

Application of four-membered ring chalcogenation reagents to the synthesis of new phosphorus-chalcogen heterocycles

Guoxiong Hua, David B. Cordes, Alexandra M. Z. Slawin, and J. Derek Woollins*

EaStCHEM School of Chemistry, University of St Andrews, Fife, KY16 9ST, U.K.

Email: jdw3@st-and.ac.uk

Dedicated to Prof. Oleg A. Rakitin on the occasion of his 65th birthday

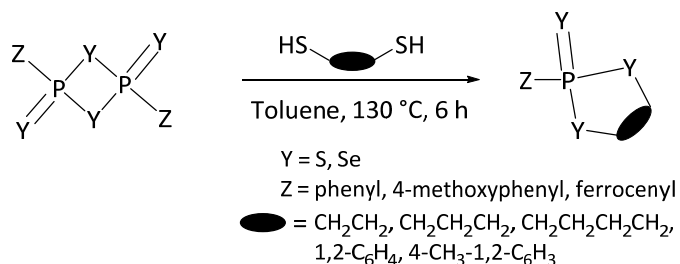
Received 07-20-2016

Accepted 08-16-2016

Published on line 08-29-2016

Abstract

The reaction of four-membered ring chalcogenation reagents such as Lawesson's reagent, 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (the ferrocene analogy of Lawesson's reagent) and Woollins' reagent with alkyl- or aryl-dithiols in refluxing toluene gave a series of five- to seven-membered organo-phosphorus-chalcogen heterocycles in 24% to 87% yields. Five representative X-ray structures confirm the formation of these five- to seven-membered heterocycles.



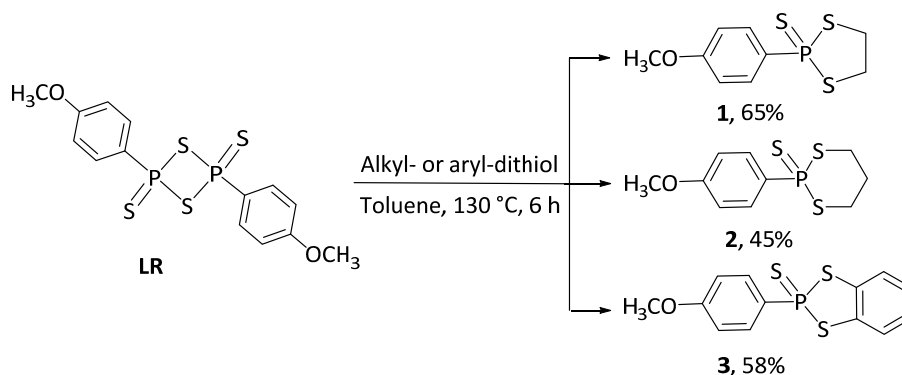
Keywords: Lawesson's reagent; Woollins' reagent, phosphorus-chalcogen heterocycles, chalcogenation; dithiols

Introduction

The chemistry of organophosphorus-chalcogen heterocycles has attracted extensive attention for several decades. Heterocycles with small ring systems have found many applications both as useful starting materials in the synthesis of more elaborate structures and as valuable targets of organic and inorganic synthesis.¹ A variety of organophosphorus-chalcogen heterocycles including three- to ten-membered ring systems has been developed due to their wide-ranging applications in synthetic chemistry.²⁻⁵ The most important RP/S(Se) heterocycles are the four-membered ring compounds, Lawesson's reagent (**LR**, R = *p*-C₆H₄OMe), a highly efficient thionation reagent,⁶⁻¹¹ 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (**FcLR**, a ferrocene analogy of Lawesson's reagent), another alternatively efficient thionation reagent,¹²⁻¹⁶ and 2,4-diphenyl-1,3-diselenadiphosphetane 2,4-diselenide [{PhP(Se)(μ -Se)}₂] (Woollins' reagent, **WR**, R = Ph, a selenium counterpart of Lawesson's reagent), as a highly efficient selenation reagent.¹⁷⁻²⁵ Very recently, we have reported these chalcogenation reagents used as efficient building blocks for the synthesis of a series of phosphorus-chalcogen macrocycles incorporating two phosphorus atoms and four chalcogen atoms [X₂-P₂-X₂ (X = O, S, Se)] in the central ring.²⁶⁻²⁸ In order to enrich further the library of organo phosphorus-chalcogen heterocycles, herein we report the preparation of a series of small organo phosphorus-chalcogen heterocycles from the reaction of chalcogenation reagents (**LR**, **FcLR** and **WR**) with alkyl-dithiol or aryl-dithiols, and five representative X-ray structures.

Results and Discussion

Treating Lawesson's reagent with two molar equivalents of alkyl- or aryl-dithiol in refluxing toluene gave the corresponding five- and six-membered ring heterocycles **1–3** in 45% to 65% yields, respectively, as shown in Scheme 1. Heterocycles **1–3** were obtained as white solids or pastes in good yields, and are soluble in normal organic solvents such as dichloromethane, chloroform, THF, acetonitrile, acetone and so on. All of the above heterocycles were found to be air-stable both as solids and in solution. The identity of **1–3** was determined through a combination of mass spectrometric (EI or CI) techniques, and NMR (¹H, ¹³C and ³¹P) spectroscopy. In all cases mass spectrometry found the expected [M]⁺ or [M+H]⁺. The ¹H and ¹³C spectra of **1–3** show clearly the presence of both the aromatic and alkoxy substituents displaying the expected coupling constants. Singlets at 71.4, 64.7 and 88.4 ppm were observed respectively in their ³¹P{¹H} NMR spectra. Attempts to prepare ring systems of more than six-members from the reaction of **LR** with longer-chain [(-CH₂)_n, n > 3] dithiol precursors failed and always led to very messy products.



Scheme 1. Synthesis of phosphorus-sulfur heterocycles **1–3** from **LR** and alkyl- or aryl-diols.

