





## Synthesis and Characterization of Novel Organic Heteroatom Compounds from Reaction of Woollins' Reagent with Various Organic Substrates

Guoxiong Hua, Junyi Du, David B. Cordes, Kasun S. A. Arachchige, Alexandra M. Z. Slawin & J. Derek Woollins

**To cite this article:** Guoxiong Hua, Junyi Du, David B. Cordes, Kasun S. A. Arachchige, Alexandra M. Z. Slawin & J. Derek Woollins (2015): Synthesis and Characterization of Novel Organic Heteroatom Compounds from Reaction of Woollins' Reagent with Various Organic Substrates, *Phosphorus, Sulfur, and Silicon and the Related Elements*, DOI: [10.1080/10426507.2015.1072184](https://doi.org/10.1080/10426507.2015.1072184)


**To link to this article:** <http://dx.doi.org/10.1080/10426507.2015.1072184>

 View supplementary material 

 Accepted online: 02 Oct 2015.

 Submit your article to this journal 

 Article views: 2

 View related articles 

 View Crossmark data 

# Synthesis and Characterization of Novel Organic Heteroatom Compounds from Reaction of Woollins' Reagent with Various Organic Substrates

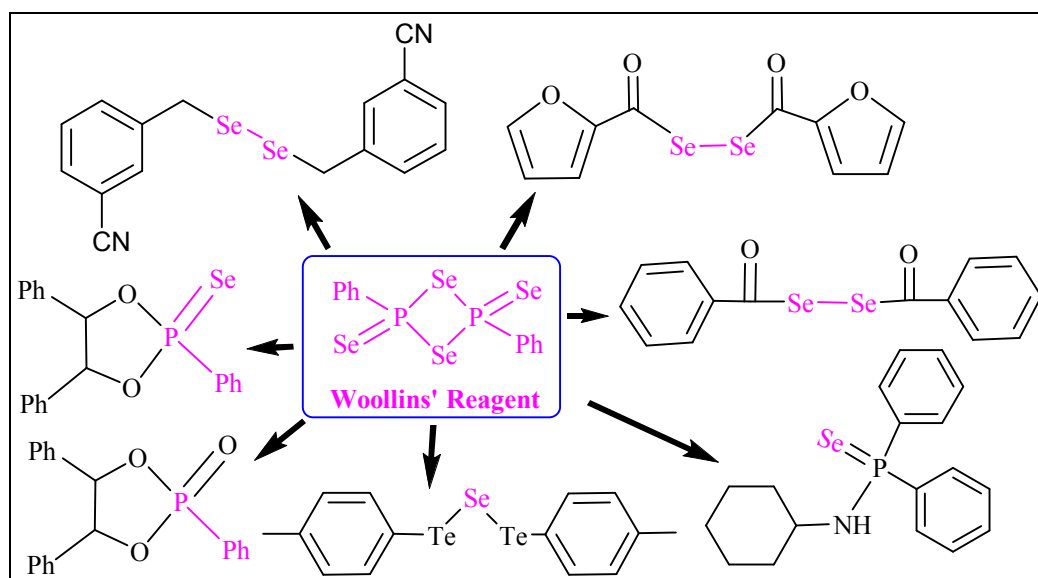
Guoxiong Hua, Junyi Du, David B. Cordes, Kasun S. A. Arachchige, Alexandra M. Z. Slawin  
and J. Derek Woollins\*

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

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

## Abstract

A series of new selenium-containing heteroatom compounds were synthesized in good yields by the reactions of Woollins' reagent with various organic substrates such as cyclohexylamine, *N*-benzoylbenzamide, benzoic anhydride, 4-fluoro-*N*-(2-oxo-2-phenylethyl)benzamide, *N*-benzoylbenzamide, benzoic anhydride, 3-(bromomethyl)benzonitrile, 1,2-diphenylethane-1,2-diol and sodium alcoholate. Three representative X-ray structures are described.



***Key words***

*Woollins' reagent / Benzamides / Diselenoperoxyanhydrides / Heteroatom compounds / Single crystal structures*

## INTRODUCTION

Following the discovery of seleno-enzymes, selenium-containing compounds have been studied extensively because of their interesting reactivity profile and potential applications in many areas such as organic synthesis,<sup>1</sup> biochemistry,<sup>2</sup> xerography,<sup>3</sup> the synthesis of conducting materials,<sup>4</sup> semiconductors,<sup>5</sup> ligand synthesis<sup>6</sup> and cancer therapy.<sup>7</sup> A wide range of selenation reagents can introduce selenium into organic substrates by both nucleophilic and electrophilic pathways, and the resulting selenium-containing products can be further converted into useful targets that may or may not retain the selenium atom.<sup>8</sup> 2,4-Bis(phenyl)-1,3-diselenadiphosphethane-2,4-diselenide [ $\{\text{PhP}(\text{Se})(\mu\text{-Se})\}_2$ ] (Woollins' reagent, **WR**, a selenium counterpart of Lawesson's reagent) has proved in recent years to be an efficient selenation reagent in organic synthetic chemistry due to its ready preparation and ease of handling.<sup>9-21</sup> Herein, we report the synthesis of a series of novel selenium-containing heteroatom compounds from the reaction of Woollins' reagent with various organic substrates such as alkylamine, benzamides, benzoic anhydride, benzonitrile, 1,2-diol, sodium alkyl-alcoholate and three representative single crystal X-ray structures.

