Synthesis and Structure of Sulphur Derivatives of a Methylenephosphine

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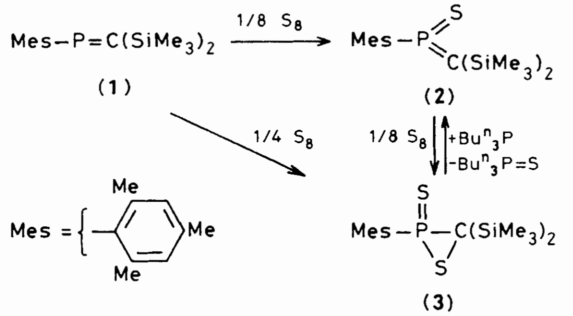
The methylenephosphine MesP=C(SiMe$_3$)$_2$ [(**1**) Mes = mesityl] is smoothly oxidized by elemental sulphur to the 3-membered ring system MesP(=S)–S–C(SiMe$_3$)$_2$, (**3**), which, upon treatment with Bu$^n{}_3$P, is converted into the 3-co-ordinate phosphorane MesP(=S)=C(SiMe$_3$)$_2$, (**2**); the nearly isostructural nature of compounds (**2**) and (**3**) is confirmed by their *X*-ray crystallographic analyses.

There has been considerable interest recently in π-bonded phosphorus compounds such as the methylenephosphines and their related oxidation products.[1,2] We report here the synthesis and the crystal structure analyses of the products of the oxidation of mesityl[bis(trimethylsilyl)methylene]phosphine, (**1**),[3] by elemental sulphur.

Treatment of (**1**) with one equivalent of sulphur resulted in an inseparable mixture of the methylene(thioxo)phosphorane (**2**), the thiaphosphirane (**3**), and starting material (**1**). Addition of a second equivalent of sulphur afforded complete conversion of the mixture into (**3**). A pure sample of (**2**) was then obtained by the reaction of (**3**) with Bu$^n{}_3$P.† ^{1}H and ^{13}C n.m.r. data for (**2**) and (**3**) are in Table 1.



Compound (**2**) represents a stable analogue of the proposed intermediate, [(*o*-Me)$_2$C$_6$H$_3$]P(=S)=CPh$_2$[2b] (^{31}P n.m.r. δ 140.6 p.p.m.),[4] in the oxidation of methylenephosphines by sulphur. Stable, non-crystalline analogues of both (**2**) and (**3**), R$_2$N–P(=S)=CHR and R$_2$N-P(=S)–S–CHR (R = Me$_3$Si), have been prepared by Niecke and Wildbredt[2a] using a similar procedure. The crystal structure of (**3**) is the first for a P–C–S

Table 1. N.m.r. spectroscopic data.[a,b]

Compd.	Signal	^{1}H N.m.r. δ	^{13}C N.m.r. δ	^{13}C N.m.r. J_{PC}
(2)	Me$_3$Si	−0.22	2.11	
		0.39	2.56	
	P–C		126.00	34.2
	o-Me	2.23	22.50	7.3
	p-Me	2.51[d]	21.48	
(3)	Me$_3$Si	−0.26	0.14	3.1
		0.38	1.66	3.4
	P–C		26.39	8.6
	o-Me[c]	2.66[e]	22.76	4.3
		2.57[f]	22.19	5.5
	p-Me	2.20	21.15	1.2

[a] Chemical shifts downfield from Me$_4$Si; coupling constants in Hz. Solvents: ^{1}H, CH$_2$Cl$_2$; ^{13}C, CDCl$_3$. [b] Data for phenyl signals to be published.[3] [c] Non-equivalent *o*-Me groups due to hindered rotation about P–C(ring) bond. [d] *J*(P–H) 1.5 Hz. [e] *J*(P–H) 1.5 Hz. [f] *J*(P–H) 1.1 Hz.

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† ^{31}P N.m.r. (CDCl$_3$) (**2**), δ 190.9 p.p.m.; (**3**), δ 2.6 p.p.m. (downfield from H$_3$PO$_4$).