The X-ray structures of heterocycles **1–3** reveal (Figures 1–3 and Tables 1 and 2) that all compounds crystallize with one independent molecule in the unit cell. **1–3** adopt puckered conformations with **1** being a pseudo-chair arrangement and **2,3** being open envelope conformations. Compared to the structures of **2** and **3**, the structure of **1** is highly symmetrical with the mean plane of newly formed ring being perpendicular to the aryl ring. In comparison, the mean planes of the newly formed ring and the aryl ring in **2** and **3** are rotated with the dihedral angles of 87.70° and 80.98°, respectively. In the newly formed ring the central phosphorus atom lies 0.195 Å in **1**, 0.349 Å in **2** and 0.332 Å in **3** out of the P-S-S-C_n (n = 2, 3) mean plane. The P=S double bond lengths in the structures of **1–3** are 1.934(2) Å, 1.9390(10) Å and 1.9351(7) Å, respectively, cf dithiophosphono disulfides [1.9203(14) – 1.9303(7) Å],^{29–31} are slightly shorter than that in other terminal phosphine sulphide bond lengths in the Cambridge Crystallographic Database (average 1.965 Å).³²

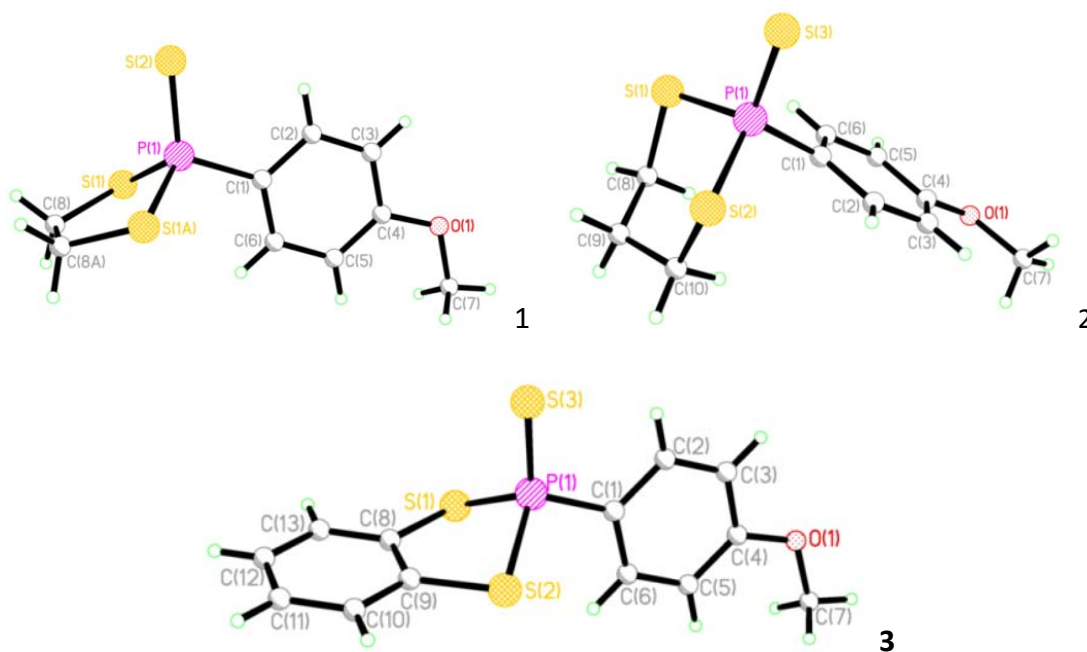
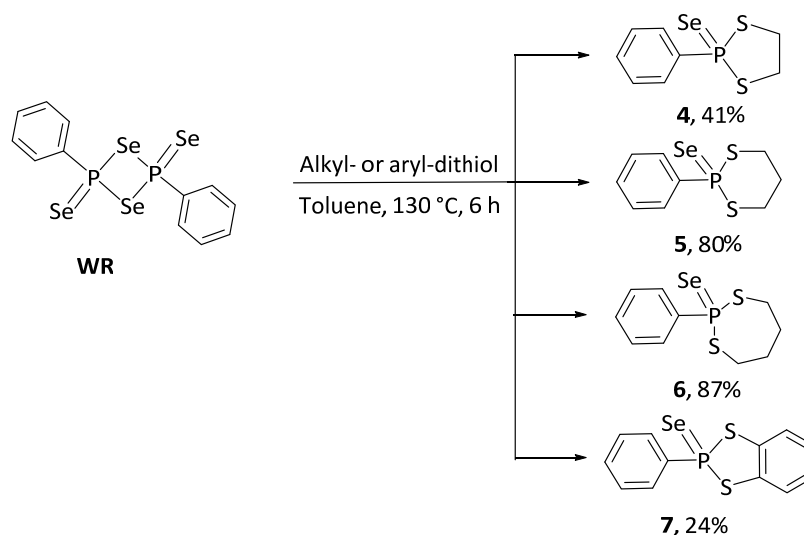


Figure 1. Single crystal X-ray structures of compounds **1**, **2** and **3**.

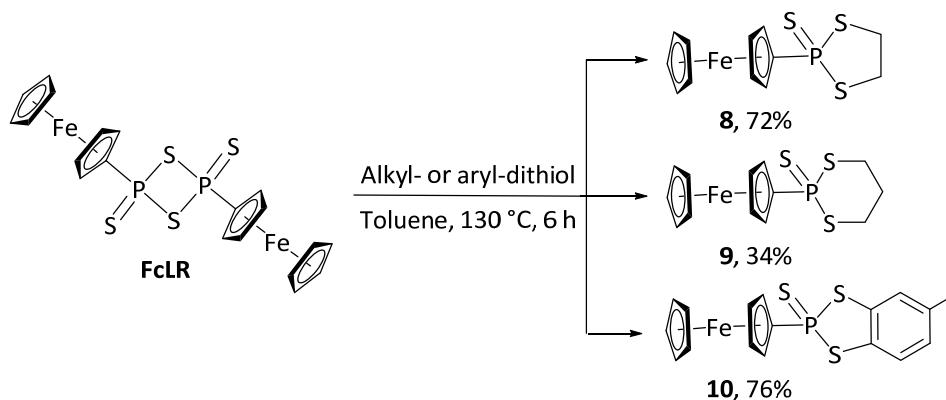
The reaction of **WR** and alkyl- or aryl-dithiol was carried out under identical condition. Phosphorus-selenium heterocycles **4–6** were obtained by the reaction of **WR** with the corresponding alkyl-dithiols in good to excellent yields (Scheme 3). Meanwhile, the reaction of **WR** with two equivalents of aryl-dithiol afforded as the sole product seven-membered ring heterocycle **7** in very low yield (24%). The results indicated that the stability of heterocycles is affected by the replacement of sulfur by selenium in the phosphorus center; the P(Se)-containing heterocycles seem to be more stable than those with a P(S) motif. Furthermore, the building block with π -system such as phenyl ring is less favorable than building block such as linear CH₂CH₂CH₂CH₂ chain system. Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio for seven-membered heterocycle **6** due to its highly twisted newly formed ring. In all cases mass spectrometry found the expected [M]⁺ or [M+H]⁺, with the matching isotope distributions as the expected patterns. The ¹H and ¹³C spectra of heterocycles **4–7** confirm the presence of phenyl ring showing the expected coupling constants. The ³¹P NMR spectra of heterocycles **4–7** display sharp singlets at 73.1, 46.2, 70.5 (65.3) and 70.6 ppm, respectively, and each signal is accompanied by one set of selenium satellites (816 Hz for **4**, 786 Hz for **5**, 808 and 789 Hz for **6**, and 833 Hz for **7**), indicating that in each compound there is a P=Se double bond present. This is further substantiated by the