## RESULTS AND DISCUSSION

Treatment of Woollins' reagent with an equi-molar amount of *N*-benzoylbenzamide (**1**)<sup>22</sup> in refluxing toluene solution led to the formation of benzoic diselenoperoxyanhydride (**2**) in 53% isolated yield. Alternatively, applying Woollins' reagent with an equivalent of benzoic anhydride under identical conditions gave the same product (**2**) in 72% isolated yield (Scheme 1). This efficient method is very simple and easy to control, and avoids using harsh selenation reagents

such as LiAlHSeH for the synthesis of various diacyl selenides, diacyl diselenides and selenocarboxylates.<sup>23</sup>

Similarly, furan-2-carboxylic diselenoperoxyanhydride (**4**) could be prepared by the reaction of Woollins' reagent with an equi-molar amount of *N*-(furan-2-carbonyl)furan-2-carboxamide (**3**)<sup>24</sup> under identical conditions in 61% isolated yield (Scheme 2). We confirmed the nature of **4** by a single crystal X-ray structure obtaining similar results to those reported elsewhere.<sup>25</sup>

An attempt to synthesize selenoamide (**5**) by treating 3-(bromomethyl)benzonitrile with Woollins' reagent/H<sub>2</sub>O in refluxing toluene failed, instead, 3,3'-(diselanediyldis(methylene))dibenzonitrile (**6**) was unexpectedly isolated in excellent yield (93%) as shown in Scheme 3. The result is in contrast with the previous report that the nitrile reacted with Woollins' reagent/H<sub>2</sub>O leading to the formation of 3-(bromomethyl)benzoselenoamide (**5**).<sup>26</sup> Surprisingly, 3,3'-(diselanediyldis(methylene))dibenzonitrile (**6**) formed with the CN group being intact. The mechanism for this reaction is not clear so far and further investigation is underway. The IR spectrum of **6** shows a strong band at 2225 cm<sup>-1</sup> resulting from the  $\nu(\text{C-N})$  and is characteristic of the C $\equiv$ N group. The <sup>77</sup>Se NMR spectrum of **6** displays a singlet signal at 419.0 ppm, comparable to the related diselenides.<sup>27</sup> A single crystal structure confirmed the formation of the compound **6** (Figure 1).<sup>28</sup>

Breaking the four-membered ring in Woollins' reagent with two molar equivalents of sodium methanolate generated the sodium *O*-methyl phenylphosphonodiselenoate **7**,<sup>29</sup> the latter was further stirred with an equivalent of trichloro(*p*-tolyl)- $\lambda^4$ -tellane in dry THF for 24 h at room temperature delivering bis(*p*-tolyltellanyl)selane (**8**) in 47% isolated yield as depicted in Scheme 4. Compound **8** was spectrally characterized by multi-nuclear NMR and IR spectroscopy and

accurate mass measurement. Two stereoisomers were observed from multinuclear NMR spectra which show very close chemical shifts in both the  $^{77}\text{Se}$  NMR spectrum ( $\delta_{\text{Se}}$  265.4 and 265.5 ppm) and the  $^{125}\text{Te}$  NMR spectrum ( $\delta_{\text{Te}}$  423.5 and 423.8 ppm). According to the literature, compound **8** is new though similar compounds can be obtained by reaction of diaryl ditelluride with  $\text{SeO}_2$  in pyridine.<sup>30</sup> However, we have found no published X-ray crystal structure data for this kind of compound, therefore, we report the new single crystal structure here (Figure 2).<sup>28</sup> The single crystal structure adopts a symmetric framework. The Te-Se single bond length [2.5216(16) Å] is significantly longer than the Se-Se single bond distance [2.3088(9) Å] in the structure of **6**, reflecting the big difference of the formation of the single bond between a selenium atom and a tellurium atom.

Stirring a mixture of diphenylethane-1,2-diol with an equimolar amount of Woollins' reagent in refluxing toluene for 3 h afforded two five-membered heterocycles **9** and **10** in 14% and 31% yields, respectively, after work up in air (Scheme 5). We presume that Woollins' reagent in toluene solution at elevated temperature is in equilibrium with a diselenaphosphorane  $\text{PhP}(\text{Se})_2$  (**I**), which is believed to be a true reactive species (Scheme 6).<sup>31</sup> We suggest that the initial step involves the reaction of intermediate **I** with diphenylethane-1,2-diol to give a five-membered ring **9** via an intramolecular cyclization by eliminating a molecule of  $\text{H}_2\text{Se}$ ; then, compound **9** could be readily oxidized by air to give another five-membered ring **10** (Scheme 6).

Monophosphorus **9** and **10** are soluble in organic solvents and air-stable. The  $^{31}\text{P}$  NMR spectra of **9** and **10** show sharp singlets at 107.9 and 34.9 ppm, however, one pair of satellites for the exocyclic selenium atom [ $^1J(\text{P}, \text{Se}_{\text{exo}})$ : 925 Hz] was only found in **9**, thus indicating the presence of the double  $\text{P}=\text{Se}$  bond in this structure. The  $^{77}\text{Se}$  NMR spectrum of **9** contains one doublet

signal ( $\delta_{\text{Se}} = -186.0$  ppm) with a matching coupling constant further confirming the presence of the only P=Se double bond. The single crystal X-ray structure has been reported elsewhere<sup>32</sup> and confirmed the formation of compound **10**.

