Unexpected four- and eight-membered organo P–Se heterocycles†‡

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

Reaction of [PhP(Se)(μ-Se)]₂ (Woollins' reagent, WR) with symmetrically disubstituted diynes: five-membered P(Se)Se₂C₂ heterocycles and bis-heterocycles with two five-membered P(Se)Se₂C₂ rings connected through a C–C single bond; ᵗBu–C≡C–C≡C–ᵗBu reacts differently to afford an unprecedented four-membered P(Se)SeC₂ heterocycle with one unreacted triple bond and a fused bis-heterocycle containing two five-membered P(Se)SeC₃ rings fused at the middle two carbons of the diyne to give a heterocyclic analogue of pentalene, [3.3.0]octa-1,6-diene.

Interest in organoselenium compounds has increased in recent years because of their unique chemo-, regio- and stereoselective reactions as well as their potential biological and pharmaceutical properties.[1] However, synthesis of selenium-containing organic heterocycles is not always easy due to the inconvenience of selenium reagents such as H_2Se, NaHSe, $(Me_3Si)_2Se$, potassium selenocyanate and tetraethylammonium tetraselenotungstate $[Et_4N]_2WSe_4$, each exhibiting its own problems including toxicity, solubility, difficulty in handling and poor reactivity. 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [PhP(Se)(μ-Se)]₂, known as Woollins' reagent (WR), is a selenium analogue of the well-known Lawesson's reagent, $[p-MeOC_6H_4P(S)(μ-S)]_2$. Compared to other selenium reagents, the deep-red crystals of WR have less unpleasant chemical properties. Though it is best stored under nitrogen it can be easily prepared and is safely handled in air. WR has proved to be an efficient selenium source for the synthesis of a wide range of selenoamides and selenoaldehydes by simple oxygen/selenium exchange reaction or reaction with ArCN followed by hydrolysis[4,5] as well as a useful source of a variety of P–Se heterocycles.[6–13] In this work, we report on the reactivity of WR towards 1,4-disubstituted-1,3-butadiynes (RC≡C–C≡CR). Apart from some five-membered rings, an unprecedented C₂PSe heterocycle, and a remarkable fused system have been obtained.

In a typical procedure, 1 mmol of 1,4-disubstituted-1,3-butadiyne and 2 mmol of WR [*i.e.* 4 equivalents of PhPSe₂] were refluxed in toluene under a N₂ atmosphere for 10 h. After cooling to room temperature, the resulting deep coloured solution was passed through a pad of Celite to remove traces of selenium and purified by column chromatography (SiO₂, toluene as eluent) to afford two major products: a single heterocycle and a bis-heterocycle.

*School of Chemistry, University of St Andrews, Fife, UK KY16 9ST.
E-mail: jdw3@st-and.ac.uk; Tel: (+44)-1334-463384*
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‡ The HTML version of this article has been enhanced with colour images.

Eqn (1) shows the products from the reaction of 1,4-diphenyl-1,3-butadiyne and 1,4-bis(trimethylsilyl)-1,3-butadiyne with WR.

$$\text{(1)}$$

1 R = Ph
3 R = Si(CH₃)₃
2a,b R = Ph
4a,b R = Si(CH₃)₃
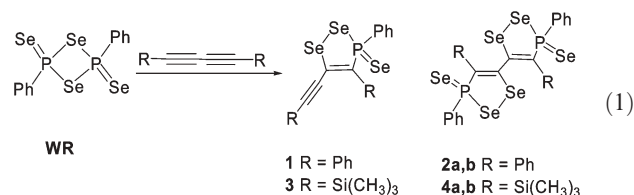
In both cases, cycloaddition at one triple bond gives five-membered P(Se)Se₂C₂ heterocycles 1 (yield 19%) and 3 (yield 23.5%), whereas reaction at both triple bonds leads to two five-membered rings in the same molecule (2 and 4); reduced amounts of WR in the reaction did not improve the yield of 1 and 3. We tested if formation of 1 and 3 might be a result of deficiency of WR, however, increasing the amount of WR to 3 equivalents did not change the product distribution except for the fact that other unidentified impurities increased. Both 2 and 4 display two phosphorus signals with similar selenium satellites, as would be expected for diastereoisomers. Further purification of 2 by recrystallization from CH₂Cl₂–petroleum ether gave 2a (22% yield) and 2b (10% yield). However, the same treatment with 4 only afforded the major product 4a (17% yield). The structure of 2a was confirmed by X-ray crystallography (Fig. 1).§ The almost planar P(Se)Se₂C₂ heterocycle has a similar geometry to previously obtained systems.[9]
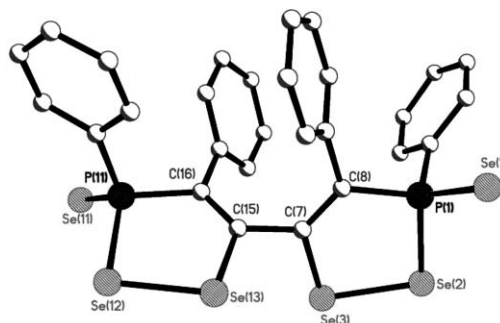