^{77}Se NMR spectra, which display a doublet with matching coupling constants, indicating the presence of a P=Se double bond in each compound.



Scheme 2. Synthesis of phosphorus-sulfur-selenium heterocycles **4–7** from **WR** and alkyl- or aryl-dithiols.

Analogous reactions were carried out by using **FcLR**^{29,30} and dithiols. The reaction of **FcLR** with two molar equivalents of alkyl- or aryl-dithiols in refluxing toluene afforded five or seven-membered ring heterocycles **8–10** in good yields as shown in Scheme 2. The yields suggest that the ring size of the newly formed ring plays a key role in the formation of heterocyclic compounds **8–10**, the formation of five-membered rings **8** and **10** are favoured compared the formation of seven-membered ring **9**. Though the ^{31}P NMR spectrum of the reaction mixture did suggest the formation of the corresponding six-membered ring heterocycle ($\delta_p = 71.9$ ppm), the reaction of **FcLR** with 1,3-propane-dithiol did not lead to any isolatable pure product. The heterocycles **8–10** were found to be air stable both as solids and in solution. Two signals were found in *ca.* 3 : 2 intensity ratio for seven-membered heterocycle **9** and we speculate that there are conformational isomers present with selenium/phenyl substituents being able to occupy axial or equatorial positions though we have not conducted VT NMR experiments. ^1H NMR and ^{13}C NMR spectra of compounds **8–10** were as expected confirming the presence of all the characteristic peaks of the ferrocene backbones. The ^{31}P NMR spectra of **8–10** exhibit sharp singlets in the range of $\delta = 81.4$ to 93.6 ppm, the values are consistent with those in heterocycles **1–3**.



Scheme 3. Synthesis of phosphorus-sulfur heterocycles **8–10** from **FcLR** and alkyl- or aryl-dithiols.

The X-ray structures of **5** and **10** were obtained and show that the PhP=X (X = S or Se) is attached across the dithiol in a newly formed five-membered C₂PS₂ ring or six-membered C₃PS₂ ring as shown in Figure 2 and Tables 1 and 2. Compound **10** crystallizes with one independent molecule within the unit cell; compound **5** crystallizes with two independent molecules within the unit cell. Both structures adopt the envelope like conformation, having very similar structural motif to the structure of **3**. The newly formed five-membered ring P(S)-S₂-C₂ in **10** is nearly planar with a mean deviation of 0.1522 Å; however, the newly formed six-membered ring P(Se)-S₂-C₃ in **5** is highly puckered. The P-S single bond lengths in **10** [2.1045(14) and 2.1048(14) Å] are comparable to the P-S single bond lengths in **3** [2.1028(8) and 2.1038(7) Å], but considerably longer than the corresponding P-S single bond lengths in **1** [2.0899(17) Å], **2** [2.0724(9) and 2.0665(9) Å] and in the similar five-membered P(S)₂C₂ ring structures: for example, 2,5-dithia-1-phenyl-1-thiophosphorus(V)-cyclopentane [2.087 Å],³³ 4,5-diphenyl-2-ferrocenyl-1,3,2-dithiaphosphane 2-sulfide [2.095(2) and 2.089(2) Å],³⁴ 2-*t*-butyl-2-thioxo-1,3,2-dithiaphospholane [2.096(1) and 2.081(1) Å] and 2-(3,5-dimethylphenyl)-2-thioxo-1,3,2-dithiaphospholane [2.084(1) and 2.078(1) Å],³⁵ but is considerably shorter than the corresponding P-S single bond lengths in 2-(1,1-dimethylethyl)-2-sulfide-4,5-[1,2-dicarbacloso-dodecaborano(12)]-1,3,2-dithiaphospholane [2.1335 (16) and 2.1429(17) Å];³⁶ meanwhile, the P=Se double bond [1.9233(17) Å] is substantially shorter than that in **1–3** [1.934(2) to 1.9390(10) Å] and in the similar structures [1.932(1) – 1.938(2) Å].^{33–36} The plane of the phenyl ring is almost perpendicular [87.98°] to the C_p ring attached to phosphorus atom. The P-S single bond distances in **5** [2.0688(10) - 2.0793(11) Å] are consistent with those in **2** [2.0793(11) and 2.0665(9) Å]. However, they are marginally shorter than the P-S single bond distances in **1, 3** [2.0899(17) - 2.1038(7) Å] and in similar structures [2.081(1) – 2.1429(17) Å].^{33–36} The P=Se double bond distances in **5** [2.1020(9) [2.1011(8)] Å] are close to the P=Se double bond distances in the five-membered ring P(Se)C₄ systems such as 1,1'-bis(2,5-dimethylphospholanyl)ferrocene-*P,P'* 1,1'-diselenide [avg. 2.1066 Å] and 1,1'-bis(2,5-diethylphospholanyl)ferrocene-*P,P'* 1,1'-diselenide [2.0978(6) Å].³⁷ The P(Se)S₂C₃ ring in **5** adopts a chair geometry with the substituent phenyl ring in an axial site.