Reaction of Woollins' reagent with two molar equivalents of cyclohexylamine at room temperature for 1 h gave the ammonium phenylphosphonamidodiselenoates **11** in almost quantitative yield;<sup>22</sup> the latter was further treated with one molar equivalent of chlorodiphenylphosphane but did not result in the expected compound **12**, instead *N*-cyclohexyl-*P,P*-diphenylphosphinoselenoic amide (**13**) formed in 72% isolated yield as displayed in Scheme 7. The <sup>31</sup>P NMR spectrum has a sharp singlet at 54.4 ppm, which is accompanied by one set of satellite for the exocyclic selenium atom [ $^1J(\text{P}, \text{Se}_{\text{exo}})$ : 751 Hz], indicating the presence of double P=Se bond. The <sup>77</sup>Se NMR spectrum reveals a set of signals at  $\delta_{\text{Se}} = -252.7$  Hz with matching coupling constant further confirming the presence of only the P=Se double bond. Single crystal structure analysis further confirmed the formation of the compound **13** (Figure 3).<sup>28</sup> The single crystal structure of **13** adopts a distorted tetrahedral conformation. The dihedral angles between the mean plane of cyclohexyl ring and two phenyl rings are 86.3 and 36.0°. The P(1)-Se(1) distance [2.139(3) Å] is marginally longer than the normal P=Se double bond length [ca. 2.08 Å]<sup>33</sup> and the P–N single bond length [1.672(7) Å] is significantly shorter, compared to the other typical P–N single bond system [ca. 1.80 Å],<sup>34</sup> suggesting some delocalization.

## EXPERIMENTAL

Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work

up procedures were performed in air.  $^1\text{H}$  (400.1 MHz),  $^{13}\text{C}$  (100.6 MHz),  $^{31}\text{P}$ - $\{^1\text{H}\}$  (162.0 MHz) and  $^{77}\text{Se}$ - $\{^1\text{H}\}$  (51.5 MHz referenced to external  $\text{Me}_2\text{Se}$ ) NMR spectra were recorded at 25 °C (unless stated otherwise). IR spectra were recorded as KBr pellets in the range of 4000-250  $\text{cm}^{-1}$  on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea. X-ray crystal structures were determined for compounds **6**, **8** and **13** at -148(1) °C on a Rigaku ACTOR-SM, Saturn 724 CCD area detector [the St Andrews Automated Robotic Diffractometer (STANDARD)]<sup>27a</sup> with SHINE optic using Mo Ka radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were corrected for Lorentz, polarisation and absorption. The data was collected and processed using CrystalClear (Rigaku).<sup>35</sup> The structures were solved by direct methods<sup>36</sup> and expanded using Fourier techniques.<sup>37</sup> Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure<sup>38</sup> and SHELXL 97.<sup>39</sup> These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](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](mailto:deposit@ccdc.cam.ac.uk). CCDC 1054712-1054714. The Supplemental Materials contains sample  $^1\text{H}$  and  $^{13}\text{C}$  spectra for compounds **2**, **6**, **8**, **9**, **10** and **13** (Figures S 1 – S 12)

### Benzoic diselenoperoxyanhydride (**2**). *Method 1*

A suspension of *N*-benzoylbenzamide (0.225 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in toluene (15 mL) was refluxed for 15 h. Upon cooling to room temperature and removing toluene the residue was dissolved in dichloromethane and purified by silica gel (dichloromethane as eluent) to afford the titled compound **2** as yellow solid (0.194 g, 53%).

**Method 2:** A red suspension of benzoic anhydride (0.226 g, 1.0 mmol) and Woollins' reagent



(0.54 g, 1.0 mmol) in dry toluene (20 mL) was refluxed for 15 h. Upon cooling to room temperature and removing toluene in vacuum, the residue was purified by silica gel column (dichloromethane as eluent) to give the titled compound **2** as yellow solid (0.266 g, 72%). M.p. 130-132 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1738(m), 1685(s), 1444(m), 1196(s), 1173(m), 866(s), 769(m), 686(m), 664(s).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 8.00 (d,  $J(\text{H,H}) = 7.6$  Hz, 4H, Ar-H), 7.65 (t,  $J(\text{H,H}) = 7.6$  Hz, 2H, Ar-H), 7.53 (t,  $J(\text{H,H}) = 7.6$  Hz, 4H, Ar-H) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 187.2, 136.8, 134.5, 129.1, 128.1 ppm.  $^{77}\text{Se}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 614.1 ppm. MS ( $\text{Cl}^+$ ,  $m/z$ ), 371  $[\text{M}+\text{H}]^+$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{Se}_2$  (368.15): C, 45.7; H, 2.7. Found: C, 46.0; H, 2.8.

#### **Furan-2-carboxylic diselenoperoxyanhydride (4)**

A red suspension of *N*-(furan-2-carbonyl)furan-2-carboxamide (0.205 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in dry toluene (20 mL) was refluxed for 10 h. Upon cooling to room temperature and removing toluene in vacuum the residue was purified by silica gel column (1 : 1 hexane / dichloromethane as eluent) to give the titled compound **4** as a pale yellow solid (0.213 g, 61%). M.p. 156-157 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1740(m), 1683(s), 1195(s), 1178(m), 867(s), 770(m), 690(m), 665(s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ), 7.78 (d,  $J(\text{H,H}) = 3.6$  Hz, 2H, Furan-H), 7.51 (d,  $J(\text{H,H}) = 3.7$  Hz, 2H, Furan-H), 6.65 (dd,  $J(\text{H,H}) = 3.7$  Hz,  $J(\text{H,H}) = 3.6$  Hz, 2H, Furan-H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ), 155.5, 149.9, 146.1, 124.7, 113.3 ppm.  $^{77}\text{Se}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 624.5 ppm. Mass spectrum [ $\text{Cl}^+$ ,  $m/z$ ]: 351  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{Cl}^+$ ,  $m/z$ ]: 350.8667  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{10}\text{H}_7\text{O}_4\text{Se}_2\text{H}$ : 350.8673.

