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A New Synthesis of $(PhPSe_2)_2$ (Woollins Reagent) and Its Use in the Synthesis of Novel P–Se Heterocycles

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Abstract: A new and improved method for the preparation of $(PhPSe_2)_2$ (Woollins reagent (WR), **1**) is reported. Reaction of dichlorophenylphosphine with Na_2Se, (prepared from the reaction of elemental selenium and sodium in liquid ammonia) gives WR with excellent purity, high yield and on a larger scale than was previously possible. Four novel phosphorus–selenium heterocycles, including a spirocyclic heterocycle exhibiting a four-membered P_2SeC ring, were obtained from the reaction of WR with two reactive substrates (diphenylcyclopropenone and methyl phenylpropiolate). Useful selenocarbonyl and thiocarbonyl compounds were obtained from the reaction of both WR and Lawesson's reagent with diphenylcyclopropenone. All new compounds were characterised spectroscopically and three demonstrative X-ray structures are reported.

Keywords: heterocycles · phosphorus · selenium · Woollins reagent · X-ray structure

Introduction

The synthesis and wide variety of reactions of dithiadiphosphetane disulfides has been the subject of many reviews, articles and communications over many years.[1] In contrast, their selenium analogues, the diselenaphosphetane diselenides, have received very little attention. Shore et al.[2] reported the synthesis of $(t\mathrm{BuPSe}_2)_2$ from dichloro-*tert*-butylphosphine and Li_2Se_2, and, although this compound was studied crystallographically, its potential chemistry has been overlooked. Hahn and co-workers were also able to obtain this compound and its methyl and phenyl analogues[3] from the reaction of the silyl esters of the triselenophosphonic acids and DMSO, although no detailed experimental procedure or spectroscopic data was reported. Karaghiosoff and co-workers[4] and Woollins et al.[5] have reported a range of diselenaphosphetane diselenides synthesised from the oxidation of the corresponding homocyclic pentamers $(PR)_5$ (R = Me, Et, 4-$Me_2NC_6H_4$, An and Ph) by 10 equivalents of elemental selenium, including WR (R = Ph).

In recent years, the chemistry of $(PhPSe_2)_2$ **1** (which has become known as Woollins reagent, WR) has been the subject of a few reports. Baxter et al.,[6] Bhattacharyya et al.[7] and Bethke et al.[8a] have reported the selenation reactions of WR in the synthesis of selenoketenyl complexes and a range of selenoamides and selenoaldehydes, and Knapp and Darout very recently described its use for the selenation of carboxylic acids.[8b] We have also reported the use of WR in the preparation of novel phosphorus–selenium heterocycles by the reaction with several organic substrates containing reactive unsaturated C=C double bonds, C≡C triple bonds and C≡N triple bonds.[9] A further range of novel phosphorus–selenium heterocycles were prepared by treating WR with dibasic nucleophiles.[10]

Results and Discussion

To date, no suitable general method for the synthesis of diselenaphosphetane diselenides has been established. Here, we describe a new method that gives WR with excellent purity and high yield. Reactions were carried out with WR and two reactive substrates to yield four new phosphorus–selenium heterocycles and a useful selenocarbonyl compound. As a direct comparison, the reaction between one of these substrates, diphenylcyclopropenone, and Lawesson's reagent was performed and gave the analogous thiocarbonyl compound in high yield.

Preparation of Woollins reagent from $(PhP)_5$: WR is usually prepared from the pentamer $(PhP)_5$ by following the litera-

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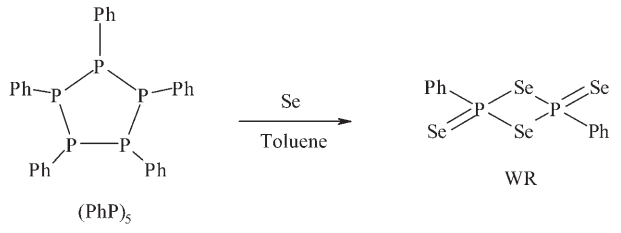
ture procedure[5c] (Scheme 1). Although this method produces the desired product, as indicated by the results of microanalysis and IR spectra, it has limitations. The pentamer is a highly unpleasant compound, is air-sensitive and has a lingering stench. One other major limitation of this method is that the pentamer can be readily prepared on a small scale only (5–10 g), which makes it an unsuitable precursor for large-scale synthesis.



Scheme 1.

Preparation of WR from $PhPCl_2$ and Na_2Se: We have employed a new method to synthesise WR, producing material of high purity in high yield. Elemental selenium was added to sodium metal dissolved in liquid ammonia at −78 °C, and was allowed to reflux at −34 °C. Once the ammonia was removed, Na_2Se was obtained as an off-white solid. The ammonia was replaced by toluene, $PhPCl_2$ was added and the mixture was heated to reflux. The reaction was filtered to remove the precipitated NaCl byproduct from the yellow solution. A second portion of selenium was added and reflux was continued. WR was isolated as red crystals in very high yield (86 %), which were identified by performing microanalysis, IR spectroscopy, mass spectrometry, powder diffraction and ^{31}P solid-state NMR spectroscopy. The IR and solid-state ^{31}P NMR[11] spectra are identical to those obtained for WR by using the previous method, and also to literature values.

