Six-membered cyclic phosphate–phosphonates: synthesis and stereochemistry of *cis*/*trans*-2-phosphorylbenzyloxy-4-aryl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-thiones (selones)

Jia Zhou * and Ruyu Chen

Institute of Elemento-Organic Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, PR China

A study on the synthesis and stereochemistry of the novel six-membered cyclic phosphate–phosphonates, *cis*/*trans*-2-phosphorylbenzyloxy-4-aryl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-thiones (selones) 7a–f has been carried out. The title compounds were obtained in good overall yields by a one-pot procedure using tris(diethylamino)phosphine activated by iodine as the phosphorylating and ring-closing reagent. Their geometric stereoisomers were isolated and characterized. A *cis*-configuration and a preferred chair conformation of one isomer of 7b have been established by X-ray diffraction analysis. This study also gives a good explanation for the correlation between the configurational assignments and the chemical shifts of C_4-H and ^{31}P, which shows some difference from previously reported results.

Introduction

1,3,2-Dioxaphosphorinane derivatives are an important class of organophosphorus heterocycles, which continue to attract considerable interest due to their unique stereochemical features and diverse potential biological importance.[1–4] It has been found that the stereochemistry is important for the bioactivities and many biochemical interactions of 1,3,2-dioxaphosphorinane compounds, especially those involving enzymes.[5,6] Consequently, the development of new stereoselective methods to obtain a variety of these kinds of molecules is highly desirable. To the best of our knowledge, 1,3,2-dioxaphosphorinane derivatives have generally been prepared by the phosphorylation with phosphorus trichloride or (thio)phosphoryl chloride.[7,8] However, studies on the synthesis and stereochemistry of 1,3,2-dioxaphosphorinane-2-thiones (selones) by the tris(diethylamino)phosphine method are rare.

The phosphoryl group is of fundamental significance in many of the most important molecules that control molecular replication, cell biochemistry and metabolic processes in all living species.[9] Succeeding the more extensively studied α-amino phosphoryl compounds, α-hydroxy phosphonate compounds have recently been proved to be biologically active[10] and have been shown to inhibit the enzymes renin, EPSP synthase and HIV protease.[11] Therefore, a large number of thio (seleno) phosphate–phosphonate derivatives, bearing a P–O–C–P bond structure, were synthesized and their significant herbicidal, antiviral and fungicidal activities were reported for the first time.[12] In continuation of our work on elaborating phosphate–phosphonates into a variety of heterocyclic systems of biological and stereochemical interest, we herein describe an efficient, one-pot synthesis of the novel cyclic phosphate–phosphonates *cis*- and *trans*-**7a**–**f**, and their stereochemistry. Configurational and conformational analyses are also discussed.