#### **3,3'-(Diselanediylobis(methylene))dibenzonitrile (6).**

A red suspension of 2-(bromomethyl)benzonitrile (0.195 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in dry toluene (20 mL) was refluxed for 6 h. Upon cooling to below 100 °C

water (1.0 mL) was added, the mixture then was allowed to refluxing for another 2 h. After cooling to room temperature and removing toluene in vacuum the residue was purified by silica gel column (dichloromethane as eluent) to give the titled compound **6** as orange solid (0.35 g, 93%). The crystals for X-ray determination were obtained from the diffusion of the dichloromethane solution of the compound into hexane. M.p. 176-178 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 2225(s), 1579(m), 1478(s), 1415(m), 1292(m), 1177(s), 1087(m), 896(s), 829(m), 801(vs), 688(vs), 532(s), 437(s).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 7.82-7.43 (m, 8H, Ar-H), 3.82 (s, 4H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 140.8, 133.3, 132.3, 130.8, 129.4, 118.5, 112.6, 31.1 ppm.  $^{77}\text{Se}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 419.4 ppm. Mass spectrum [ $\text{Cl}^+$ ,  $m/z$ ]: 393 [ $\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{Cl}^+$ ,  $m/z$ ]: 392.9404 [ $\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{Se}_2\text{H}$ : 392.9408.

### Synthesis of bis(*p*-tolyltellanyl)selane (**8**)

Small pieces of sodium (0.046 g, 2.0 mmol) were stirred in dry methanol (40 mL) at room temperature until fully dissolved. To this mixture Woollins' reagent (0.54 g, 1.0 mmol) was added and continued stirring for 3 h. The resulting green solution was filtered through a small Celite pad from the reaction mixture. The filtrate was concentrated under vacuum to *ca.* 5 mL and hexane (10 mL) was added to precipitate the salt as a white solid. Then, the above salt in THF (30 mL) was added dropwise to a solution of trichloro(*p*-tolyl)- $\lambda^4$ -tellane (0.312 g, 1.0 mmol) in THF (20 mL) at room temperature. The mixture was stirred at room temperature for another 24 h. After removing solvent in vacuum the residue was purified by silica gel column (dichloromethane as eluent) to give the titled compound **8** as red paste (0.120 g, 47%). Two diastereomers were found in multi-NMR spectra. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1479(m), 1439(m),

1207(m), 1183(m), 1135(m), 1046(s), 984(s), 796(s), 751(s), 696(s), 560(m), 524(s), 477(m).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 7.79-7.60 (m, 4Hx2, Ar-H), 7.09-6.99 (m, 4Hx2, Ar-H), 2.37 (s, 3H,  $\text{CH}_3$ ), 2.30 (s, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 138.3, 138.0, 132.4, 131.4, 131.3, 130.2, 128.6, 128.4, 21.0, 20.9 ppm.  $^{77}\text{Se}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 265.5 and 263.0 ppm.  $^{125}\text{Te}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 423.7 and 423.6 ppm. Mass spectrum [ $\text{Cl}^+$ ,  $m/z$ ]: 521 [ $\text{M}+\text{H}^+$ ]. Accurate mass measurement [ $\text{Cl}^+$ ,  $m/z$ ]: 520.8442 [ $\text{M}+\text{H}^+$ ], calculated mass for  $\text{C}_{14}\text{H}_{14}\text{SeTe}_2\text{H}$ : 520.8445.

### Reaction of Woollins' Reagent with diphenylethane-1,2-diol

A mixture of diphenylethane-1,2-diol (0.214 g, 1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in dry toluene (20 mL) was stirred at room temperature for 3 h. Then the mixture was heated to 60 °C and kept stirring for 2 h. The red suspension disappeared and a greyish green solution formed. Upon cooling to room temperature and removing the solvent in vacuum the residue was purified by silica gel column (dichloromethane as eluent) to give the compounds **9** and **10**.

### 2,4,5-Triphenyl-1,3,2-dioxaphospholane 2-selenide (**9**)

Pale green solid (0.055 g, 14%). M.p. 186-188 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1587(w), 1496(m), 1436(m), 1454(m), 1112(m), 980(s), 856(m), 716(s), 692(s), 637(s), 575(m,  $\text{P}=\text{Se}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 8.10-7.95 (m, 2H, Ar-H), 7.70-7.59 (m, 2H, Ar-H), 7.73-7.15 (m, 11H, Ar-H), 5.89 (dd,  $J(\text{P},\text{H}) = 13.6$  Hz,  $J(\text{H},\text{H}) = 2.3$  Hz, 2H, CH) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 134.4 (d,  $J(\text{P},\text{C}) = 5.0$  Hz), 133.3 (d,  $J(\text{P},\text{C}) = 3.3$  Hz), 131.9 (d,  $J(\text{P},\text{C}) = 10.4$  Hz), 130.5 (d,  $J(\text{P},\text{C}) = 8.9$  Hz), 128.9 (d,  $J(\text{P},\text{C}) = 15.5$  Hz), 128.4, 128.0, 126.9, 83.9 ppm.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 107.9 (s,  $J(\text{P},\text{Se}) = 925$  Hz) ppm.  $^{77}\text{Se}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), -186.0 (d,  $J(\text{P},\text{Se}) = 925$  Hz) ppm. Mass

spectrum  $[Cl^+, m/z]$ : 401  $[M+H]^+$ . Accurate mass measurement  $[Cl^+, m/z]$ : 401.0203  $[M+H]^+$ , calculated mass for  $C_{20}H_{17}O_2PSeH$ : 401.0210.