The powder diffraction pattern of the product of this reaction was compared to a theoretical pattern calculated from single crystal data, unambiguously showing it to be Woollins reagent (Figure 1). A low intensity peak, due to an unidentified impurity, was also observed with 2θ at 49°. A powder diffraction pattern was also collected for a sample produced by the pentamer method, and showed it to contain a significant amount of red selenium.

The use of ^{31}P NMR spectroscopy allows us to monitor the course of the reaction (Scheme 2). After 18 h of the initial reflux, a ^{31}P NMR spectrum was recorded (Figure 2), which shows the presence of both **2** ($\delta = 102.3$, 101.1, 89.9, 82.9 ppm) and **3** ($\delta = 119.0$, 108.8, 106.2, 92.8, 90.1 ppm), the chemical shifts and coupling constants in accordance with known literature values.[4,5] The spectrum also shows the presence of the starting $PhPCl_2$ ($\delta = 161.5$ ppm) and $PhP(Se)Cl_2$ ($\delta = 58.3$ ppm) (Figure 2). This suggests that the reactive heterocycles **2** and **3** are formed by the reaction of

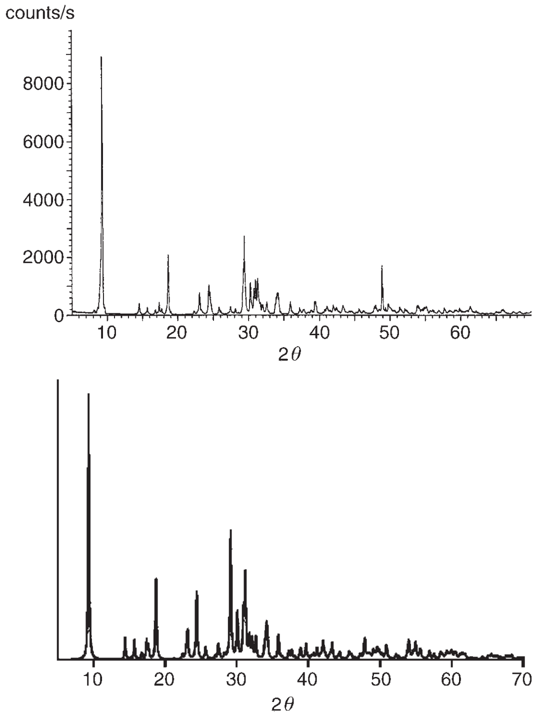
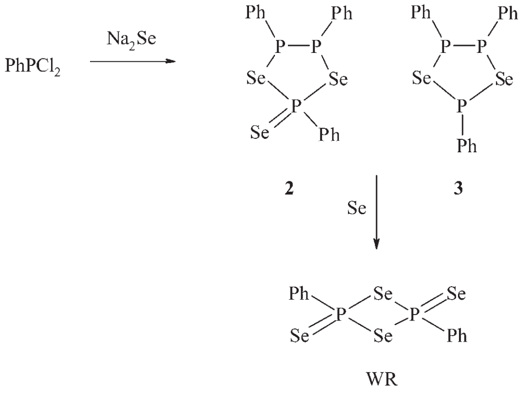


Figure 1. The upper spectrum shows the actual powder diffraction pattern obtained for **1**; the lower spectrum shows the powder diffraction pattern simulated from single crystal data of **1**.



Scheme 2.

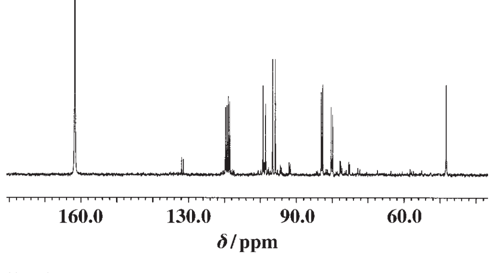
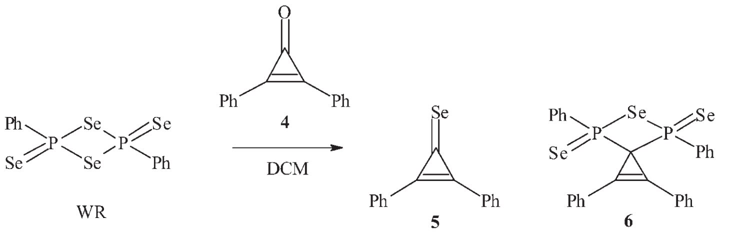


Figure 2. ^{31}P-{^{1}H} NMR spectrum obtained after 18 h of reflux of Na_2Se and $PhPCl_2$ in toluene.

$PhPCl_2$ with Na_2Se, and upon further addition of selenium, they are converted to WR.

This new method involves the use of the unpleasant dichlorophenylphosphine and the potentially hazardous liquid ammonia; however, it bypasses the handling of the pentamer $(PhP)_5$. In addition, it produces a product of high purity, in higher yield and by a cleaner process, but the real advantage of this method is that it can be conducted on a much larger scale (~150 g).



Scheme 3.