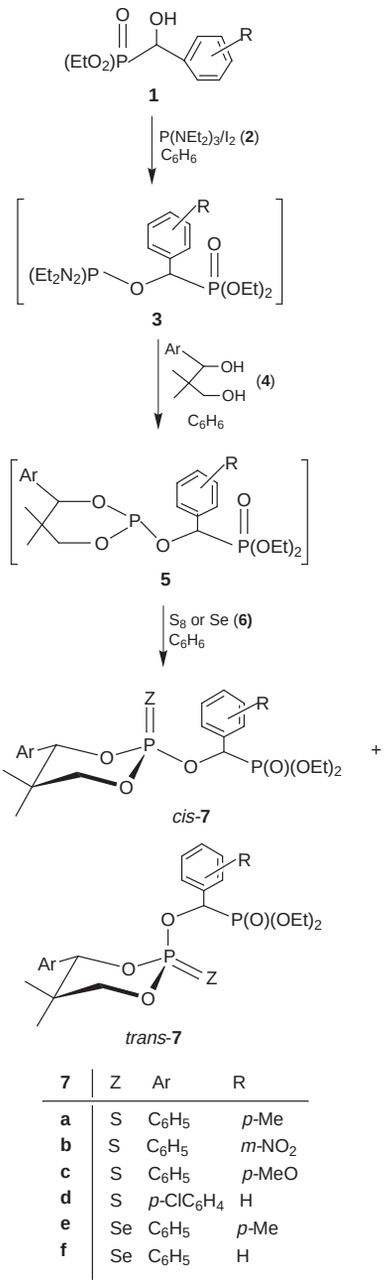
Results and discussion

The six-membered cyclic phosphate–phosphonates, *cis*/*trans*-2-phosphorylbenzyloxy-4-aryl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-thiones (selones) **7a**–**f** were synthesized by a multistep, one-pot procedure under mild conditions (Scheme 1). The starting materials α-hydroxy phosphonates **1** were prepared through base-catalysed hydrophosphonylation (the Pudovik reaction) of aldehydes with dialkyl phosphites.[13] The phosphorylation of **1** was carried out with tris(diethylamino)-phosphine activated by iodine to give the resultant phosphite–phosphonates **3** in nearly quantitative yields. Intermediates **3** underwent the ring-closing reaction with 1-aryl-2,2-dimethylpropane-1,3-diol **4** to produce the cyclic phosphite–phosphonate **5**, which was then treated with sulfur or grey selenium to afford the desired title compounds **7a**–**f** as a mixture of the two possible diastereoisomers in overall yields of 85.7–90.8%.

The ratios of geometric isomers given in Table 1 were determined by integration of suitable signals in the ^{1}H NMR spectra or the ^{31}P NMR spectra of the crude products. The results obtained show that unfortunately the synthetic reactions are not significantly stereoselective affording the products, which might be the result of a thermodynamic equilibrium system (see Scheme 2), as a nearly equimolar mixture of diastereoisomers. However, the reaction provides a convenient method to synthesize the *cis* and *trans* stereoisomers at the same time. The isolation of the diastereoisomers was accomplished by column chromatography on silica gel and their structures were characterized by ^{1}H NMR, ^{31}P NMR, IR, MS and elemental analysis. A comparison of the spectra of the isomers displayed a consistent difference in the chemical shifts of C_4-H and ^{31}P. The isomer with the lower polarity, on the basis of the chromatographic separation, has a smaller δ value of C_4-H (shift difference $\Delta\delta$ 0.05–0.08 ppm) and larger ^{31}P δ values ($\Delta\delta$ 1–2 ppm) than the other isomers. However, analogues described in the literature[14] have δ (*cis*) larger than δ (*trans*) for both C_4-H and ^{31}P. Thus the correlation between the δ values and configuration does not allow an accurate configurational assignment of the isomers.

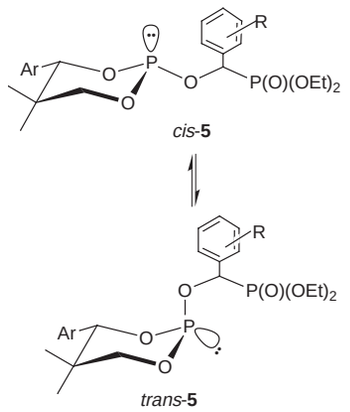
At this point in the study it was considered necessary to carry out a single-crystal X-ray diffraction analysis of one isomer. Our intention was to obtain conclusive evidence on the configuration and, at the same time, to get a reasonable explanation for the correlation mentioned above. The structural analysis of the lower polarity isomer of **7b** proved its configuration unambiguously to be *cis*, for which the 4-proton and ^{31}P appear at a higher field and lower field, respectively. A comparison of the NMR spectrum of the crystal sample before and after X-ray diffraction indicates that the solid state NMR spectra display anisotropic chemical shifts and the chemical shift of the C_4-H proton is not changed and, therefore, no configurational

conversion has occurred during the analysis. The molecular structure obtained for *cis*-**7b** is shown in Fig. 1, together with the atomic numbering scheme. Fig. 2 depicts the preferred chair conformation of *cis*-**7b** adopted in the solid state and, the relative locations between C_4-H and P=S double bond, which reveal the fact that C_4-H is within the shielding region of the