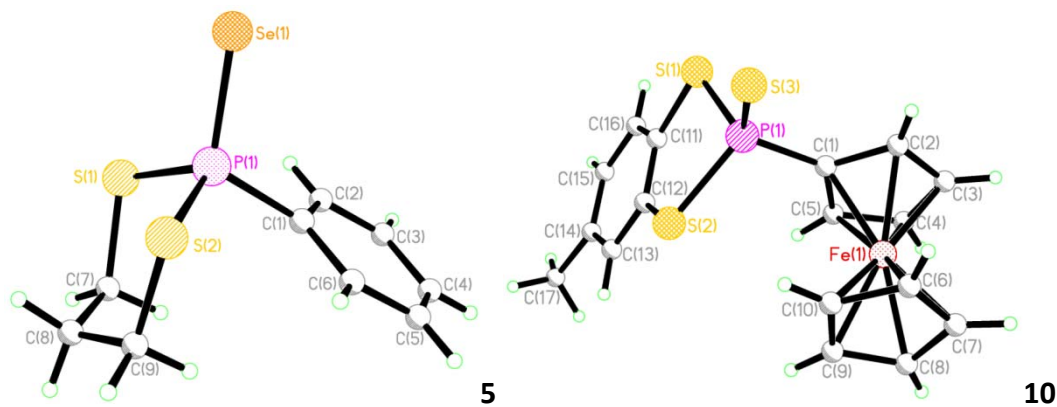


Figure 2. Single crystal X-ray structures of compounds **5** and **10**.

Table 1. Details of the X-ray data collections and refinements for compounds **1**, **2**, **3**, **5** and **10**

Compound	1	2	3	5	10
Formula	C ₉ H ₁₁ OPS ₃	C ₁₀ H ₁₃ OPS ₃	C ₁₃ H ₁₁ OPS ₃	C ₉ H ₁₁ PS ₂ Se	C ₁₇ H ₁₅ FePS ₃
<i>M</i>	262.34	276.37	310.38	293.24	402.31
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>Pnma</i>	<i>P2₁/c</i>	<i>P-1</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	20.961(7)	11.526(2)	7.6496(18)	11.287(6)	12.407(5)
<i>b</i> /Å	6.993(3)	11.228(2)	8.2387(13)	6.901(2)	9.349(3)
<i>c</i> /Å	8.166(3)	10.470(2)	11.274(2)	20.754(7)	15.176(8)
α	90	90	75.0145(10)	90	90
β	90	113.301(5)	89.379(10)	108.245(9)	108.086(12)
γ	90	90	84.850(11)	90	90
<i>U</i> /Å ³	1197.0(4)	1244.5(4)	683.5(2)	2351.4(13)	1673.3(12)
<i>Z</i>	4	4	2	8	4
μ /mm ⁻¹	7.178	6.945	6.419	36.388	13.617
Reflections collected	7313	19224	11162	36172	13116
Independent reflections	1183	2279	2493	4294	3077
<i>R</i> _{int}	0.0300	0.1766	0.0279	0.0828	0.0757
<i>R</i> 1	0.0709	0.0449	0.0226	0.0280	0.0393
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.1893	0.1430	0.0831	0.0653	0.0794

Table 2. Selected bond lengths (Å) and angles (°) for the structures of **1–3**, **5** and **10**

	1	2	3	5	10
P(1)-S(1)	2.0899(17)	2.0724(9)	2.1028(8)	2.0712(11) [2.0793(11)]	2.1045(14)
P(1)-S(2)		2.0665(9)	2.1038(7)	2.0703(12) [2.0688(10)]	2.1048(14)
P(1)-X(3)	1.934(2)	1.9390(10)	1.9351(7)	2.1020(9) [2.1011(8)]*	1.9233(17)
P(1)-C(1)		1.804(3)	1.7917(19)	1.816(2) [1.818(3)]	1.773(3)
S(1)-P(1)-S(2)	98.90(8)	106.14(4)	95.90(3)	106.86(4) [106.10(4)]	97.86(6)
S(1)-P(1)-X(3)		110.11(5)	115.51(3)	110.16(4) [109.08(4)]*	112.87(6)
S(2)-P(1)-X(3)	115.05(7)	110.98(4)	115.74(3)	110.46(4) [111.15(4)]*	115.70(6)
X(3)-P(1)-C(1)	113.3(2)	114.25(8)	114.15(6)	114.90(9) [116.46(8)]*	113.80(13)
S(1)-P(1)-C(1)	106.58(13)	107.29(8)	108.12(7)	106.03(8) [107.49(7)]	107.91(12)
S(2)-P(1)-C(1)		107.68(9)	105.55(6)	108.04(9) [106.01(8)]	107.32(12)

* X = S or Se.

In summary, we have successfully developed an efficient route for synthesis of a series of organo phosphorus-chalcogen heterocycles *via* the reaction of four-membered ring thionation reagent, 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (**LR**, Lawesson's reagent) or 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (**FcLR**, a ferrocene analogue of Lawesson's reagent) and 2,4-bis(phenyl)-1,3-diselenadiphosphethane-2,4-diselenide [$\{\text{PhP}(\text{Se})(\mu\text{-Se})_2\}$] (Woollins' reagent, **WR**, R = Ph, a selenium counterpart of Lawesson's reagent) with alkenyl-dithiols or aryl-dithiols in refluxing toluene solution. Five representative X-ray structures are discussed to confirm the formation of these heterocycles. It is anticipated that this route would be a convenient pathway to synthesize novel macrocyclic compounds. This method allows P-S or P-Se heterocycles to be easily available for further investigations into their chemistry and biological properties.

Experimental Section

General. Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques; subsequent chromatographic and work up procedures were performed in air. All commercially available reagents including alkyldithiols and aryldithiols were used as supplied without further purification unless stated otherwise. ^1H (400.1 MHz), ^{13}C (100.6 MHz), ^{31}P - $\{^1\text{H}\}$ (162.0 MHz) and ^{77}Se - $\{^1\text{H}\}$ (51.5 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise). IR spectra were recorded as KBr pellets in the range of 4000-250 cm^{-1} . Mass spectrometry (m/z, HRMS) data was performed using either atmospheric pressure chemical ionization (APCI) or electron ionization (EI) using a TOM mass analyzer.

The X-ray crystal structure for compound **1** was collected at 173 K using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system, and the structures for compounds **2**, **3**, **5** and **10** were collected using a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics and Rigaku XtaLAB P200 system, both with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). Intensity data were collected using both ω and ϕ steps (**1**), or ω steps alone (**2**, **3**, **5**, **10**), 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 using CrystalClear.³⁸ Structures were solved by charge-flipping (Superflip: **1**),³⁹ direct (SIR-2011: **2**, **3**, **10**)⁴⁰ or Patterson (PATY: **5**)⁴¹ methods and refined by full-matrix least-squares against F^2 (SHELXTL).⁴² Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. All calculations were performed using the CrystalStructure⁴³ interface. 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. CCDC Nos 1494991-1494996.