Reaction of WR with diphenylcyclopropenone: WR and diphenylcyclopropenone **4** were stirred together at 100 °C in dichloromethane (in a sealed tube) resulting in a very dark red solution plus a small amount of black selenium (Scheme 3). Column chromatography (silica gel, toluene) produced an orange fraction followed by a purple fraction. The orange fraction proved to be the expected selenation product, the selenocarbonyl compound **5**. This was isolated in moderate yield (27 %) as an orange, air-stable, solid. The identity of **5** was confirmed by microanalysis, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy, IR spectroscopy and mass spectrometry. The values obtained matched literature data from previous studies of this selenocarbonyl species. This compound is of interest in organometallic chemistry as it has been reported to undergo insertion reactions with metal carbonyl compounds.[12]

The second, purple fraction proved to be a new and unusual phosphorus–selenium heterocycle **6**. This was isolated in low yield (5 %) as a purple solid and was found to degrade in the presence of air and moisture over approximately two weeks. The ^{31}P NMR spectrum of **6** shows a sharp singlet at $\delta = 66.1$ ppm, accompanied by an unusual pattern of selenium satellites. There appeared to be three sets of satellites associated with each phosphorus atom, with ^{31}P,^{77}Se couplings of 304, 693 and 938 Hz, respectively. Closer inspection suggests that the pattern is actually a $^{1}J(^{31}P,^{77}Se)$ coupling of 304 Hz attributed to the P–Se single bonds, and a $^{1}J(^{31}P,^{77}Se)$ coupling of 816 Hz attributed to the P=Se double bonds, which is split by a $^{2}J(^{31}P,^{31}P)$ coupling of 124 Hz. This assignment is further substantiated by ^{77}Se NMR studies. The ^{77}Se NMR spectrum displays two distinct signals; a doublet at $\delta = -34.1$ ppm with a $^{1}J(^{31}P,^{77}Se)$ coupling constant of 820 Hz and a triplet at $\delta = 507$ ppm with a $^{1}J(^{31}P,^{77}Se)$ coupling constant of 306 Hz, assigned as P=Se and P–Se, respectively. Results of ^{1}H NMR spectroscopy showed that only phenyl protons are present. Unfortunately, the low yield meant that a suitable ^{13}C NMR spectrum could not be obtained.

Crystals suitable for X-ray analysis were grown by layering of a dichloromethane solution with hexane, allowing us to unambiguously identify the structure of **6** as a four-membered P_2SeC ring fused at the carbon atom to a three-membered cyclopropene ring (Figure 3). The structure shows that the exocyclic selenium atoms exist in a *trans* conformation, consistent with all known four-membered phosphorus–selenium ring systems of this type. The C=C double bond of the cyclopropene ring remains unchanged. The P_2SeC ring adopts a planar conformation that has been shown to be favoured by similar ring systems, WR,[9a] tBuP_2Se_4[2] and PhP(Se)(μ-NPh)P(Se)Ph.[9a] The internal P-Se-P bond angle in **6** (78.83(9)°) is substantially smaller than in WR (85.45(9)°) and is closer to the values found for $Ph_2P_2Se_3CMe_2$[13] (77.73(7)°) and PhP(Se)(μ-NPh)P(Se)Ph[9a] (75.28(4)°), indicating that the reduction in angle size is due to the introduction of the smaller heteroatom (C or N). Only two other examples of P_2SeC four-membered rings have been discovered; $Ph_2P_2SeCH_2$[13] and $Ph_2P_2SeCMe_2$.[13] These are consistent with the above structure, but no three-membered ring has been shown to fuse to such a system.

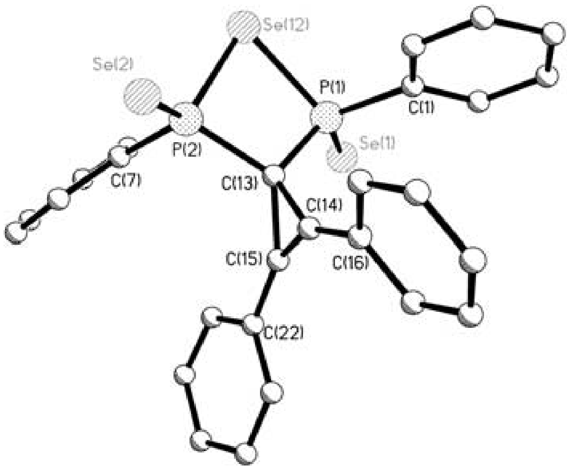
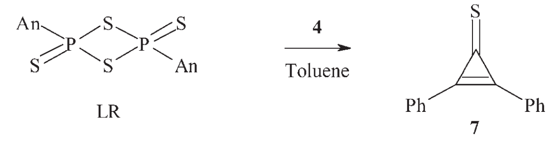


Figure 3. The X-ray structure of **6**. Selected bond lengths (Å) and angles (°) (esd's in parentheses): P(1)–Se(1) 2.089(3), P(1)–Se(12) 2.265(2), P(1)–C(1) 1.826(10), P(1)–C(13) 1.840(9), C(13)–C(15) 1.507(12), C(14)–C(15) 1.290(12), P(1)-Se(12)-P(2) 78.83(9), P(1)-C(13)-P(2) 102.0(4).