7	Z	Ar	R
a	S	C_6H_5	*p*-Me
b	S	C_6H_5	*m*-NO_2
c	S	C_6H_5	*p*-MeO
d	S	*p*-ClC_6H_4	H
e	Se	C_6H_5	*p*-Me
f	Se	C_6H_5	H

Scheme 1



Scheme 2

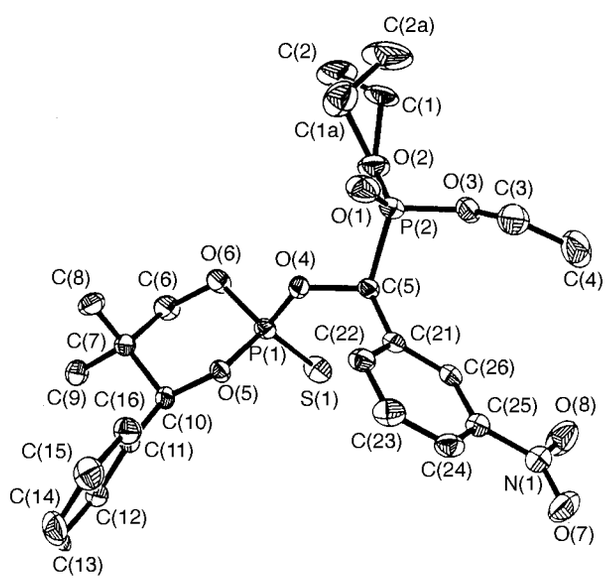


Fig. 1 Molecular structure of compound *cis*-**7b** showing the atomic numbering. Selected bond lengths (Å) and angles (°): P(1)–S(1) 1.908(3), P(1)–O(4) 1.573(4), P(1)–O(5) 1.573(4), P(1)–O(6) 1.557(5), O(4)–C(5) 1.443(7), P(2)–O(1) 1.452(5), P(2)–O(2) 1.573(6), P(2)–O(3) 1.537(5), P(2)–C(5) 1.814(6); S(1)–P(1)–O(4) 115.9(2), S(1)–P(1)–O(5) 116.1(2), O(4)–P(1)–O(5) 101.4(2), S(1)–P(1)–O(6) 117.5(2), O(4)–P(1)–O(6) 100.0(2), O(5)–P(1)–O(6) 103.4(2), O(1)–P(2)–O(3) 115.8(3), O(1)–P(2)–C(5) 114.1(3), O(2)–P(2)–C(5) 100.3(3), P(1)–O(4)–C(5) 122.1(4), P(1)–O(5)–C(10) 117.3(3), P(1)–O(6)–C(6) 114.3(4), P(2)–C(5)–O(4) 105.9(4).

Table 1 Experimental data of compounds *cis*- and *trans*-**7a**–**f**

Compound	Yield (%)	Ratios of *cis* : *trans*	*cis*		*trans*	
			δ_H(4-H) (ppm)	δ_P (ppm)	δ_H(4-H) (ppm)	δ_P (ppm)
7a	88.4	59.58 : 40.42	5.31 (d)	68.79 (d) 16.42 (d)	5.36 (d)	67.99 (d) 16.11 (d)
7b	85.7	55.71 : 44.29	5.32 (d)	70.47 (d) 16.96 (d)	5.41 (d)	69.62 (d) 14.96 (d)
7c	86.1	53.38 : 46.62	5.31 (d)	68.85 (d) 16.52 (d)	5.37 (d)	68.15 (d) 16.27 (d)
7d	88.7	48.08 : 51.92	5.28 (d)	68.76 (d) 16.13 (d)	5.33 (d)	67.44 (d) 15.75 (d)
7e	89.9	51.97 : 48.03	5.33 (d)	73.09 (d) 16.13 (d)	5.39 (d)	72.20 (d) 15.84 (d)
7f	90.8	46.91 : 53.09	5.33 (d)	73.24 (d) 15.98 (d)	5.40 (d)	72.20 (d) 15.68 (d)