**2,4,5-Triphenyl-1,3,2-dioxaphospholane 2-oxide (10)**

Pale white solid (0.105 g, 31%). M.p. 206-207 °C. Selected IR (KBr,  $cm^{-1}$ ): 1439(m), 1269(m), 1133(m), 992(s), 870(m), 840(m), 716(s), 693(s), 510(m).  $^1H$  NMR ( $CD_2Cl_2$ ,  $\delta$ ), 8.06-7.94 (m, 2H, Ar-H), 7.71-7.55 (m, 2H, Ar-H), 7.23-7.05 (m, 11H, Ar-H), 6.74 (dd,  $J(P,H) = 9.2$  Hz,  $J(P,H) = 1.4$  Hz, 2H, CH) ppm.  $^{13}C$  NMR ( $CD_2Cl_2$ ,  $\delta$ ), 134.4, 131.9, 130.9, 130.6, 129.1, 128.4, 121.1 (d,  $J(P,C) = 2.4$  Hz), 110.5 (d,  $J(P,C) = 8.3$  Hz), 84.0 ppm.  $^{31}P$  NMR ( $CD_2Cl_2$ ,  $\delta$ ), 39.4 ppm. Mass spectrum  $[Cl^+, m/z]$ : 377  $[M+H]^+$ . Accurate mass measurement  $[Cl^+, m/z]$ : 377.0989  $[M+H]^+$ , calculated mass for  $C_{20}H_{17}O_3PH$ : 377.0992.

**N-Cyclohexyl-P,P-diphenylphosphinoselenoic amide (13)**

A red mixture of cyclohexylamine (0.396 g, 4.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in tetrahydrofuran (60 mL) was stirred at room temperature for 1 h. The red suspension became pale yellow suspension. Then diphenylchlorophosphine (0.600 g, 2.0 mmol) was added and the mixture was continued stirring at room temperature overnight. Upon filtering to remove insoluble solid and drying in vacuum the residue was purified by silica gel column (1 : 1 hexane / dichloromethane as eluent) to give the titled compound **13** as a greenish yellow paste (0.260 g, 72%). Selected IR (KBr,  $cm^{-1}$ ): 1477(m), 1434(s), 1306(m), 1180(m), 1097(s), 879(s), 744(s), 689(vs), 540(s), 516(s), 489(s).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ ), 8.02-7.93 (m, 4H, Ar-H), 7.44-7.40 (m, 6H, Ar-H), 2.30-2.15 (m, 1H, cyclohexyl-H), 1.98 (dd,  $J(H,H) = 8.0$  Hz, 1H, NH), 1.61-1.05 (m, 10H, cyclohexyl-H) ppm.  $^{13}C$  NMR ( $CDCl_3$ ,  $\delta$ ), 134.7 (d,  $J(P,C) = 92.4$  Hz), 132.4 (d,  $J(P,C) = 3.1$  Hz), 131.8 (d,  $J(P,C) = 11.4$  Hz), 128.4 (d,  $J(P,C) = 12.5$  Hz), 52.1, 35.9, 29.1, 25.5, 25.2 ppm.

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ), 54.4 (s,  $J(\text{P},\text{Se}) = 751$  Hz) ppm.  $^{77}\text{Se}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), -252.7 (d,  $J(\text{P},\text{Se}) = 751$  Hz). Mass spectrum [ $\text{Cl}^+$ ,  $m/z$ ]: 364 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement ( $\text{Cl}^+$ ): 364.0731, calculate mass for  $\text{C}_{18}\text{H}_{23}\text{NPSe}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 364.0733.

## ACKNOWLEDGEMENTS

We are grateful to the University of St Andrews for financial support and the EPSRC National Mass Spectrometry Service Centre (Swansea) for mass spectral measurements.

REFERENCES AND NOTES

1. (a) Wirth, T. *Tetrahedron* **1999**, *55*, 1-28. (b) Wirth, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3740-3749. (c) Freudendahl, D. M.; Shahzad, S. A.; Wirth, T. *Eur. J. Org. Chem.* **2009**, 1649-1664. (d) Freudendahl, D. W.; Santoro, S.; Shshzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8409-8411.
2. (a) Mugesh, G.; du Mont, W. W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125-2179. (b) Chasteen, T. G.; Bentley, R. *Chem. Rev.* **2003**, *103*, 1-25. (c) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255-6285. (d) Zeni, G.; Ludtke, D. S.; Pnatieri, R. B.; Braga, A. L. *Chem. Rev.* **2006**, *106*, 1032-1076.
3. Berger, S. B. *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *38*, 375-379.
4. Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355-390.
5. Kanatzidis, M. G.; Huang, S. *Coord. Chem. Rev.* **1994**, *130*, 509-621.
6. English, U.; Ruhlandt-Senge, K. *Coord. Chem. Rev.* **2000**, *210*, 135-179.
7. (a) Liang, Y. W.; Zheng, J. S.; Li, X. L.; Zheng, W. J.; Chen, T. F. *Eur. J. Med. Chem.* **2014**, *84*, 335-342. (b) Seng, H. L.; Tiekink, E. R. T. *Appl. Organomet. Chem.* **2012**, *26*, 655-662. (c) Mukherjee, A. J.; Zade, S. S.; Singh, H. B.; Sunoj, R. B. *Chem. Rev.* **2010**, *110*, 4357-4416.
8. (a) Wirth, T. *Top. Curr. Chem.* **2000**, *208*, 1-5. (b) Iwaoka, M.; Tomoda, S. *Top. Curr. Chem.* **2000**, *208*, 55-80. (c) Back, T. G. *Organoselenium Chemistry-A Practical Approach*; Oxford Press: New York, **2000**.
9. Gray, I. P.; Bhattacharyya, P.; Slawin, A. M. Z.; Woollins, J. D. *Chem. Eur. J.* **2005**, *11*, 6221-6227.