Reaction of Lawesson's reagent with diphenylcyclopropenone: As a direct comparison, the reaction between diphenylcyclopropenone and Lawesson's reagent (LR) was performed (Scheme 4) to give **7** as the only product (confirmed by microanalysis, ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy and mass spectrometry).[11] Like its selenium analogue, **7** has been reported to undergo similar insertion reactions with metal carbonyl compounds.[11] Unlike the corresponding reaction with Woollins reagent, there was no sign



Scheme 4.

of the formation of any phosphorus-containing heterocyclic products. Although this reaction did not produce any novel heterocycles, it clearly demonstrates a novel and simple route to this useful thiocarbonyl compound.

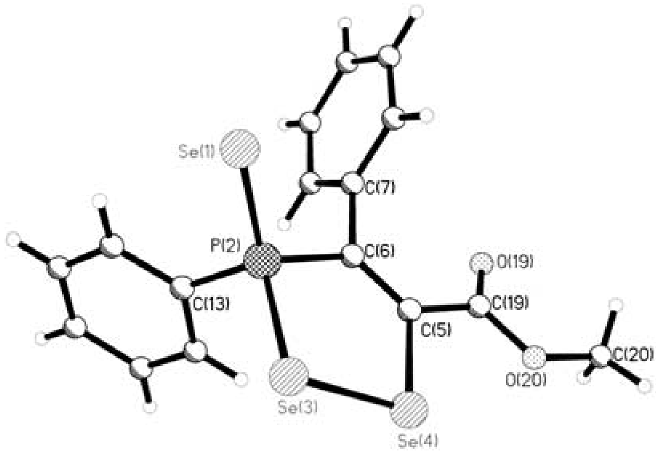
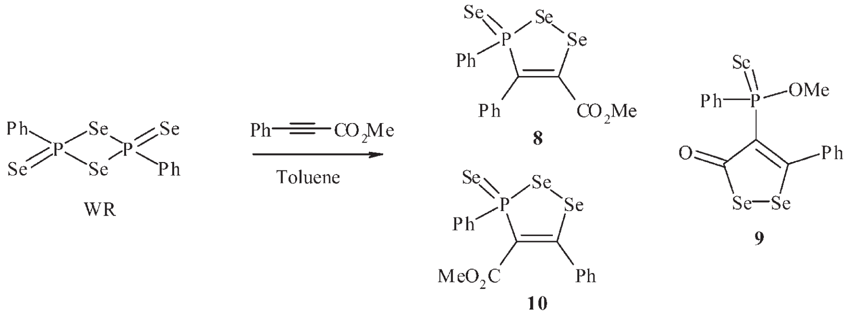


Figure 4. The X-ray structure of **8**. Selected bond lengths [Å] and angles [°] (esd's in parentheses): Se(1)−P(2) 2.096(2), P(2)−Se(3) 2.2387(19), Se(3)−Se(4) 2.3286(11), Se(4)−C(5) 1.924(6), C(5)−C(6) 1.323(9); Se(1)-P(2)-Se(3) 112.21(9), P(2)-Se(3)-Se(4) 94.78(5), C(5)-Se(4)-Se(3) 96.1(2), C(5)-C(6)-P(2) 112.3(4), C(6)-C(5)-Se(4) 123.8(5).



Scheme 5.

Reaction of WR with methyl phenylpropiolate: WR and methyl phenylpropiolate were heated to reflux in toluene, resulting in a red solution. The use of column chromatography (silica gel, toluene) afforded four phosphorus-containing fractions, from which compounds **8**–**10** were obtained in 20–26% isolated yields (Scheme 5). Compounds **8**–**10** were found to be solids that were moderately stable in air, degrading over a period of several weeks with the obvious expulsion of red selenium. They are soluble in chloroform, tetrahydrofuran and dichloromethane and insoluble in diethyl ether and hexane. The mass spectra of these compounds all contain molecular ion peaks at *m*/*z* 506, corresponding to $PhPSe_3(PhC{=}C{-}CO_2Me)$, which is supported by microanalyses.

The ^{31}P NMR spectra of **8** and **10** display sharp singlets at $\delta = 76.0$ and 71.4 ppm, respectively, and each signal is accompanied by two sets of selenium satellites (789 and 366 Hz for **8**, 798 and 343 Hz for **10**), indicating that in each compound there is a P−Se single bond and a P=Se double bond present. This is further substantiated by the ^{77}Se NMR spectrum, which displays three doublets, due to ^{31}P,^{77}Se coupling, and indicates the presence of a PhP(Se)-Se-Se chain, a fragment present in the products obtained from the reaction of WR with dimethyl acetylenedicarboxylate, norbornadiene and norbornene.[9a,b] The X-ray structure of **8** (Figure 4) was obtained unambiguously and shows that the PhP(Se)-Se-Se chain is attached across the C=C double bond in a five-membered ring. The structure also shows that in **8**, the ester group is *trans* to the phosphorus atom, thus **10** is assigned as the *cis* isomer. This assignment of these isomers is also reinforced by the ^{13}C NMR data, which revealed the expected differences in chemical shift and ^{31}P,^{13}C coupling constants. The ^{1}H NMR spectra show that in both molecules there are two phenyl groups and one methoxy group present.