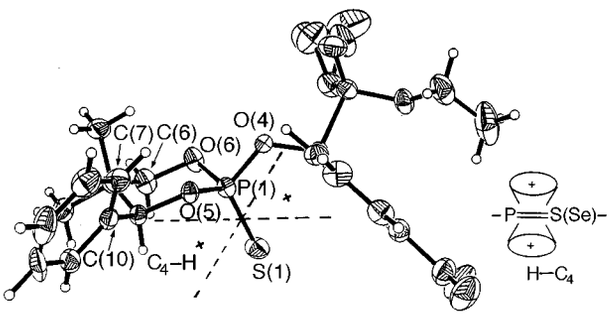


Fig. 2 The preferred chair conformation of *cis*-**7b** and the relative locations between C_4-H and the P=S double bond. Selected torsion angles (°): S(1)–P(1)–O(4)–C(5) −7.6(1), O(5)–P(1)–O(4)–C(5) 117.7(1), O(6)–P(1)–O(4)–C(5) −136.1(1), S(1)–P(1)–O(5)–C(10) −78.2(1), O(4)–P(1)–C(5)–C(10) 156.9(1), O(6)–P(1)–O(5)–C(10) 52.0(1), S(1)–P(1)–O(6)–C(6) 76.2(1), O(4)–P(1)–O(6)–C(6) −157.5(1), O(5)–P(1)–O(6)–C(6) −52.5(1), P(1)–O(4)–C(5)–P(2) 154.5(1), P(1)–O(5)–C(10)–C(7) −58.1(2), P(1)–O(5)–C(10)–C(11) 177.5(1), P(1)–O(6)–C(6)–C(7) 59.3(2), O(6)–C(6)–C(7)–C(8) 69.1(2), O(6)–C(6)–C(7)–C(9) −177.2(2), O(6)–C(6)–C(7)–C(10) −58.6(2), C(6)–C(7)–C(10)–O(5) 57.8(2), C(6)–C(7)–C(10)–C(11) 176.2(1), C(8)–C(7)–C(10)–O(5) −65.7(2), C(8)–C(7)–C(10)–C(11) 52.7(2), C(9)–C(7)–C(10)–O(5) 173.3(1).

P=S or P=Se group and as a result, its chemical shift is at a higher field (δ 5.280–5.335 ppm). In contrast to the analogues in previous studies,[14] the 1,3-diaxial shielding effects of the axial P=X (X = O, S, Se) group on the axial C_4-H proton are evident for compounds *cis*-**7** perhaps due to the favourably short distance between the two, which is mainly attributed to the repulsion of the bulky phosphono(substituted)benzyloxy group to the axial P=X group.

In the ^{1}H NMR spectra of *cis*- and *trans*-**7a**–**f**, the difference between the chemical shifts of the two methyls at the C-5 position of the ring in the *cis*-isomer is larger than that in the *trans*-one (0.02–0.05 ppm). The corresponding methyl and methylene protons of the two ethoxy groups are magnetically nonequivalent and display two sets of signals, respectively. The α-methylidyne proton in the P–O–C–P moiety of *cis*- or *trans*-**7a**–**f** exhibits a dd peak due to the coupling effects of two phosphorus atoms (*J* 13.56 Hz). Similarly, the ^{31}P NMR spectra display a dd peak owing to the ^{31}P–^{31}P coupling with the $^3J_{P1P2}$ of 41.4–44.8 Hz and, the coupling constants in the *cis*-isomers are slightly larger than those in the *trans*. The IR spectra of *cis*- and *trans*-**7a**–**f** show normal stretching absorption bands, indicating the existence of P=O (1247–1256 cm^{-1}) and P–O–C (1175–920 cm^{-1}) groups. In the *cis*-isomers the P=S or P=Se absorption bands generally appear at smaller wavenumbers than those in the *trans*-isomers, consistent with the reported results.[15] The EIMS spectra of **7a**–**f** show the existence of strong molecular ion peaks, indicating that the heterocyclic skeletons have some stability. However, it is worth mentioning that the observed molecular ions of selenium-containing compounds such as **7e** and **7f** are 1 larger than their corresponding calculated molecular weight due to the highest natural abundance of ^{80}Se atoms.

Conclusions

In summary, we have carried out a study on the synthesis and stereochemistry of a series of novel six-membered cyclic phosphate–phosphonates. A convenient and efficient one-pot approach to the *cis*- and *trans*-4-aryl-5,5-dimethyl-1,3,2-dioxaphosphorinanes containing thio (seleno) phosphate–phosphonate linkages in good yields under mild conditions has been developed. The results obtained show that configurational assignments based on comparisons of the chemical shifts of C_4-H and ^{31}P should be treated with caution until supported by X-ray diffraction studies.

Experimental

Melting points were determined using a Yanaco MP-500 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu-435 spectrometer, and band positions are reported in wavenumbers (cm^{-1}). NMR spectra were taken on JEOL-FX-90Q and Bruker AC-P200 spectrometers. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H NMR, and 85% H_3PO_4 was used as an external standard for ^{31}P NMR spectroscopy. The nuclei that are deshielded relative to their respective standards are assigned a positive chemical shift. Coupling constants, *J*, are given in Hz. Mass spectra were recorded on a Hewlett-Packard 5988 instrument. Elemental analyses were carried out on a Yana MT-3 instrument. Column chromatography was performed using silica gel H (10–40 μm, Haiyang chemical Factory of Qingdao).

