 1657-1669.
3. J. Garin, *Adv. Heterocycl. Chem.* **1995**, *62*, 249-304.
4. *Organoselenium Chemistry. A practical Approach* (Ed.: T. G. Back), Oxford University Press, Oxford **1999**; J. Mlochowski, *Phosphorus, Sulfur, Silicon* **1998**, *191*, 136-138; M. Tiecco, *Top. Curr. Chem.* **2000**,

- 208, 7-54; T. Wirth, *Angew. Chem. Int. Ed.* **2000**, *39*, 3740-3749; J. Mlochowski, M. Brzascz, M. Giurg, J. Palus, H. Wojtowicz, *Eur. J. Org. Chem.* **2003**, 4329-4339.
5. I. P. Gray, P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.* **2005**, *11*, 6221-6227.
 6. A. Rothenberger, W. Shi, M. Shafaei-Fallah, *Chem. Eur. J.* **2007**, *13*, 5974-5981; W. Shi, M. Shafaei-Fallah, L. Zhang, E. Matern, A. Rothenberger, *Chem. Eur. J.* **2007**, *13*, 598-603.
 7. G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Org. Lett.* **2006**, *8*, 5251-5254; G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Eur. J. Inorg. Chem.* **2007**, 891-897; G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.* **2007**, 1465-1468; G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Dalton Trans.* **2007**, 1477-1480; G. Hua, J. D. Woollins. *Angew. Chem., Int. Ed.* **2009**, *48*, 1368-1377.
 8. P. Bhattacharyya, A. M. Z. Slawin, and J. D. Woollins, *J. Organomet. Chem.* **2001**, *623*, 116-119.
 9. P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.* **2002**, *8*, 2705-2711; P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Dalton Trans.* **2001**, 300-303; P. Bhattacharyya, J. Novosad, J. R. Phillips, A. M. Z. Slawin, D. J. William and D. J. Woollins, *Dalton Trans.* **1995**, 1607-1613.
 10. J. T. Shore, W. T. Pennington, M. C. Noble and A. W. Cordes, *Phosphorus, Sulfur Silicon Relat. Elem.* **1988**, *39*, 153-157.
 11. S. Parveen, P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2006**, 2586-2590.
 12. P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem. Int. Ed.* **2000**, *39*, 1973-1975.
 13. I. P. Parkin, M. J. Pilkington, A. M. Z. Slawin, J. D. Williams, J. D. Woollins, *Polyhedron* **1990**, *9*, 987-990.
 14. Rigaku (2006). *Crystal Structure*, Version 3.8. Single Crystal Structure Analysis Software. Rigaku/MS, 9009 TX, USA 77381-5209. Rigaku, Tokyo 196-8666, Japan.
 15. Rigaku (2004). *CrystalClear*. Version 1.36. Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
 16. G. M. Sheldrick, *SHELXL97*. *Acta Cryst.* **2008**, *A64*, 112-122.