The X-ray structure of **8** confirms the formation of a five-membered C_2PSe_2 ring. The ring is essentially planar with a mean deviation of 0.06 Å; however, this was not found to be the case for heterocycles containing similar ring systems formed from the reaction of WR with dimethyl acetylenedicarboxylate (C_2PSe_2 and C_2PSe_2) and bicyclo[2.2.1]hept-2-ene (C_2PSe_2), which have envelope conformations.[9a–c] The Se(3)−Se(4) bond length (2.3266(11) Å) is comparable to the Se−Se bond lengths found in $(PhPSe)_2CH_2Se_2$ (2.338(1) Å)[9b] and PhP(Se)-$Se_2(C_2\{CO_2Me\}_2)$ (2.359(2) Å)[9c], with the plane of the phenyl group attached to C(6) lying almost perpendicular to the central C_2PSe_2 ring (C(5)-C(6)-C(7)-C(12) torsion angle of 80.9(10)°).

Despite the similarities in the molecular ions and microanalyses of **9**, and **8** and **10**, the spectra of **9** display a somewhat different pattern to those of **8** and **10**. The ^{31}P spectrum of **9** again displays a sharp singlet ($\delta = 85.7$ ppm), but in this case, only one set of selenium satellites is observed, with a ^{31}P,^{77}Se coupling constant of 822 Hz. This would indicate the presence of a P=Se double bond and the absence of any P−Se single bonds, therefore, compound **9** must adopt a different structural motif to that of **8** and **10**. The ^{77}Se NMR spectrum displays a doublet at $\delta = 207$ ppm with a ^{31}P,^{77}Se coupling constant of 823 Hz, confirming the presence of a P=Se bond. There are also two distinct singlets at $\delta = 688$ and 519 ppm, respectively. The ^{1}H NMR spectrum shows that the molecule contains two phenyl groups and one methoxy group, with a ^{1}H,^{31}P coupling constant of 15 Hz.

The X-ray structure of **9** was obtained (Figure 5) and was, as expected, very different from that of **8**. The molecule possesses a planar C_3Se_2 ring, with exocyclic CPh and PhP(Se)OMe substituents arranged in a *cis* geometry with respect to one another. The structure shows that, in contrast to **8**, the ester group of the starting material has not remained unchanged, with the methoxy group having migrated to form a bond to the phosphorus atom. The data obtained from the ^{13}C NMR spectrum of **9** is that expected for this structure.

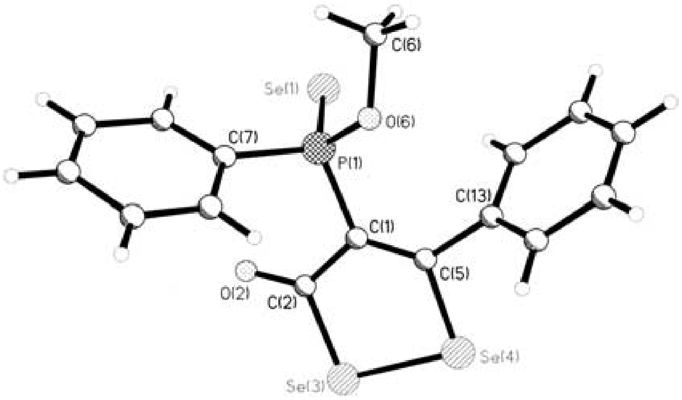


Figure 5. The X-ray structure of **9**. Selected bond lengths [Å] and angles [°] (esd's in parentheses). Se(1)–P(1) 2.096(3), P(1)–O(6) 1.591(7), C(2)–Se(3) 1.948(10), Se(3)–Se(4) 2.3082(16), Se(4)–C(5) 1.895(10), O(6)–C(6) 1.469(13), C(2)–O(2) 1.202(12); C(1)-P(1)-Se(1) 113.1(3), C(5)-C(1)-P(1) 126.6(8), C(2)-C(1)-P(1) 112.9(7), C(2)-C(1)-P(1) 112.9(7), O(2)-C(2)-C(1) 126.4(9), O(2)-C(2)-Se(3) 119.7(8), C(1)-C(2)-Se(3) 113.9(7), C(2)-Se(3)-Se(4) 92.4(3), C(5)-Se(4)-Se(3) 91.1(3), C(1)-C(5)-Se(4) 122.0(8)C(5)-C(1)-C(2) 120.3(9).

In **8** and **9**, the C–Se (1.895(10), 1.948(10) Å) and P–Se bond lengths (ca. 2.10 Å for P=Se double bonds and 2.24 Å for P–Se single bonds) and the angles at internal selenium atoms (91.1(3) to 96.1(2)°) are consistent with those found for similar ring systems. There are no notable intermolecular contacts within either structure.

Conclusion

We have described a new method for the preparation of WR, which gives a product of excellent purity and high yield, and which can be applied to syntheses on a much larger scale than that previously employed. Reactions were carried out with Woollins reagent and two reactive substrates (diphenylcyclopropenone and methyl phenylpropiolate) to yield four new isolable phosphorus–selenium heterocycles, including the novel spirocyclic compound **6**.

Experimental Section

General: Unless otherwise stated, experiments were performed under an oxygen-free nitrogen atmosphere by using predried solvents and standard Schlenk techniques. All reagents were purchased from Aldrich, Acros or Lancaster and were used as received. IR spectra were recorded as KBr discs in the range 4000–350 cm^{-1} by using a Perkin–Elmer System 2000 Fourier-transform spectrometer; ^{1}H, ^{31}P, ^{13}C and ^{77}Se NMR spectra were recorded by using a Jeol GSX Delta 270 FT NMR spectrometer. Solid-state ^{31}P NMR spectra were recorded by using an Infinityplus 500 MHz solid-state NMR spectrometer. Microanalyses were performed by the University of St. Andrews microanalysis service. Mass spectra were recorded by both the University of St. Andrews mass spectrometry service and the Swansea mass spectrometry service.