General Procedure for Preparation of Heterocycles 1–10. A white or brown suspension of **LR** or **FcLR** or **WR** (1.0 mmol) and alkyl- or aryl-dithiol (2.0 mmol) in dry toluene (20 mL) was heated at 130 °C for 6 h. Upon cooling to room temperature and removing unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (*ca.* 2 mL) and loaded onto a silica gel column (1 : 1 hexane/dichloromethane or dichloromethane as eluent) to give compounds **1–10**.

2-(4-Methoxyphenyl)-1,3,2-dithiaphospholane 2-sulfide (1). White solid (65% yield). Selected IR (KBr, cm^{-1}): 1434(m), 1414(m), 1279(m), 1201(m), 1088(s), 995(m), 936(m), 745(s), 686(s), 566(vs), 528(s), 472(s). ^1H NMR (CD_2Cl_2 , δ), 7.98 (dd, $J(\text{P},\text{H}) = 20.7 \text{ Hz}$, $J(\text{H},\text{H}) = 8.0 \text{ Hz}$, 2H), 6.91 (dd, $J(\text{P},\text{H}) = 7.6 \text{ Hz}$, $J(\text{H},\text{H}) = 8.0 \text{ Hz}$, 2H), 3.78 (s,

3H), 3.72-3.53 (m, 4H) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 164.6 (d, $J(\text{P},\text{C}) = 105$ Hz), 135.2, 129.4, 114.7, 56.5, 43.9 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 71.4 ppm. Mass spectrum (EI^+ , m/z), 262 $[\text{M}]^+$. Accurate mass measurement $[\text{EI}^+$, m/z]: 261.9707 $[\text{M}]^+$, calculated mass for $\text{C}_9\text{H}_{11}\text{OPS}_3$: 261.9710.

2-(4-Methoxyphenyl)-1,3,2-dithiaphosphinane 2-sulfide (2). White paste (45% yield). Selected IR (KBr, cm^{-1}): 1588(s), 1562(m), 1493(s), 1461(m), 1419(m), 1289(m), 1256(s), 1179(s), 1095(s), 1016(s), 831(s), 799(m), 677(s), 637(m), 622(m), 561(s), 509(s). ^1H NMR (CDCl_3 , δ), 8.12 (dd, $J(\text{P},\text{H}) = 14.6$ Hz, $J(\text{H},\text{H}) = 8.0$ Hz, 2H), 7.05 (dd, $J(\text{P},\text{H}) = 3.2$ Hz, $J(\text{H},\text{H}) = 8.0$ Hz, 2H), 3.89 (s, 3H), 3.59-3.50 (m, 2H), 3.15-3.04 (m, 2H), 2.29-2.07 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , δ), 163.4 (d, $J(\text{P},\text{C}) = 3.5$ Hz), 133.2 (d, $J(\text{P},\text{C}) = 14.0$ Hz), 124.7 (d, $J(\text{P},\text{C}) = 93.3$ Hz), 114.5 (d, $J(\text{P},\text{C}) = 15.6$ Hz), 55.6, 31.1 (d, $J(\text{P},\text{C}) = 3.4$ Hz), 25.8 (d, $J(\text{P},\text{C}) = 4.7$ Hz) ppm. ^{31}P NMR (CDCl_3 , δ), 64.7 ppm. Mass spectrum (Cl^+ , m/z), 277 $[\text{M}+\text{H}]^+$. Accurate mass measurement $[\text{Cl}^+$, m/z]: 276.9940 $[\text{M}+\text{H}]^+$, calculated mass for $\text{C}_{10}\text{H}_{13}\text{OPS}_3\text{H}$: 276.9939.

2-(4-Methoxyphenyl)-1,3,2-benzodihydrodithiaphosphole 2-sulfide (3). White paste (58% yield). Selected IR (KBr, cm^{-1}): 1589(s), 1494(m), 1444(s), 1295(m), 1262(s), 1181(m), 1096(s), 1021(s), 928(m), 839(s), 800(m), 748(s), 691(s), 624(s), 540(s), 514(s), 396(m). ^1H NMR (CDCl_3 , δ), 8.23 (dd, $J(\text{P},\text{H}) = 15.3$ Hz, $J(\text{H},\text{H}) = 8.0$ Hz, 2H), 7.45-7.37 (m, 2H), 7.24-7.16 (m, 2H), 7.10-7.00 (m, 2H), 3.89 (s, 3H) ppm. ^{13}C NMR (CDCl_3 , δ), 163.6 (d, $J(\text{P},\text{C}) = 3.5$ Hz), 134.2 (d, $J(\text{P},\text{C}) = 14.8$ Hz), 131.2, 130.3 (d, $J(\text{P},\text{C}) = 92.9$ Hz), 127.3, 126.8, 125.9 (d, $J(\text{P},\text{C}) = 8.8$ Hz), 55.7 ppm. ^{31}P NMR (CDCl_3 , δ), 88.4 ppm. Mass spectrum (Cl^+ , m/z), 311 $[\text{M}+\text{H}]^+$. Accurate mass measurement $[\text{Cl}^+$, m/z]: 310.9784 $[\text{M}+\text{H}]^+$, calculated mass for $\text{C}_{13}\text{H}_{11}\text{OPS}_3\text{H}$: 310.9782.

2-Phenyl-1,3,2-dithiaphospholane 2-selenide (4). Pale orange paste (41% yield). Selected IR (KBr, cm^{-1}): 1590(s), 1496(s), 1404(m), 1303(m), 1264(s), 1186(s), 1121(m), 1096(s), 1020(m), 922(s), 821(m), 747(m), 686(s), 531(m), 437(m). ^1H NMR (CD_2Cl_2 , δ), 8.07-7.99 (m, 2H), 7.44-7.40 (m, 3H), 3.74-3.50 (m, 4H) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 138.5 (d, $J(\text{P},\text{C}) = 101.5$ Hz), 133.0 (d, $J(\text{P},\text{C}) = 3.1$ Hz), 132.0 (d, $J(\text{P},\text{C}) = 13.0$ Hz), 129.3 (d, $J(\text{P},\text{C}) = 14.3$ Hz), 44.8 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 73.1 (s, $J(\text{P}=\text{Se}) = 816$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 389.5 (d, $J(\text{P}=\text{Se}) = 816$ Hz) ppm. Mass spectrum (EI^+ , m/z), 275.9(20%), 276.9(19%), 277.9(49%), 279.9(100%), 281.9(27%) $[\text{M}]^+$. Accurate mass measurement $[\text{EI}^+$, m/z]: 279.9045 $[\text{M}]^+$, calculated mass for $\text{C}_8\text{H}_9\text{PS}_2\text{Se}$: 279.9048.