10. Mohanakrishnan, A. K.; Amaladass, P. *Tetrahedron Lett.* **2005**, *46*, 7201-7204.
11. G. Hua, Y. Li, A. M. Z. Slawin, J. D. Woollins, *Tetrahedron* **2008**, *64*, 5442-5448.
12. Gómez Castaño, J. A.; Romano, R. M.; Beckers, H.; Willner, H.; Boese, R.; Della Védova, C. O. *Angew. Chem., Int. Ed.* **2008**, *47*, 10114-10118.
13. (a) Hua, G.; Henry, J. B.; Li, Y.; Mount, A. R.; Slawin, A. M. Z.; Woollins, J. D. *Org. Biomol. Chem.* **2010**, *8*, 1655-1660. (b) Hua, G.; Woollins, J. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1368-1377.
14. G. Hua, Y. Li, A. L. Fuller, A. M. Z. Slawin, J. D. Woollins, *Eur. J. Org. Chem.* **2009**, 1612-1618.
15. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *New J. Chem.* **2010**, *34*, 1565-571.
16. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Org. Chem.* **2010**, 2707-2615.
17. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2011**, *30*, 805-808.
18. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Org. Chem.* **2011**, 3067-3073.
19. Hua, G.; Griffin, J. M.; Ashbrook, S. E.; Slawin, A. M. Z.; Woollins, J. D. *Angew. Chem. Int. Ed.* **2011**, *50*, 4123-4126.
20. Hua, G.; Cordes, D. B.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Tetrahedron Lett.* **2011**, *52*, 3311-3314.

21. Kaschel, J.; Schmidt, C. D.; Mumby, M.; Kratzert, D.; Stalke, D.; Werz, D. B. *Chem. Commun.* **2013**, 4403-4405.
22. Josee Voorstad, P.; Chapman, J. M.; Cocolas, G. H.; Wyrick, S. D.; Hall, I. H. *J. Med. Chem.* **1985**, 28, 9-12.
23. Koketsu, M.; Nada, F.; Hiramatsu, S.; Ishihara, H. *J. Chem. Soc., Perkin Trans. 1*, **2002**, 737-740.
24. Thomp, Q. *J. Am. Chem. Soc.* **1951**, 73, 5841-5846.
25. Cordes, D. B.; Hua, G.; Slawin, A. M. Z.; Woollins, J. D. *Acta Cryst.* **2011**, E67, o1586.
26. Hua, G.; Slawin, A. M. Z.; Woollins, J. D. *Org. Lett.* **2006**, 8, 5251-5254.
27. (a) Fuller, A. L.; Scott-Hayward, L. A. S.; Li, Y.; Buhl, M.; Slawin, A. M. Z.; Woollins, J. D. *J. Am. Chem. Soc.* **2010**, 132, 5799-5802. (b) Hua, G.; Fuller, A. L.; Slawin, A. M. Z.; Woollins, J. D. *Acta Cryst.* **2010**, E66, o2579. (c) Lari, A.; Rominger, F.; Gleiter, R. *Acta Cryst.* **2009**, E65, o400. (d) Aucott, S. M.; Milton, H. L.; Robertson, S. D.; Slawin, A. M. Z.; Woollins, J. D. *Heteroat. Chem.* **2004**, 15, 531-542.
28. **Single crystal structure of 6:** yellow prism crystal 0.120 x 0.120 x 0.030 mm, C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>Se<sub>2</sub>, M = 390.20, monoclinic, space group P2<sub>1/n</sub>, a = 8.723(3), b = 8.258(2), c = 20.888(7) Å, α = 90°, β = 99.221(10)°, γ = 90°, V = 1485.2(8) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.745 gcm<sup>-3</sup>, μ = 49.701 cm<sup>-1</sup>, 9275 reflections collected, 2689 unique [R<sub>(int)</sub> = 0.0314], R<sub>1</sub> = 0.0344, wR2 = 0.0769. CCDC 1054712.
- Single crystal structure of 8:** red needle crystal 0.100 x 0.020 x 0.010 mm, C<sub>14</sub>H<sub>14</sub>SeTe<sub>2</sub>, M = 516.42, orthorhombic, space group Pbcn, a = 32.991(14), b = 7.223(3), c = 6.083(3) Å, α = 90°, β = 90°, γ = 90°, V = 1449.6(11) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 2.366 gcm<sup>-3</sup>, μ = 65.132 cm<sup>-1</sup>, 6774

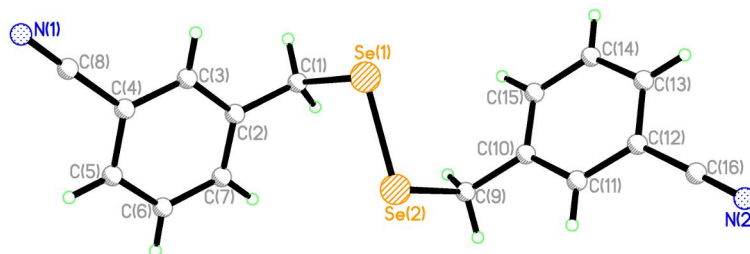


reflections collected, 1306 unique [ $R_{\text{(int)}} = 0.0978$ ],  $R_1 = 0.0584$ ,  $wR2 = 0.1507$ . CCDC 1054713.

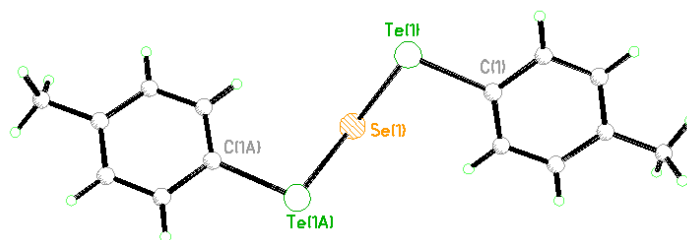
**Single crystal structure of 17:** colorless chunk crystal 0.210 x 0.110 x 0.070 mm,  $\text{C}_{18}\text{H}_{21}\text{NPSe}$ ,  $M = 361.30$ , monoclinic, space group  $C2/c$ ,  $a = 17.178(8)$ ,  $b = 10.958(5)$ ,  $c = 18.744(11)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 98.37(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3491(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.375$  gcm<sup>-3</sup>,  $\mu = 22.371$  cm<sup>-1</sup>, 14083 reflections collected, 3049 unique [ $R_{\text{(int)}} = 0.1317$ ],  $R_1 = 0.0747$ ,  $wR2 = 0.2569$ . CCDC 1054714.