Fig. 1 Molecular structure of 2a (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses); P(1)–Se(1) 2.113(3), P(1)–Se(2) 2.252(3), Se(2)–Se(3) 2.3401(14), Se(3)–C(7) 1.914(9), C(7)–C(8) 1.348(12), P(1)–C(8) 1.821(10), P(11)–Se(11) 2.104(3), P(11)–Se(12) 2.260(3), Se(12)–Se(13) 2.3447(15), Se(13)–C(15) 1.923(9), C(15)–C(16) 1.331(14), P(11)–C(16) 1.833(10); Se(1)–P(1)–C(1) 113.4(3), Se(1)–P(1)–C(8) 114.4(3), Se(1)–P(1)–Se(2) 111.91(12), P(1)–Se(2)–Se(3) 94.83(8), Se(2)–Se(3)–C(7) 96.6(3), Se(3)–C(7)–C(8) 124.5(7), C(7)–C(8)–P(1) 121.4(7), S(11)–P(11)–C(23) 113.5(3), Se(11)–P(11)–Se(12) 112.75(11), Se(11)–P(11)–C(16) 113.7(3), P(11)–Se(12)–Se(13) 94.27(8), Se(12)–Se(13)–C(15) 96.3(3), Se(13)–C(15)–C(16) 124.7(8), C(15)–C(16)–P(11) 121.2(8), C(16)–P(11)–Se(12) 102.2(3).

In contrast to the above reactions, refluxing a toluene solution of 2,2,7,7-tetramethyl-3,5-octadiynebutadiyne with two equivalents of WR [eqn. (2)] resulted in two unusual products, the four-membered heterocycle **5** in a yield of 18% and a bis-heterocycle **6** with two fused five-membered rings.

$$(2)$$
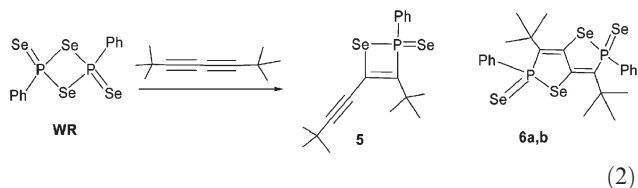
There is no precedent for either of these ring systems. $^{31}P\{^1H\}$ NMR suggests there are isomers in **6**; we observed two distinct phosphorus signals (intensity ratio 5 : 3) with the expected selenium satellites [δ_P 56.3 ppm with ^1J(PSe) 352, 801 Hz and δ_P 54.8 ppm with ^1J(PSe) 350, 803 Hz]. Further purification of **6** by crystallisation gave **6a** (7% yield) free of **6b**.