Synthesis

Preparation of $(PhP)_5$: $PhPCl_2$ (8.9 g, 50 mmol) and Mg turnings (1.2 g, 50 mmol) were stirred together in THF (50 cm^3) for 4 h. Room temperature was maintained by some external cooling. Acetone (5 cm^3) was added and excess Mg was filtered off. Upon the addition of water (2× 30 cm^3), an oily off-white precipitate formed. The mixture was stirred vigorously for 40 min. The product was collected by suction filtration and dried in vacuo to give a white solid (1.41 g, 26 % yield).

*Preparation of $(PhPSe_2)_2$ (**1**): From $(PhP)_5$*: $(PhP)_5$ (1.01 g, 1.87 mmol) and selenium (1.49 g, 18.7 mmol) were refluxed with stirring in toluene (30 cm^3) for 5 h. The reaction mixture was allowed to cool to room temperature. The product was collected by suction filtration, washed with toluene (2×15 cm^3) and dried in vacuo to give a red solid (1.96 g, 78 % yield); IR (KBr disc): $\tilde{\nu} = 1433$ (s), 1300 (mw), 1280 (w), 1155 (w), 1108 (w), 1078 (s), 994 (m), 917 (w), 841(w), 744 (m), 734 (s), 702 (m), 678 (s), 615 (m), 508 (s, br), 486 (s), 430 cm^{-1} (s); elemental analysis calcd (%) for $C_{12}H_{10}P_2Se_4$: C 27.09, H 1.89; found: C 26.62, H 1.80; EIMS (positive mode): m/z: 534 $[M]^+$.

*Preparation of $(PhPSe_2)_2$ (**1**): From $PhPCl_2$*: Na (1.2 g, 52.2 mmol) was dissolved in liquid NH_3 (50 cm^3) at −78 °C. Se (2.061 g, 26.1 mmol) was added, resulting in a dark red mixture. After 15 min of stirring, the NH_3 was allowed to evaporate and was replaced by toluene (50 cm^3). An excess of $PhPCl_2$ (6.60 cm^3) was added and refluxed for 64 h. The progress of the reaction was monitored by ^{31}P NMR analysis. Se (3.435 g, 43 mmol) was added and the mixture was refluxed for 3.5 h. The product was collected by suction filtration, washed with toluene (2×15 cm^3) and dried in vacuo to give a red solid (5.68 g, 82 % yield); ^{31}P NMR (solid state): $\delta = 18.7$ ppm (s); IR (KBr disc): $\tilde{\nu} = 1434$ (s), 1302 (mw), 1280 (w), 1154 (w), 1109 (w), 1077 (s), 994 (m), 917 (w), 744 (m), 734 (s), 704 (m), 679 (s), 614 (m), 508 (s, br), 486 (s), 432 cm^{-1} (s); elemental analysis calcd (%) for $C_{12}H_{10}P_2Se_4$: C 27.09, H 1.89; found: C 27.12, H 1.41; EIMS (positive mode): m/z: 534 $[M]^+$.

This reaction can be performed on a scale 20 times greater than that described above, and by taking suitable handling precautions. Attempts were made to repeat this procedure using a) Li (0.362 g, 52.2 mmol) and b) $(nBu_4N)BH_4$ (13.421 g, 52.2 mmol) instead of Na, however, both attempts proved unsuccessful.

Reaction of WR with diphenylcyclopropenone—synthesis of 5 and 6: WR (**1**), (0.2 g, 37.3 mmol) and diphenylcyclopropenone (0.154 g, 74.6 mmol) were stirred in dichloromethane (3 cm^3) at 100 °C in a sealed tube for 5 min, producing a dark red solution plus a tiny amount of black solid (selenium). Column chromatography (silica gel, toluene) produced an orange fraction and a subsequent purple fraction. These were dried in vacuo and produced an orange solid, **5**, and a purple solid, **6**.

Compound **5** (0.054 g, 27 % yield, based on ketone); ^{1}H NMR ($CDCl_3$): $\delta = 7.61$–8.25 ppm (m, 10 H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 173.1$ (s, C=Se), 159.9 (s, Ph C-1), 134.6 (s, p-Ph), 132.4 (s, m-Ph), 129.7 (o-Ph), 122.8 ppm (s, C-Ph); ^{77}Se NMR ($CDCl_3$): $\delta = 330.0$ ppm (s); IR: (KBr disc): $\tilde{\nu} = 3463$ (s, br), 1780 (m), 1596 (m), 1360 (m), 1331 (s), 1310 (s), 1287 (s), 1171 (m), 764 (s), 685 cm^{-1} (s); elemental analysis calcd (%) for $C_{15}H_{10}Se$: C 66.92, H 3.74; found: C 66.74, H 3.51; EIMS (positive mode): m/z: 270 $[M]^+$.