29. Gray, I. P.; Slawin, A. M. Z.; Woollins, J. D. *Dalton* **2005**, 2188-2194.
30. Dereu, N. L. M.; Zingaro, R. A.; Meyers, E. A. *Organometallics* **1982**, *1*, 111-115.
31. Pilkington, M. J.; Slawin, A. M. Z.; Williams, D. J.; Wood, P. T.; Woollins, J. D. *Heteroatom Chem.* **1990**, *1*, 351-355.
32. Cordes, D. B.; Hua, G.; Slawin, A. M. Z.; Woollins, J. D. *Acta Cryst.* **2011**, *E67*, o1790.
33. Nguyen, C. Q.; Adeogun, A.; Afzaal, M.; Malik, M. A.; O'Brien, P. *Chem. Commun.* **2006**, 2179-2181.
34. Cameron, T. S.; Chan, C.; Chute, W. J. *Acta Crystallogr.* **1980**, *B36*, 2391-2393.
35. CrystalClear 2.0, Rigaku Corporation, *CrystalClear Software User's Guide*, Molecular Structure Corporation, © 2010; Flugrath, J.W.P. *Acta Cryst.* **1999**, *D55*, 1718-1725.
36. SIR97, Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.
37. DIRDIF99, Beurskens, P.T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Israel, R.; Smits, J. M. *The DIRDIF-99 Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1999**.

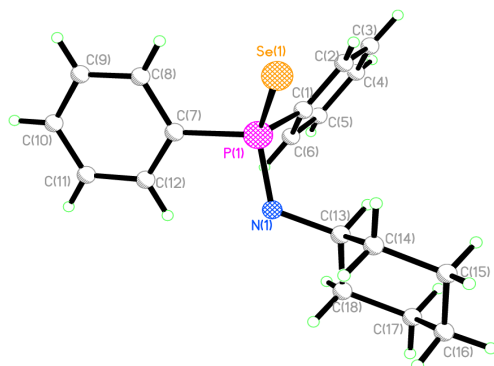
38. CrystalStructure 3.8.1, *Crystal Structure Analysis Package, Rigaku and Rigaku/MS* (2000–2006), 9009 New Trails Dr, The Woodlands, TX 77381, USA.
39. Sheldrick, G. M. *SHELXL97. Acta Cryst.* **2008**, *A64*, 112-122.



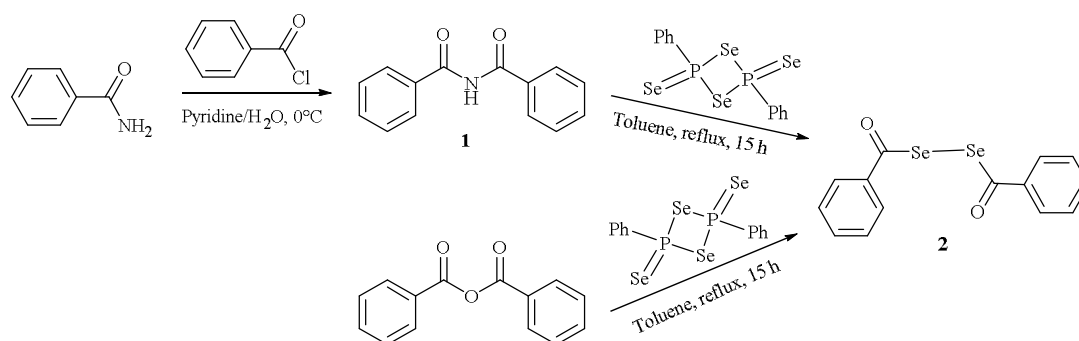
**Figure 1** Single crystal structure of compound **6**. Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-Se(2) 2.3088(9), C(1)-Se(1) 1.977(3), C(9)-Se(2) 1.992(3); C(1)-Se(1)-Se(2) 100.97(11), Se(1)-C(1)-C(2) 112.8(2), C(9)-Se(2)-Se(1) 101.95(11), Se(2)-C(9)-C(10) 112.6(2).



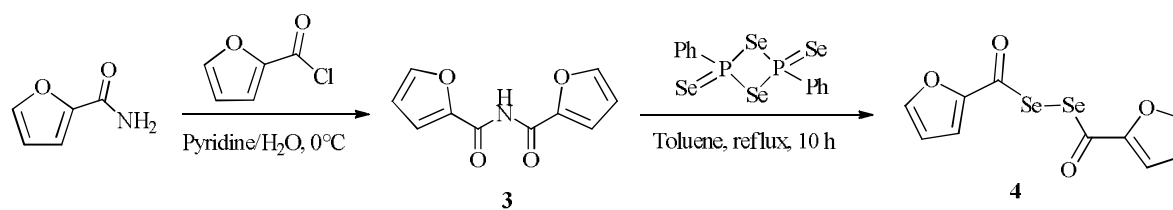
**Figure 2** Single crystal structure of compound **8**. Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-Te(1) 2.5216(16), Te(1)-C(1) 2.130(10); Te(1)-Se(1)-Te(1A) 107.02(9), C(1)-Te(1)-Se(1) 96.0(3).