The identities of **1**, **2a**, **2b**, **3**, **4a**, **5** and **6a** were confirmed by microanalysis, ^1H, ^{13}C, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ NMR, IR and mass spectrometry. Satisfactory microanalysis and mass spectra were obtained for all compounds. The IR spectra show $\nu_{P=Se}$ bands at 514–561 cm^{-1} for all of the compounds and $\nu_{C\equiv C}$ bands at 2067–2145 cm^{-1} in **1**, **3** and **5**. The ^1H NMR spectra of **1–6a** were as expected confirming the presence of the phenyl or methyl moieties. The $^{31}P\{^1H\}$ NMR spectra of **1**, **2a**, **2b**, **3** and **4** display sharp singlets at δ_P 67.7, 72.7, 71.2, 87.7, 87.5 ppm respectively, flanked by appropriate selenium satellites with $^1J\{^{31}P^{77}Se\}$ coupling constants in the ranges 767–798 and 330–362 Hz, similar to those found in other P–Se systems,[9,11,12,14,15] and their $^{77}Se\{^1H\}$ NMR spectra show three sharp doublets, the values suggesting that similar P(Se)Se$_2$C$_2$ ring systems are present. However, the $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra of **5** and **6a** suggest quite different structural motifs. **5** is formulated (*vide infra*) as a 1,2-selenaphosphetene with an unusual four-membered C$_2$P(Se)Se ring, the very small $^1J\{^{31}P^{77}Se\}$ single bond coupling of 106 Hz being attributed to the acute angles in the four-membered ring. **6a** is composed of two fused C$_3$P(Se)Se rings [δ_P 56.3 ppm $^1J\{^{31}P^{77}Se\}$ 352 and 801 Hz, δ_{Se} doublets at 399.1 and −161.4 ppm]. Compounds **2**, **5** and **6a**, have been characterized crystallographically (Fig. 1–3).

The structure of **2a** (Fig. 1) contains two five-membered C$_2$P(Se)Se$_2$ rings with the phenyl substituent on the phosphorus

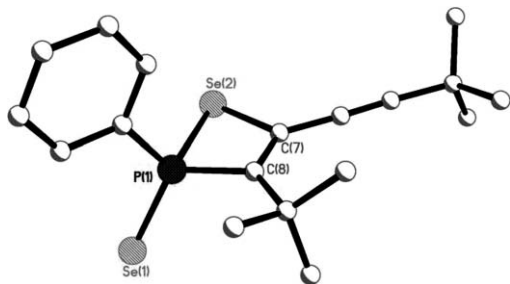**Fig. 2** Molecular structure of **5** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses); P(1)–Se(1) 2.0941(11), P(1)–C(8) 1.818(4), P(1)–Se(2) 2.2828(10), Se(2)–C(7) 1.964(4), C(7)–C(8) 1.361(5); Se(1)–P(1)–C(1) 114.77(13), Se(1)–P(1)–C(8) 118.59(13), P(1)–C(8)–C(7) 100.9(3), C(8)–C(7)–Se(2) 107.0(3), C(7)–Se(2)–P(1) 70.62(11), Se(2)–P(1)–C(8) 81.37(5).
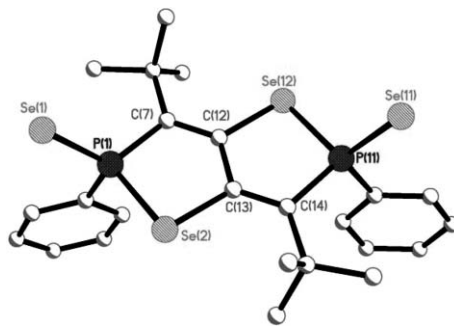

Fig. 3 Molecular structure of **6a** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses); Se(1)–P(1) 2.1027(15), P(1)–Se(2) 2.2364(15), Se(2)–C(13) 1.920(5), C(13)–C(12) 1.489(7), C(12)–C(7) 1.360(7), C(7)–P(1) 1.821(5), C(12)–Se(12) 1.923(5), Se(12)–P(11) 2.2386(15), P(11)–Se(11) 2.1012(15), P(11)–C(14) 1.823(5), C(14)–C(13) 1.348(8); C(1)–P(1)–Se(1) 113.85(18), Se(1)–P(1)–C(7) 120.86(17), Se(1)–P(1)–Se(2) 111.02(6), P(1)–Se(2)–C(13) 91.76(16), Se(2)–C(13)–C(12) 112.1(4), C(13)–C(12)–C(7) 124.4(5), C(12)–C(7)–P(1) 114.6(4), C(13)–C(12)–Se(12) 112.1(4), C(12)–Se(12)–P(11) 91.50(16), Se(12)–P(11)–C(14) 96.74(17), Se(12)–P(11)–Se(11) 113.01(7), Se(11)–P(11)–C(14) 118.51(18), P(11)–C(14)–C(13) 115.0(4), C(14)–C(13)–C(12) 124.4(5), C(13)–C(12)–Se(12) 112.1(4).