Compound **6** (0.012 g, 5 % yield, based on WR): Yellow crystals suitable for X-ray analysis were grown by layering a dichloromethane solution with hexane; ^{1}H NMR (CDCl$_3$): $\delta = 7.16$–7.37 ppm (m, 20H; Ph); ^{31}P NMR (CDCl$_3$): $\delta = 66.1$ ppm (s, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 304.2$ Hz, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 815.5$ Hz), $^{2}J(^{31}\mathrm{P},^{31}\mathrm{P}) = 124.4$ Hz; ^{77}Se NMR (CDCl$_3$): $\delta = -34.1$ (d, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 820.2$ Hz), 506.9 ppm (t, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 306.1$ Hz); IR (KBr disc): $\tilde{\nu} = 3048$ (s), 1445 (m), 1435 (s), 1305 (w), 1086 (s), 754 (s), 727 (m), 706 (m), 685 (s), 541 cm^{-1} (s, P=Se); elemental analysis calcd (%) for $C_{27}H_{20}P_2Se_3$: C 50.41, H 3.13; found: C 50.11, H 3.04; EIMS (positive mode): *m*/*z*: 643 $[M]^+$.

Reaction of Lawesson's reagent with diphenylcyclopropenone—synthesis of 7: LR (0.133 g, 37.3 mmol) and diphenylcyclopropenone (0.154 g, 74.6 mmol) were refluxed in toluene (3 cm^3) for 3 min, producing a brown/orange solution. Column chromatography (silica gel, toluene) produced a yellow fraction. This was dried in vacuo to give a yellow solid (0.121 g, 74 % yield); ^{1}H NMR (CDCl$_3$): $\delta = 7.25$–7.85 ppm (m, 10H; Ph); ^{13}C NMR (CDCl$_3$): $\delta = 178.5$ (s, *C*=S), 153.8 (s, Ph C-1), 133.8 (s, *p*-Ph), 132.1 (s, *m*-Ph), 129.6 (*o*-Ph), 122.9 ppm (s, *C*-Ph); IR (KBr disc): $\tilde{\nu} = 3449$ (s, br), 1780 (m), 1595 (m), 1352 (s), 1331 (s), 1314 (m), 1298 (m), 1172 (m), 762 (s), 688 cm^{-1} (s); elemental analysis calcd (%) for $C_{15}H_{10}S$: C 81.04, H 4.53; found: C 80.72, H 4.26; EIMS (positive mode): *m*/*z*: 222 $[M]^+$.

Reaction of WR (1) with methyl phenylpropiolate: A mixture of Woollins reagent (0.300 g, 0.56 mmol) and methyl phenylpropiolate (0.18 cm^3) in toluene (7 cm^3) was heated at reflux for 21 h resulting in a red solution. After cooling to room temperature, the solution was subjected to column chromatography (silica gel, toluene) and afforded successively yellow, orange (**8**), yellow (**9**) and orange (**10**) eluates. Compounds **8**–**10** were precipitated as yellow (**8** and **9**) or orange (**10**) solids following the addition of hexane to dichloromethane solutions.

Compound **8** (0.073 g, 26 % yield): Yellow crystals suitable for X-ray analysis were grown by layering of a dichloromethane solution with hexane; ^{1}H NMR (CDCl$_3$): $\delta = 8.02$ (m, 2H; Ph), 7.44 (m, 3H; Ph), 7.18 (m, 3H; Ph), 7.01 (m, 2H; Ph), 3.61 ppm (s, 3H; CH$_3$); ^{13}C NMR (CDCl$_3$): $\delta = 178.6$ (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 9.3 Hz, *C*=O), 162.9 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 26.0 Hz, *C*-C=O), 144.5 (d, $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 60.2 Hz, P-*C*(Ph)=C), 133.7 (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 10.4 Hz, C-Ph-*o*), 132.8 (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 12.5 Hz, P-Ph-*m*), 131.1 (d, $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 70.6 Hz, P-Ph C-1), 129.7 (d, $^{4}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 5.2 Hz, C-Ph-*m*), 129.6 (d, $^{4}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 5.2 Hz, P-Ph-*p*), 128.9 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 29.1 Hz, C-Ph C-1), 128.5 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 14.5 Hz, P-Ph-*o*), 127.8 (s, C-Ph-*p*), 53.3 ppm (s, O*C*H3); ^{31}P NMR (CDCl$_3$): $\delta = 76.0$ ppm (s, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 789.2$ and 365.9 Hz); ^{77}Se NMR (CDCl$_3$): $\delta = 525.8$ (d, $^{2}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 9.5$ Hz, C-Se), 341.4 (d, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 367.2$ Hz, P-Se), 26.8 ppm (d, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 796.3$ Hz, P=Se); selected IR data (KBr): $\tilde{\nu} = 1742$ (s, C=O), 1224 (m, C–O), 523 cm^{-1} (m, P=Se); elemental analysis calcd (%) for $C_{16}H_{13}O_2PSe_3$: C 38.04, H 2.59; found: C 38.47, H 2.30; EIMS (positive mode): 506 $[M]^+$.