2-Phenyl-1,3,2-dithiaphosphinane 2-selenide (5). Pale pink solid (80% yield). M.p. 100-102 °C. Selected IR (KBr, cm^{-1}): 1475(w), 1431(s), 1415(m), 1265(s), 1175(m), 1089(s), 997(s), 895(m), 857(s), 743(s), 689(s), 615(s), 551(vs), 492(s), 329(m). ^1H NMR (CDCl_3 , δ), 8.21-8.15 (m, 2H), 7.60-7.54 (m, 3H), 3.44-3.34 (m, 2H), 3.08-2.98 (m, 2H), 2.27-2.12 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , δ), 133.1 (d, $J(\text{P},\text{C}) = 73.9$ Hz), 132.9 (d, $J(\text{P},\text{C}) = 3.6$ Hz), 131.1 (d, $J(\text{P},\text{C}) = 12.0$ Hz), 129.2 (d, $J(\text{P},\text{C}) = 14.1$ Hz), 31.9 (d, $J(\text{P},\text{C}) = 3.7$ Hz), 25.3 (d, $J(\text{P},\text{C}) = 5.2$ Hz) ppm. ^{31}P NMR (CDCl_3 , δ), 46.2 (s, $J(\text{P},\text{Se}) = 786$ Hz) ppm. ^{77}Se NMR (CDCl_3 , δ), -27.3 (d, $J(\text{P},\text{Se}) = 786$ Hz) ppm. Mass spectrum (EI^+ , m/z), 290.9(18%), 291.9(16%), 292.9(48%), 294.9(100%), 296.9(21%) $[\text{M}]^+$. Accurate mass measurement $[\text{Cl}^+$, m/z]: 294.9275 $[\text{M}+\text{H}]^+$, calculated mass for $\text{C}_9\text{H}_{11}\text{PS}_2\text{SeH}$: 294.9276.

2-Phenyl-1,3,2-dithiaphosphepane 2-selenide (6). Milky paste (87% yield). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio in multi-NMR spectra. Selected IR (KBr, cm^{-1}): 1541(m), 1434(s), 1303(s), 1092(s), 746(s), 687(s), 617(m), 575(s), 528(s), 475(s), 352(m), 279(s). ^1H NMR (CDCl_3 , δ), 8.22 (m, 4H), 7.59-7.48 (m, 6H), 3.40-3.20 (m, 2H), 2.98-2.89 (m, 2H), 2.60-2.47 (m, 4H), 2.38-2.11 (m, 2H), 1.85-1.60 (m, 2H), 1.44-1.32 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , δ), 135.5 (d, $J(\text{P},\text{C}) = 74.3$ Hz), 134.0 (d, $J(\text{P},\text{C}) = 76.5$ Hz), 132.7 (d, $J(\text{P},\text{C}) = 3.7$ Hz), 132.4 (d, $J(\text{P},\text{C}) = 3.5$ Hz), 131.3 (d, $J(\text{P},\text{C}) = 12.5$ Hz), 131.1 (d, $J(\text{P},\text{C}) = 12.5$ Hz), 35.0 (d, $J(\text{P},\text{C}) = 3.3$ Hz), 33.1 (d, $J(\text{P},\text{C}) = 3.8$ Hz), 32.7, 32.6, 30.4, 28.4 (d, $J(\text{P},\text{C}) = 5.0$ Hz), 24.1, 24.0 ppm. ^{31}P NMR (CDCl_3 , δ), 70.5 (s, $J(\text{P},\text{Se}) = 808$ Hz), 65.3 (s, $J(\text{P},\text{Se}) = 789$ Hz) ppm. ^{77}Se NMR (CDCl_3 , δ), -10.7 (d, $J(\text{P},\text{Se}) = 789$ Hz), -139.6 (d, $J(\text{P},\text{Se}) = 808$ Hz) ppm. Mass spectrum (EI^+ , m/z), 304.9(19%), 305.9(17%), 306.9(47%), 308.9(100%), 310.9(19%) $[\text{M}]^+$. Accurate mass measurement $[\text{Cl}^+$, m/z]: 308.9433 $[\text{M}+\text{H}]^+$, calculated mass for $\text{C}_{10}\text{H}_{13}\text{PS}_2\text{SeH}$: 308.9433.

2-Phenyl-1,3,2-benzodithiaphosphole 2-selenide (7). Pale red paste (24% yield). Selected IR (KBr, cm^{-1}): 1440(s), 1303(m), 1260(m), 1090(s), 1027(m), 802(m), 748(s), 705(m), 687(m), 617(m), 573(s), 535(m), 480(m), 454(m), 421(m). ^1H NMR (CDCl_3 , δ), 8.23 (dd, $J(\text{P,H}) = 16.6$ Hz, $J(\text{H,H}) = 8.3$ Hz, 2H), 7.59-7.49 (m, 3H), 7.40 (dd, $J(\text{P,H}) = 3.2$ Hz, $J(\text{H,H}) = 6.3$ Hz, 2H), 7.21 (d, $J(\text{H,H}) = 6.3$ Hz, 2H) ppm. ^{13}C NMR (CDCl_3 , δ), 135.8, 135.5 (d, $J(\text{P,C}) = 69.1$ Hz), 133.0 (d, $J(\text{P,C}) = 3.6$ Hz), 131.4 (d, $J(\text{P,C}) = 13.1$ Hz), 128.6 (d, $J(\text{P,C}) = 14.6$ Hz), 127.4, 125.6 (d, $J(\text{P,C}) = 8.3$ Hz) ppm. ^{31}P NMR (CDCl_3 , δ), 70.6 (s, $J(\text{P,Se}) = 833$ Hz) ppm. ^{77}Se NMR (CDCl_3 , δ), -13.3 (d, $J(\text{P,Se}) = 834$ Hz) ppm. Mass spectrum (EI^+ , m/z), 323.9(18%), 324.9.9(17%), 325.9(49%), 327.9(100%), 329.9(20%) [M] $^+$. Accurate mass measurement [Cl^+ , m/z]: 328.9122 [$\text{M}+\text{H}$] $^+$, calculated mass for $\text{C}_{12}\text{H}_9\text{PS}_2\text{SeH}$: 328.9126.