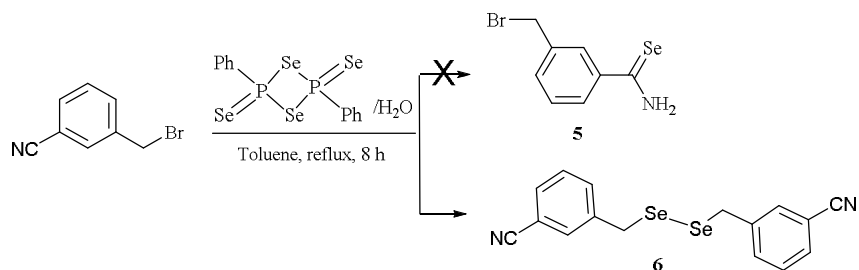
**Figure 3** Single crystal structure of compound **13**. Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.139(3), P(1)-N(1) 1.672(7), P(1)-C(1) 1.839(9), P(1)-C(7) 1.819(9); Se(1)-P(1)-N(1) 119.6(3), Se(1)-P(1)-C(1) 111.5(3), Se(1)-P(1)-C(7) 112.4(3), N(1)-P(1)-C(1) 104.6(4), N(1)-P(1)-C(7) 102.3(4), C(1)-P(1)-C(7) 105.0(4).



**Scheme 1** Reaction of Woollins' reagent and *N*-benzoylbenzamide or benzoic anhydride

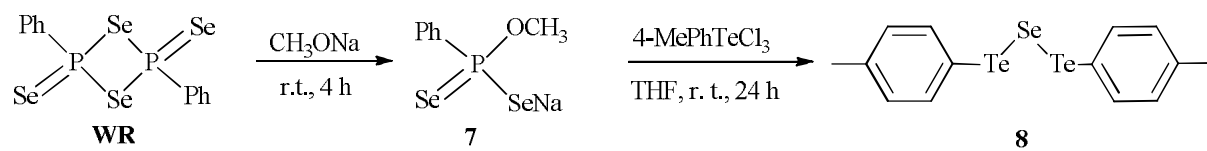


**Scheme 2** Reaction of Woollins' reagent and *N*-(furan-2-carbonyl)furan-2-carboxamide

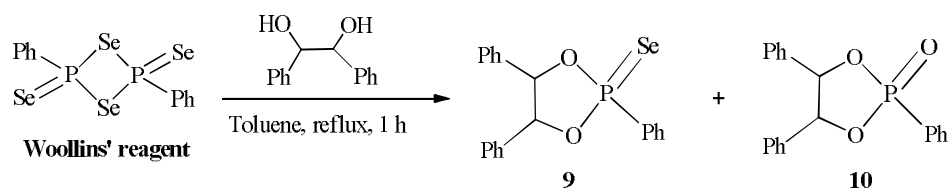


**Scheme 3** Reaction of Woollins' reagent and 3-(bromomethyl)benzonitrile

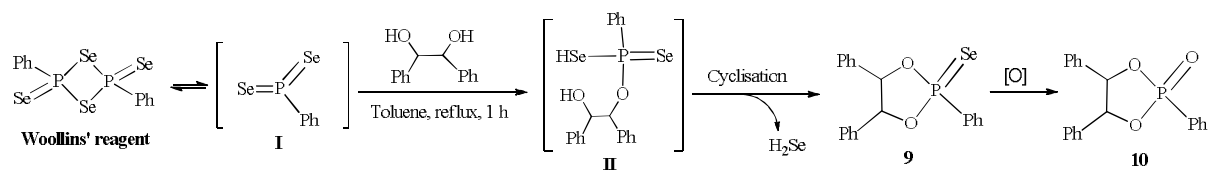




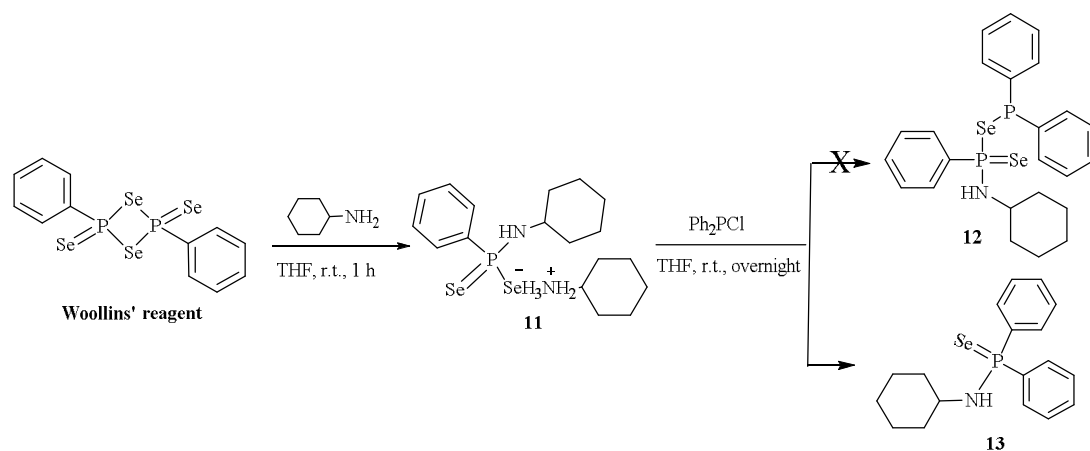
**Scheme 4.** Reaction of Woollins' reagent and sodium methanolate/ trichloro(*p*-tolyl)- $\lambda^4$ -tellane



**Scheme 5** Reaction of Woollins' reagent and 1,2-diphenylethane-1,2-diol



**Scheme 6** Possible mechanism for the formation of compounds **9** and **10**



**Scheme 7** Reaction of Woollins' reagent and cyclohexylamine/chlorodiphenylphosphane