α-Hydroxy phosphonates,[5] tris(diethylamino)phosphine[16] and 1-aryl-2,2-dimethylpropane-1,3-diol[7] were prepared according to the previously published procedure. All the reaction solvents were anhydrous and were dried according to conventional methods before use.

General procedure for the synthesis of six-membered cyclic phosphate–phosphonates *cis*/*trans*-7a–f

A mixture of tris(diethylamino)phosphine (0.78 g, 3.15 mmol) and iodine (0.038 g, 0.15 mmol) in 50 mL of anhydrous benzene was heated at 70 °C under a stream of nitrogen for approximately 20 min until the precipitate dissolved. The solution was cooled to ambient temperature, and α-hydroxy phosphonate **1** (3.0 mmol) was added. The reaction mixture was maintained at 75 °C for 1.5 h, and then cooled to room temperature when 1-aryl-2,2-dimethylpropane-1,3-diol **4** (3.0 mmol) was added. The reaction mixture was then heated at 75 °C for 2.5 h. Transformation to the desired compounds **7** was accomplished by the addition of sulfur (0.15 g, 4.69 mmol) or grey selenium (0.38 g, 4.81 mmol) and the mixture was kept at 72–78 °C for 1 h or 3 h. The solvent was removed under reduced pressure and the compound was extracted from the residue with 10 mL of acetone. After filtration, the solvent was distilled off *in vacuo* and purification of the product by silica gel flash column chromatography using ethyl acetate–light petroleum (bp 60–90 °C) (1 : 6, v/v) as the eluent, afforded **7a**–**f** as a mixture of geometric stereoisomers. The yields and the ratios of *cis*- and *trans*-isomers are listed in Table 1. After further column chromatography, eluting with ethyl acetate–light petroleum (1 : 20, v/v), the two isomers were isolated in pure form. The physical and chemical data of *cis*/*trans*-**7a**–**f** are given below.

***cis*-2-(α-Diethoxyphosphoryl-4-methylbenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-thione *cis*-7a.** White solid, mp 150–151 °C; ν_{max}(KBr)/cm^{-1} 3405, 3113, 2968, 1626, 1556, 1524, 1453 (s), 1252 (s, P=O), 1061, 1020, 979, 950 (s, P–O–C), 827 (s), 735 (s) and 662.8 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.78 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 1.25 (m, 6 H, 2 CH_3), 2.31 (s, 3 H, CH_3), 3.82–4.50 (m, 6 H, 3 CH_2), 5.31 (d, 1 H, CH, *J* 3.12), 5.95 (dd, 1 H, CH, *J* 13.6) and 6.92–7.59 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 16.42 (d), 68.79 (d) and $^3J_{P1P2}$ 43.55 (Found: C, 55.80; H, 6.60. $C_{23}H_{32}O_6P_2S$ requires C, 55.40; H, 6.48%).

***trans*-2-(α-Diethoxyphosphoryl-4-methylbenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-thione *trans*-7a.** White solid, mp 139–140 °C; ν_{max}(KBr)/cm^{-1} 3405, 3113, 2968, 1626, 1556, 1524, 1452 (s), 1255 (s, P=O), 1061, 1020, 979, 950 (s, P–O–C), 827 (s), 735 (s) and 698.5 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.77 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 1.23 (m, 6 H, 2 CH_3), 2.37 (s, 3 H, CH_3), 3.84–4.52 (m, 6 H, 3 CH_2), 5.36 (d, 1 H, CH, *J* 3.14), 5.95 (dd, 1 H, CH, *J* 13.6) and 6.92–7.58 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 16.11 (d), 67.99 (d) and $^3J_{P1P2}$ 42.04 (Found: C, 55.69; H, 6.28. $C_{23}H_{32}O_6P_2S$ requires C, 55.40; H, 6.48%).