2-Ferrocenyl-1,3,2-dithiaphospholane 2-sulfide (8). Pale yellow solid (72% yield). Selected IR (KBr, cm^{-1}): 1411(m), 1368(m), 1190(s), 1107(m), 1030(m), 939(vs), 892(s), 823(m), 794(m), 754(s), 669(s), 488(m), 468(s), 466(s). ^1H NMR (CD_2Cl_2 , δ), 4.92-4.48 (m, 4H), 4.35 (s, 5H), 4.30-4.24 (m, 4H) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 81.7 (d, $J(\text{P,C}) = 130.4$ Hz), 73.8 (d, $J(\text{P,C}) = 21.4$ Hz), 73.6 (d, $J(\text{P,C}) = 16.5$ Hz), 71.5, 43.6 (d, $J(\text{P,C}) = 34.3$ Hz) ppm. ^{31}P NMR (CD_2Cl_2 , δ), 93.6 ppm. Mass spectrum (EI^+ , m/z), 330 [M] $^+$. Accurate mass measurement [EI^+ , m/z]: 329.9261 [M] $^+$, calculated mass for $\text{C}_{12}\text{H}_{13}\text{FePS}_3$: 329.9266.

2-Ferrocenyl-1,3,2-dithiaphosphepane 2-sulfide (9). Yellow paste (34% yield). Two diastereoisomers were found in *ca.* 3 : 2 intensity ratio in multi-NMR spectra. Selected IR (KBr, cm^{-1}): 1433(s), 1409(m), 1282(m), 1238(m), 1172(s), 1104(m), 1024(s), 944(m), 826(s), 677(vs), 525(s), 486(s). ^1H NMR (CDCl_3 , δ), 4.75-4.64 (m, 4H), 4.58-4.51 (m, 4H), 4.40 (s, 5H), 4.38 (s, 5H), 3.35-2.90 (m, 8H), 2.61-2.53 (m, 2H), 2.27-2.11 (m, 2H), 1.97-1.72 (m, 4H) ppm. ^{13}C NMR (CDCl_3 , δ), 80.6 (d, $J(\text{P,C}) = 101.1$ Hz), 78.4 (d, $J(\text{P,C}) = 101.3$ Hz), 72.3 (d, $J(\text{P,C}) = 11.9$ Hz), 72.2 (d, $J(\text{P,C}) = 15.1$ Hz), 71.7 (d, $J(\text{P,C}) = 11.7$ Hz), 71.3 (d, $J(\text{P,C}) = 14.8$ Hz), 70.8, 70.7, 34.7 (d, $J(\text{P,C}) = 4.1$ Hz), 33.6 (d, $J(\text{P,C}) = 4.7$ Hz), 24.1 (d, $J(\text{P,C}) = 3.6$ Hz), 24.0 (d, $J(\text{P,C}) = 4.4$ Hz) ppm. ^{31}P NMR (CDCl_3 , δ), 81.7 and 81.4 ppm. Mass spectrum (Cl^+ , m/z), 369 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement [Cl^+ , m/z]: 368.9649 [$\text{M}+\text{H}$] $^+$, calculated mass for $\text{C}_{14}\text{H}_{17}\text{FePS}_3\text{H}$: 368.9652.

2-Ferrocenyl-4-methyl-1,3,2-benzodithiaphosphole 2-sulfide (10). Yellow solid (76% yield). M.p. 121-123 °C. Selected IR (KBr, cm^{-1}): 1585(m), 1457(s), 1409(m), 1387(m), 1175(s), 1118(m), 1022(s), 908(m), 824(s), 731(s), 693(vs), 682(vs), 536(s), 487(s), 450(m), 525(m). ^1H NMR (CDCl_3 , δ), 7.30 (s, 1H), 7.24-7.23 (m, 1H), 7.03-7.01 (m, 1H), 4.82-4.79 (m, 2H), 4.60-4.59 (m, 2H), 4.42 (s, 5H), 2.35 (s, 3H) ppm. ^{13}C NMR (CDCl_3 , δ), 137.3, 134.5, 131.1, 128.0, 126.5 (d, $J(\text{P,C}) = 8.1$ Hz), 125.7 (d, $J(\text{P,C}) = 8.1$ Hz), 76.9 (d, $J(\text{P,C}) = 99.4$ Hz), 73.4 (d, $J(\text{P,C}) = 16.3$ Hz), 73.4 (d, $J(\text{P,C}) = 12.7$ Hz), 70.9, 21.1 ppm. ^{31}P NMR (CDCl_3 , δ), 89.5 ppm. Mass spectrum (Cl^+ , m/z), 402 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement [Cl^+ , m/z]: 401.9412 [$\text{M}+\text{H}$] $^+$, calculated mass for $\text{C}_{17}\text{H}_{14}\text{FePS}_3\text{H}$: 401.9417.

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

1. Rotstein, B. H.; Zaretsky, S.; Rai, V.; Yudin, A. K. *Chem. Rev.* **2014**, *114*, 8323-8359. <http://dx.doi.org/10.1021/cr400615v>
2. Chivers, T.; Manners, I. *Inorganic rings and polymers of the p-block elements: from fundamentals to applications*. RSC Publishing: Cambridge, U. K., 2009, pp 256-259.