Compound **9** (0.056 g, 20 % yield): Yellow crystals suitable for X-ray analysis were grown by layering of a chloroform solution with hexane; ^{1}H NMR (CDCl$_3$): $\delta = 7.90$ (m, 2H; Ph), 7.64 (m, 2H; Ph), 7.48 (m, 6H; Ph), 3.28 ppm (d, 3H; $^{3}J(^{31}\mathrm{P},^{1}\mathrm{H})$ 15.0 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$): $\delta = 194.6$ (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 17.6 Hz, *C*=O), 178.6 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 10.4 Hz, C=*C*-Ph), 138.8 (d, $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 120.8 Hz, P-*C*=C), 136.5 (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 3.1 Hz, C-Ph C-1), 132.1 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 12.5 Hz, P-Ph-*o*), 130.4 (s, C-Ph-*o*), 130.0 (d, $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 121.4 Hz, P-Ph C-1), 129.6 (d, $^{4}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 4.2 Hz, P-Ph-*p*), 128.3 (s, C-Ph-*m*), 128.0 (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 14.5 Hz, P-Ph-*m*), 127.2 (s, C-Ph-*p*), 52.3 ppm (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 5.2 Hz, O*C*H$_3$); ^{31}P NMR (CDCl$_3$): $\delta = 85.7$ ppm (s, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 821.7$ Hz); ^{77}Se NMR (CDCl$_3$): $\delta = 687.5$ (s, C(=O)Se), 518.0 (s, C(Ph)Se), 207.0 ppm (d, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 822.5$ Hz, P=Se); selected IR data (KBr): $\tilde{\nu} = 1638$ (s, C=O), 546 cm^{-1} (m, P=Se); elemental analysis calcd (%) for $C_{16}H_{13}O_2PSe_3$: C 38.04, H 2.59; found: C 37.69, H 2.34; EIMS (positive mode): *m*/*z*: 506 $[M]^+$.

Compound **10** (0.070 g, 25 % yield); ^{1}H NMR (CDCl$_3$): $\delta = 8.18$ (m, 2H; Ph), 7.48 (m, 8H; Ph), 3.37 ppm (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$): $\delta = 165.7$ (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 10.4 Hz, C=*C*-Ph), 164.3 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 18.7 Hz, *C*=O), 133.2 (d, $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 74.9 Hz, P-Ph C-1), 132.8 (d, $^{4}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 3.1 Hz, P-Ph-*p*), 131.5 (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 13.5 Hz, P-Ph-*m*), 131.3 (s, C-Ph-*p*), 129.0 (s, C-Ph-*o*), 128.7 (d, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 10.8 Hz, C-Ph C-1), 128.6 (d, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 15.6 Hz, P-Ph-*o*), 128.5 (s, C-Ph-*m*), 126.5 (d, $^{1}J(^{31}\mathrm{P},^{13}\mathrm{C})$ 71.6 Hz, P-*C*=C), 52.3 ppm (s, O*C*H$_3$); ^{31}P NMR (CDCl$_3$): $\delta = 71.4$ ppm (s, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 798.3$ and 342.8 Hz); ^{77}Se NMR (CDCl$_3$): $\delta = 532.0$ (d, $^{2}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 7.2$ Hz, C-Se), 420.6 (d, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 343.3$ Hz, P-Se), -25.0 ppm (d, $^{1}J(^{31}\mathrm{P},^{77}\mathrm{Se}) = 798.7$ Hz, P=Se); selected IR data (KBr): $\tilde{\nu} = 1707$ (s, C=O), 1233 (s, C–O), 539 cm^{-1} (m, P=Se); elemental analysis calcd (%) for $C_{16}H_{13}O_2PSe_3$: C 38.04, H 2.59; found: C 39.01, H 2.44; EIMS (positive mode): *m*/*z*: 506 $[M]^+$.

X-ray crystallography: Table 1 list details of data collections and refinements. Data for **6** and **8** were collected at 293 K, and for **9** at 125 K by using a Bruker SMART (sealed tube) system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. The positions of the hydrogen atoms were idealised. Refinements were obtained with full-matrix least-squares based on F^2 by using SHELXTL.[14,15]

Table 1. Details of the X-ray data collections and refinements for **6**, **8** and **9**.

Compound	**6**	**8**	**9**
formula	$C_{27}H_{20}P_2Se_3$	$C_{16}H_{13}O_2PSe_3$	$C_{16}H_{13}O_2PSe_3$
crystal colour, habit	yellow, block	yellow, block	yellow, plate
crystal size [mm^3]	0.2 × 0.1 × 0.05	0.15 × 0.1 × 0.1	0.16 × 0.04 × 0.02
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$P2_1/n$
a [Å]	13.6894(8)	9.6996(10)	11.041(4)
b [Å]	11.0398(5)	9.4792(9)	7.068(3)
c [Å]	33.605(2)	19.1924(19)	22.564(8)
α [°]	90	90	90
β [°]	90.496(2)	100.033(2)	101.306(7)
γ [°]	90	90	90
V [Å^3]	5078.5(5)	1737.6(3)	1726.7(11)
Z	8	4	4
M_r	643.25	505.11	505.11
ρ [g cm^{-3}]	1.683	1.931	1.943
μ [mm^{-1}]	4.485	6.445	6.486
$F(000)$	2512	968	968
measured reflns.	10621	8260	7042
independent reflns. (R_{int})	3584(0.0301)	2368(0.0588)	2432(0.02508)
final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0623(0.1445)	0.0461, 0.1074	0.0882, 0.2010

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[15] CCDC 266199–266201 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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