***cis*-2-(α-Diethoxyphosphoryl-3-nitrobenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-thione *cis*-7b.** White solid, mp 157–158 °C; ν_{max}(KBr)/cm^{-1} 3404, 3093, 2975, 1611, 1526, 1492, 1453 (s), 1252 (s, P=O), 1044, 1016, 979, 955 (s, P–O–C), 869, 831 (s), 755 (s) and 679 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.80 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.30 (m, 6 H, 2 CH_3), 3.83–4.58 (m, 6 H, 3 CH_2), 5.32 (d, 1 H, CH, *J* 3.14), 6.16 (dd, 1 H, CH, *J* 13.56) and 7.08–8.58 (m, 9 H, C_6H_5 and C_6H_4); δ_P(36.19 MHz; $CDCl_3$) 16.96 (d), 70.47 (d) and $^3J_{P1P2}$ 44.46; *m*/*z* 529 (M^+, 18.25%), 324 (5.10), 304 (11.19), 288 (7.76), 215 (10.79), 185 (4.28), 177 (10.27), 152 (22.32), 145 (100), 143 (58.40), 136 (43.42), 129 (35.01), 115 (28.39), 107 (12.40), 105 (80.92), 91 (93.57), 79 (15.86) and 65 (63.14) (Found: C, 49.69; H, 5.70; N, 2.79. $C_{22}H_{29}NO_8P_2S$ requires C, 49.90; H, 5.53; N, 2.65%).

Crystal data for cis-**7b**.—$C_{22}H_{29}NO_8P_2S$, M_w = 529.49, monoclinic, $P2_1/c$, a = 9.888(2), b = 20.831(4), c = 12.797(3) Å, β = 94.42(3)°, V = 2628(1) Å^3, Z = 4, D_c = 1.338 g cm^{-3}, $F(000)$ = 556, μ = 0.2796 mm^{-1}. Refined cell parameters were obtained from setting angles of 25 reflections. A colourless single crystal (0.3 × 0.3 × 0.4 mm) was used for the analysis.

Data collection.—Crystallographic measurements were made at room temperature using an Enraf-Nonius CAD-4 diffractometer operating in the ω–2θ scan mode. The intensity data were collected with a θ range 2–23° using graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å). Intensities of 3945 unique reflections were measured of which 1793 satisfied the criterion $I \geqslant 3\sigma(I)$.

Structure solution and refinement.—The structure was solved by direct methods employing SHELXS-86.[17] Corrections were applied for Lp but not for absorption or extinction. Positional and thermal parameters were refined by full-matrix least-squares minimizing the function $\Sigma\omega(F_o - F_c)^2$ with $\omega = 1/\sigma^2(F)$ for the observed reflections and $\omega = 0$ for unobserved reflections. Most of the non-hydrogen atoms were located from an E-map. The others were determined with successive difference Fourier syntheses. The hydrogen atoms were added theoretically. All of them were refined with fixed position parameters and thermal factors. The final refinements by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms were converged with unweighted and weighted (unit weights) agreement factors of 0.052 and 0.057, and *S* of 0.80. The highest peak on the final difference Fourier map had a height of 0.27 e Å^{-3} [$(\Delta/\sigma)_{max}$ = 0.45].

Atomic scattering factors for the compound were taken from International Tables for X-Ray Crystallography[18] and all calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/239.

***trans*-2-(α-Diethoxyphosphoryl-3-nitrobenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-dioxophosphorinane-2-thione *trans*-7b.** Colourless syrup; ν_{max}(film)/cm^{-1} 3404, 3093, 2975, 1611, 1526, 1492, 1453 (s), 1255 (s, P=O), 1044, 1016, 979, 955 (s, P–O–C), 869, 831 (s), 755 (s) and 698 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.79 (s, 3 H, CH_3), 1.0 (s, 3 H, CH_3), 1.26 (m, 6 H, 2 CH_3), 3.82–4.60 (m, 6 H, 3 CH_2), 5.41 (d, 1 H, CH, *J* 3.14), 6.18 (dd, 1 H, CH, *J* 13.6) and 7.06–8.50 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 14.96 (d), 69.62 (d) and $^3J_{P1P2}$ 42.12 (Found: C, 49.72; H, 5.84; N, 2.80. $C_{22}H_{29}NO_8P_2S$ requires C, 49.90; H, 5.53; N, 2.65%).