atom being approximately orthogonal to the newly formed ring (90.3 and 88.5°, respectively). The two five-membered rings are rotated from each other by 64.5°. The internal P(1)–Se(2), P(11)–Se(12) (single bond, 2.252(3), 2.260(3) Å) and exocyclic P(1)–Se(1), P(11)–Se(11) (double bond) distances [2.113(3) and 2.104(3) Å] are similar to those in other compounds which contain the P(Se)(μ-Se) unit.[9–13,16] However, the five-membered vinylic C$_2$P(Se)Se$_2$ rings in **2a** are much flatter than the 1,2-diselena-3-phospholane [C$_2$P(Se)Se$_2$] ring.[12]

The molecular structure of **5** (Fig. 2) contains a PhP(Se)Se moiety attached to a C=C bond to give an unusual four-membered ring [the first characterized with a C=C bond]. The internal P(1)–Se(2) length [2.2828(10)] is *ca.* 0.01–0.05 Å longer than the values in P$_2$SeC, P$_2$Se$_2$ or P$_2$SeN heterocycles.[3,12] However, the exocyclic P(1)–Se(1) distance of 2.0941(11) is slightly shorter than the corresponding values in the P$_2$Se$_2$ [2.102(3) Å] or P$_2$SeN [2.117(2) Å] and slightly longer than the value in P$_2$SeC [2.089(3) Å] systems.[4,15] The internal angles of the P(1)–Se(2)–C(7)–C(8) ring in **5** show distortion from a true square, with C(8)–P(1)–Se(2) being 81.37(5)° and P(1)–Se(2)–C(7) being 70.62(11)° , *ca.* 5–15° more acute than the angles in known P$_2$SeN [75.28(4)°], P$_2$SeC [78.83(9)°] or P$_2$Se$_2$ [85.45(9)°] rings.[3,12] It is clear that **5** must be very strained.

The structure of **6a** contains two fused rings (Fig. 3) which lie in almost the same plane (only 3° angle between rings) and form a long potentially delocalized Se(1)P(1)–C(7)–C(12)–C(13)–C(14)–P(11)–Se(11) chain, though the central C$_4$ fragment shows bond alternation with C–C bond lengths of 1.360(7), 1.489(7) and 1.348(8) Å going from C(7) to C(14). Within each C$_3$PSe ring the P(1)–C(7)–C(8)–C(13) and the P(11)–C(14)–C(13)–C(12) chains have mean deviations from planarity of 0.01 and 0.03 Å, respectively. In comparison with the nonvinylic 1,2-diselena-3-phospholane [P(Se)Se$_2$C$_2$] ring [ring Se displaced by 1.1 Å from the plane],[12] the vinylic C$_3$P(Se)Se rings [Se in P–Se single bond displaced by 0.4 (0.01) Å from the plane] in **6a** are flatter, and even
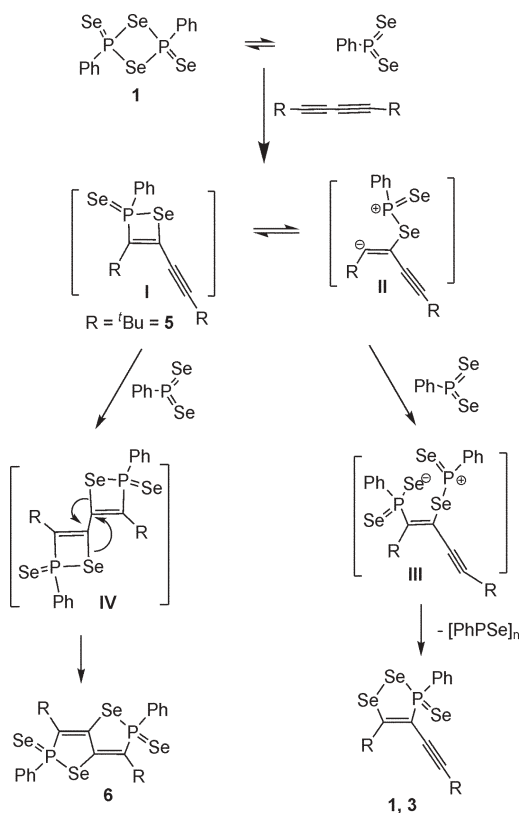
Scheme 1 Mechanism which accounts for the formation of **1–6**.

slightly flatter than the rings [Se in P–Se single bond displaced by 0.04 (0.09) Å from the plane] in **2a**. The two exocyclic P=Se bond adopt a *cis* orientation, an uncommon feature of five-membered ring systems containing a P(Se)Se linkage.[2,3,12,16] The P(1)–Se(2)–C(13) [91.76(16)°] and the P(11)–Se(12)–C(12) angles [91.50(16)°] are enlarged compared to the equivalent angle in **5** [70.62(11)°] or in the $P_2(\mu\text{-Se})_2$ ring [85.45(9)°] of WR.