3. Woollins, J. D.; Laitinen, R. S. *Selenium and tellurium chemistry: from small molecules to biomolecules and materials*. Springer, London, 2011, pp 1-40.
<http://dx.doi.org/10.1007/978-3-642-20699-3>
4. Timperley, C. M. *Best synthetic methods: Organophosphorus (V) chemistry*. Academic Press, London, 2015, pp 633-720.
5. Lecher, H. Z.; Greenwood, R. A.; Whitehouse, K. C.; Chao, T. H. *J. Am. Chem. Soc.* **1956**, *78*, 5018-5023.
<http://dx.doi.org/10.1021/ja01600a058>
6. Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061-5087.
[http://dx.doi.org/10.1016/S0040-4020\(01\)96753-5](http://dx.doi.org/10.1016/S0040-4020(01)96753-5)
7. Cherkasov, R. A.; Kuttyrev, G. A.; Pudovik, A. N. *Tetrahedron* **1985**, *41*, 2567-2569.
[http://dx.doi.org/10.1016/S0040-4020\(01\)96363-X](http://dx.doi.org/10.1016/S0040-4020(01)96363-X)
8. Jones, B. A.; Bradshaw, J. S. *Chem. Rev.* **1984**, *84*, 17-30.
<http://dx.doi.org/10.1021/cr00059a002>
9. Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2007**, *107*, 5210-5278.
<http://dx.doi.org/10.1021/cr040650b>
10. Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2010**, *110*, 3419-3478.
<http://dx.doi.org/10.1021/cr900243d>
11. Philip, J. W.; Chivers, T. *Inorg. Chem.* **2013**, *52*, 7791-7804.
<http://dx.doi.org/10.1021/ic401002b>
12. Hua, G.; Du, J.; Surgenor, B. A.; Slawin, A. M. Z.; Woollins, J. D. *Molecules* **2015**, *20*, 12175-12197.
<http://dx.doi.org/10.3390/molecules200712175>
13. van Zyl, W. E.; Woollins, J. D. *Coord. Chem. Rev.* **2013**, *257*, 718-731.
<http://dx.doi.org/10.1016/j.ccr.2012.10.010>
14. Gray, I. P., Milton, H. L., Slawin, A. M. Z.; Woollins, J. D. *Phosphorus, Sulfur, and Silicon and the Related Elements* **2004**, *179*, 969-970.
<http://dx.doi.org/10.1080/10426500490429158>
15. Gray, I. P., Slawin, A. M. Z.; Woollins, J. D. *Z. Anorg. Allgem. Chem.* **2004**, *630*, 1851-1857.
<http://dx.doi.org/10.1002/zaac.200400161>
16. Gray, I. P., Milton, H. L., Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2003**, 3450-3457.
<http://dx.doi.org/10.1039/b306387a>
17. Hua, G.; Henry, J. B.; Li, Y.; Mount, A. R., Slawin, A. M. Z.; Woollins, J. D. *Org. Biomol. Chem.* **2010**, *8*, 1655-1660.
<http://dx.doi.org/10.1039/b924986a>
18. Hua, G.; Woollins, J. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1368-1377.
<http://dx.doi.org/10.1002/anie.200800572>
19. Hua, G.; Li, Y.; Fuller, A. L.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Org. Chem.* **2009**, 1612-1618.
<http://dx.doi.org/10.1002/ejoc.200900013>
20. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *New J. Chem.* **2010**, *34*, 1565-571.
<http://dx.doi.org/10.1039/b9nj00570f>
21. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Org. Chem.* **2010**, 2707-2615.
22. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2011**, *30*, 805-808.
<http://dx.doi.org/10.1016/j.poly.2010.12.018>
23. Hua, G.; Fuller, A. L.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Org. Chem.* **2011**, 3067-3073.
<http://dx.doi.org/10.1002/ejoc.201100226>

24. Hua, G.; Griffin, J. M.; Ashbrook, S. E.; Slawin, A. M. Z.; Woollins, J. D. *Angew. Chem. Int. Ed.* **2011**, *50*, 4123-4126.
<http://dx.doi.org/10.1002/anie.201006081>
25. Hua, G.; Cordes, D. B.; Li, Y.; Slawin, A. M. Z.; Woollins, J. D. *Tetrahedron Lett.* **2011**, *52*, 3311-3314.
<http://dx.doi.org/10.1016/j.tetlet.2011.04.058>
26. Hua, G.; Slawin, A. M. Z.; Randall, R. A. M.; Corde, D. B.; Crawford, L.; Bühl, M.; Woollins, J. D. *Chem. Commun.* **2013**, *49*, 2619-2621.
<http://dx.doi.org/10.1039/c3cc40515j>
27. Hua, G.; Du, J.; Corde, D. B.; Slawin, A. M. Z.; Woollins, J. D. *J. Org. Chem.* **2016**, *81*, 4210-4225.
<http://dx.doi.org/10.1021/acs.joc.6b00573>
28. Hua, G.; Du, J.; Slawin, A. M. Z.; Woollins, J. D. *Chem. Eur. J.* **2016**, *22*, 7782-7791.
<http://dx.doi.org/10.1002/chem.201504832>
29. Foreman, M. R. St. J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc. Dalton Trans.* 1996, 3653-3657.
<http://dx.doi.org/10.1039/dt9960003653>
30. Parveen, S.; Kilian, P.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2006**, 2586-2590.
<http://dx.doi.org/10.1039/B517093A>
31. Gray, I. P.; Slawin, A. M. Z.; Woollins, J. D. *New J. Chem.* **2004**, *28*, 1383-1389.
<http://dx.doi.org/10.1039/b406007e>
32. Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 1-31.
33. Lee, J. D.; Goodacre, G. W. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *27*, 1841-1845.
<http://dx.doi.org/10.1107/S0567740871004953>
34. John Foreman, M. R. St.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc. Dalton Trans.* **1999**, 1175-1184.
<http://dx.doi.org/10.1039/a808918c>
35. Schwarz, P.; Ohms, G.; Kruger, K.; Grossmann, G.; Kaiser, V. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **1998**, *141*, 27-43.
<http://dx.doi.org/10.1080/10426509808033718>
36. Wrackmeyer, B.; Klimkina, E. V.; Milius, W. *Dalton Trans.* **2014**, *43*, 5021-5043.
<http://dx.doi.org/10.1039/C3DT52753K>
37. Mandell, C. L.; Kleinbach, S. S.; G.Dougherty, W.; Kassel, W. S.; Nataro, C. *Inorg. Chem.* **2010**, *49*, 9718-9727.
<http://dx.doi.org/10.1021/ic1016164>
38. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
<http://dx.doi.org/10.1107/S0108767307043930>
39. *CrystalClear-SM Expert v2.0 and v2.1.* Rigaku Americas, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan, 2010-2013.
40. Palatinus, L.; Chapuis, G. *J. Appl. Cryst.* **2007**, *40*, 786-790.
<http://dx.doi.org/10.1107/S0021889807029238>
41. Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2012**, *45*, 357-361.
<http://dx.doi.org/10.1107/S0021889812001124>
42. Sheldrick, G. M. *Acta Crystallogr., Sect. C.* **2015**, *71*, 3-8.
<http://dx.doi.org/10.1107/S2053229614024218>
43. *DIRDIF-99.* Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

44. *CrystalStructure* v4.1. Rigaku Americas, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan, 2013.