***cis*-2-(α-Diethoxyphosphoryl-4-methoxybenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-phosphorinane-2-thione *cis*-7c.** White solid, mp 111–112 °C, ν_{max}(KBr)/cm^{-1} 3409, 3047, 2924, 1608, 1583, 1500, 1465 (s), 1250 (s, P=O), 1172, 1017, 982, 961 (s, P–O–C), 836 (s), 755 (s) and 667.7 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.78 (s, 3H, CH_3), 0.95 (s, 3 H, CH_3), 1.17–1.33 (m, 6 H, 2 CH_3), 3.76 (s, 3 H, CH_3O), 3.80–4.48 (m, 6 H, 3 CH_2), 5.31 (d, 1 H, CH, *J* 3.13), 5.93 (dd, 1 H, CH, *J* 13.56) and 6.84–7.50 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 16.52 (d), 68.85 (d) and $^3J_{P1P2}$ 44.81 (Found: C, 53.54; H, 6.39. $C_{23}H_{32}O_7P_2S$ requires C, 53.68; H, 6.28%).

***trans*-2-(α-Diethoxyphosphoryl-4-methoxybenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-phosphorinane-2-thione *trans*-7c.** Colourless syrup, ν_{max}(film)/cm^{-1} 3394, 3058, 2946, 1608, 1584, 1494, 1460 (s), 1247 (s, P=O), 1168, 1024, 980, 958 (s, P–O–C), 838 (s), 758 (s) and 699.1 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.77 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 1.16–1.34 (m, 6 H, 2 CH_3), 3.76 (s, 3 H, CH_3O), 3.82–4.52 (m, 6 H, 3 CH_2), 5.37 (d, 1 H, CH, *J* 3.13), 5.93 (dd, 1 H, CH, *J* 13.56) and 6.82–7.50 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$), 16.27 (d), 68.15 (d) and $^3J_{P1P2}$ 43.50 (Found: C, 53.85; H, 6.50. $C_{23}H_{32}O_7P_2S$ requires C, 53.68; H, 6.28%).

***cis*-2-(α-Diethoxyphosphorylbenzyloxy)-4-(4-chlorophenyl)-5,5-dimethyl-1,3,2λ^5-phosphorinane-2-thione *cis*-7d.** Colourless syrup, ν_{max}(film)/cm^{-1} 3349, 3049, 2925, 1597, 1576, 1489, 1453 (s), 1251 (s, P=O), 1175, 1085, 1010, 981, 961 (s, P–O–C), 829 (s), 771, 739 (s) and 670.2 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.77 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 1.20–1.28 (m, 6 H, 2 CH_3), 3.76–4.48 (m, 6 H, 3 CH_2), 5.28 (d, 1 H, CH, *J* 2.80), 5.96 (dd, 1 H, CH, *J* 13.56) and 6.84–7.56 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 16.13 (d), 68.76 (d) and $^3J_{P1P2}$ 43.22 (Found: C, 51.12; H, 5.53. $C_{22}H_{29}ClO_6P_2S$ requires C, 50.91; H, 5.64%).

***trans*-2-(α-Diethoxyphosphorylbenzyloxy)-4-(4-chlorophenyl)-5,5-dimethyl-1,3,2λ^5-phosphorinane-2-thione *trans*-7d.** Colourless syrup, ν_{max}(film)/cm^{-1} 3345, 3044, 2928, 1598, 1480, 1452 (s), 1248 (s, P=O), 1174, 1085, 1020, 982, 963 (s, P–O–C), 831 (s), 770, 737 (s) and 698.0 (s, P=S); δ_H(200 MHz; $CDCl_3$) 0.76 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 1.20–1.28 (m, 6 H, 2 CH_3), 3.76–4.50 (m, 6 H, 3 CH_2), 5.33 (d, 1 H, CH, *J* 3.14), 5.96 (dd, 1 H, CH, *J* 13.56) and 6.86–7.56 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 15.75 (d), 67.44 (d) and $^3J_{P1P2}$ 41.39 (Found: C, 50.73; H, 5.45. $C_{22}H_{29}ClO_6P_2S$ requires C, 50.91; H, 5.64%).