In order to gain some mechanistic insight we examined the $^{31}P\{^1H\}$ NMR of a crude reaction mixture from the reaction of 1,4-disphenylbutadiyne with WR after 12 h reflux. Apart from the products the spectrum contained major doublets centred at 88.1, 86.9, 86.6, 82.4, 77.3, 68.9, −22.5 ppm. With $\{^{31}P^{31}P\}$ coupling of *ca.* 280 Hz, along with a $\{^{31}P^{77}Se\}$ coupling constant of *ca.* 220 Hz, suggesting a P–P–Se linkage, perhaps within a larger cyclic structure of (PhPSe)$_n$. We did show that reaction of **5** with WR under identical reaction conditions gave **6** in 69% yield, indicating a stepwise mechanism.

We propose the reaction pathway for the formation of **1–6** in Scheme 1. At elevated temperatures **WR** is in equilibrium with a diselenaphosphorane PhPSe$_2$, which is the true reactive species in refluxing solution. The first step in the reaction is a [2 + 2] cycloaddition of a P=Se bond from [PhPSe$_2$] across the C≡C bond, directly affording **5** or giving an intermediate **I**, which exists in equilibrium in solution in two valence forms: the 1,2-selenaphosphacyclobutene **I** and the dipolar species **II**. The latter reacts with PhPSe$_2$ to give s second dipolar intermediate **III**, which can eliminate [PhPSe]$_n$ and cyclise to give **1–4**. Further reaction of **5** with [PhPSe$_2$] generates an intermediate **IV**, which rapidly rearranges to **6**.

In conclusion, reaction of WR with 1,4-diphenyl-1,3-diyne or 1,4-trimethylsilyl-1,3-diyne affords the expected P(Se)Se$_2$C$_2$ heterocycles. However, 1,4-di-*tert*-butyl-1,3-diyne and WR gives an unusual four-membered P(Se)SeC$_2$ ring and a fused bis-heterocyclic compound with two five-membered P(Se)SeC$_3$ rings. The diversity of the heterocycles available from WR raises the possibility of a library of vinylic phosphorus–selenium heterocycles.

Notes and references

1 G. Mugesh, W.-W. Du Mont and H. Sies, *Chem. Rev.*, 2001, **101**, 2125–2180.

2 J. C. Fitzmaurice, D. J. Williams, P. T. Wood and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1988, 741–743.

3 I. P. Gray, P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.*, 2005, **11**, 6221–6227.

4 J. Bethke, K. Karaghiosoff and L. A. Wessjohann, *Tetrahedron Lett.*, 2003, **44**, 6911–6913.

5 G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Org. Lett.*, 2006, **8**, 5251–5254.

6 K. E. Darout, *Org. Lett.*, 2005, **7**, 203–206.

7 M. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1999, 1175–1184.

8 M. St J. Foreman, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.*, 1997, 855–856.

9 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.*, 2002, **8**, 2705–2711.

10 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem., Int. Ed.*, 2000, **39**, 1973–1975.

11 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *J. Organomet. Chem.*, 2001, **623**, 116–119.

12 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2001, 300–303.

13 P. Bhattacharyya, J. Novosad, J. R. Phillips, A. M. Z. Slawin, D. J. William and D. J. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607–1613.

14 M. J. Pilkington, A. M. Z. Slawin, D. J. Williams, P. T. Wood and J. D. Woollins, *Heteroat. Chem.*, 1990, **1**, 351–355.

15 S. W. Hall, M. J. Pilkington, A. M. Z. Slawin, D. J. Williams, P. T. Wood and J. D. Woollins, *Polyhedron*, 1991, **10**, 261–265.

16 J. T. Shore, W. T. Pennington, M. C. Noble and A. W. Cordes, *Phosporus, Sulfur Silicon Relat. Elem.*, 1988, **39**, 153.

17 SHELXTL 6.11 Bruker AXS Madison 2004.