***cis*-2-(α-Diethoxyphosphoryl-4-methylbenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-selone *cis*-7e.** White solid, mp 71–72 °C, ν_{max}(KBr)/cm^{-1} 3330, 3025, 2880, 1612, 1599, 1487, 1448 (s), 1360, 1255 (s, P=O), 1077, 1025, 975 (s, P–O–C), 784 (s), 731, 697 (s) and 550 (s, P=Se); δ_H(200 MHz; $CDCl_3$) 0.83 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 1.19–1.30 (m, 6 H, 2 CH_3), 2.31 (s, 3 H, CH_3), 3.72–4.50 (m, 6 H, 3 CH_2), 5.33 (d, 1 H, CH, *J* 3.14), 6.08 (dd, 1 H, CH, *J* 13.56) and 7.04–7.58 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 16.13 (d), 73.09 (d) and $^3J_{P1P2}$ 44.33; *m*/*z* 546 (M^+, 6.6%), 402 (0.4), 372 (1.6), 294 (5.8), 241 (17.6), 213 (42.6), 145 (12.2), 121 (14.1), 105 (100), 91 (17.1), 65 (11.0) (Found: C, 50.86; H, 5.77. $C_{23}H_{32}O_6P_2Se$ requires C, 50.64; H, 5.92%).

***trans*-2-(α-Diethoxyphosphoryl-4-methylbenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane-2-selone *trans*-7e.** Colourless syrup, ν_{max}(film)/cm^{-1} 3228, 3020, 2880, 1610, 1596, 1489, 1448 (s), 1392, 1250 (s, P=O), 1080, 1024, 980 (s, P–O–C), 783 (s), 732, 696 (s) and 558 (s, P=Se); δ_H(200 MHz; $CDCl_3$) 0.79 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 1.19–1.31 (m, 6 H, 2 CH_3), 2.35 (s, 3 H, CH_3), 3.76–4.50 (m, 6 H, 3 CH_2), 5.39 (d, 1 H, CH, *J* 3.12), 6.08 (dd, 1 H, CH, *J* 13.56) and 7.06–7.60 (m, 9 H, C_6H_5 and C_6H_4); δ_P(80.96 MHz; $CDCl_3$) 15.84 (d), 72.20 (d) and $^3J_{P1P2}$ 43.32 (Found: C, 50.92; H, 5.65. $C_{23}H_{32}O_6P_2Se$ requires C, 50.64; H, 5.92%).

***cis*-2-(α-Diethoxyphosphorylbenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-phosphorinane-2-selone *cis*-7f.** White solid, mp 96–97 °C, ν_{max}(KBr)/cm^{-1} 3390, 3105, 2966, 1608, 1490, 1466 (s), 1393, 1256 (s, P=O), 1058, 1020, 978, 922 (s, P–O–C), 735, 698 (s) and 556 (s, P=Se); δ_H(200 MHz; $CDCl_3$) 0.81 (s, 3 H,

CH_3), 0.97 (s, 3 H, CH_3), 1.18–1.28 (m, 6 H, 2 CH_3), 3.68–4.50 (m, 6 H, 3 CH_2), 5.33 (d, 1 H, CH, *J* 3.14), 6.09 (dd, 1 H, CH, *J* 13.56) and 6.96–7.58 (m, 10 H, 2 C_6H_5); δ_P(80.96 MHz; $CDCl_3$) 15.98 (d), 73.24 (d) and $^3J_{P1P2}$ 43.88 (Found: C, 49.90; H, 5.53. $C_{22}H_{30}O_6P_2Se$ requires C, 49.71; H, 5.70%).

***trans*-2-(α-Diethoxyphosphorylbenzyloxy)-4-phenyl-5,5-dimethyl-1,3,2λ^5-phosphorinane-2-selone *trans*-7f.** Colourless syrup, ν_{max}(film)/cm^{-1} 3389, 3103, 2961, 1600, 1490, 1462 (s), 1366, 1250 (s, P=O), 1056, 1018, 978, 920 (s, P–O–C), 734, 698 (s) and 562 (s, P=Se); δ_H(200 MHz; $CDCl_3$) 0.78 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 1.17–1.28 (m, 6 H, 2 CH_3), 3.70–4.50 (m, 6 H, 3 CH_2), 5.40 (d, 1 H, CH, *J* 3.12), 6.09 (dd, 1 H, CH, *J* 13.56) and 6.96–7.58 (m, 10 H, 2 C_6H_5); δ_P(80.96 MHz; $CDCl_3$) 15.68 (d), 72.20 (d) and $^3J_{P1P2}$ 42.02 (Found: C, 49.47; H, 5.58. $C_{22}H_{30}O_6P_2Se$ requires C, 49.71; H, 5.70%).

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