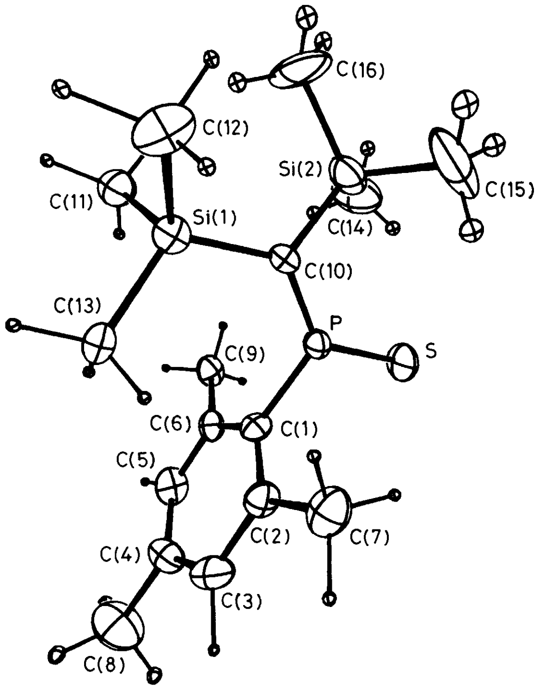

Figure 1. Molecular structure of (**2**): Mes-P(=S)=C(SiMe$_3$)$_2$. Principal bond lengths Å and angles ° are: P=S 1.925(4), P=C(10) 1.647(9), P–C(1) 1.80(1), Si(1)–C(10) 1.88(1), Si(2)–C(10) 1.89(1), S–P–C(1) 113.1(3), S–P–C(10) 127.8(4), C(1)–P–C(10) 119.0(5), P–C(10)–Si(1) 123.8(6), P–C(10)–Si(2) 115.8(6), Si(1)–C(10)–Si(2) 120.2(5). Thermal ellipsoids in both figures drawn at the 35% probability level.

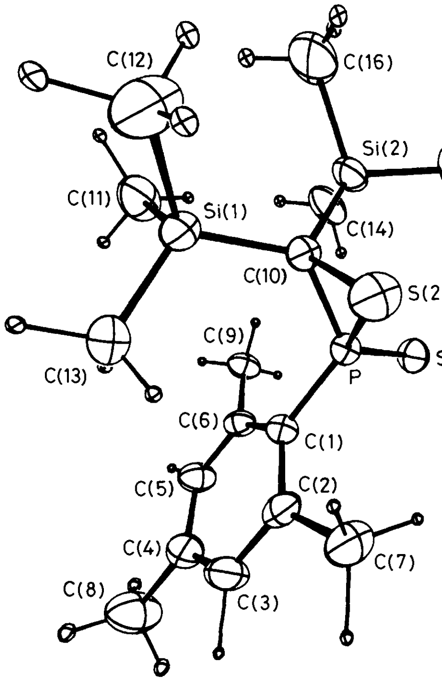

Figure 2. Molecular structure of (**3**): Mes-P(=S)-S-C(SiMe$_3$)$_2$. Principal bond lengths Å and angles ° are: P=S(1) 1.932(3), P–S(2) 2.049(3), P–C(10) 1.795(7), P–C(1) 1.793(7), S(2)–C(10) 1.918(8), Si(1)–C(10) 1.920(8), Si(2)–C(10) 1.918(7), S(1)–P–C(1) 112.7(2), S(1)–P–C(10) 123.2(3), C(1)–P–C(10) 116.3(3), P–C(10)–Si(1) 123.4(4), P–C(10)–Si(2) 115.8(4), Si(1)–C(10)–Si(2) 117.1(4), S(1)–P–S(2) 121.6(1), S(2)–P–C(1) 113.7(3), S(2)–P–C(10) 59.4(2), P–S(2)–C(10) 53.7(2), P–C(10)–S(2) 66.9(3), S(2)–C(10)–Si(1) 106.4(3), S(2)–C(10)–Si(2) 114.4(4).

three-membered ring system and that of (**2**) is one of the few[5] reported for three-co-ordinate phosphorus(v) compounds.

The molecular structures of (**2**) and (**3**) are shown in perspective views in Figures 1 and 2, respectively. They are, in fact, nearly isostructural‡ with twenty non-hydrogen atoms occuping very similar positions but with no electron density at the S(2) position in (**2**). In compound (**2**), the P=C(10) distance lies just below the lower limit of the range of P=C distances reported for methylenephosphines,[1] 1.68—1.72 Å. The sums of the valence angles subtended by atoms P and C(10) are 359.9 and 359.8°, respectively, confirming sp^2 hybridization at these centres. In contrast, atoms P and C(10) in (**3**) are pyramidallized, lying at 0.42 and 0.36 Å, respectively, above the plane of their four bonded atoms (coplanar to within 0.04 Å) in the direction of S(2).

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‡ *Crystal data* for (**2**): a = 17.539(3), b = 13.393(2), c = 8.934(2) Å, U = 2077.1(7) Å^3, orthorhombic, space group $Pn2_1a$ (standard setting $Pna2_1$), D_c = 1.089 g cm^{-3} for Z = 4, μ(Cu-K_α) = 3.02 mm^{-1}, F(000) = 736.0. *Crystal data* for (**3**): a = 17.455(4), b = 13.756(4), c = 8.973(2) Å, U = 2154.5(9) Å^3, orthorhombic, space group $Pn2_1a$, D_c = 1.149 g cm^{-3} for Z = 4, μ(Cu-K_α) = 3.80 mm^{-1}, F(000) = 800.0. Intensity data for (**2**) and (**3**) were collected at 293 K from spherically-ground crystals (average radii 0.133, 0.125 mm) mounted on a Syntex P2$_1$ automatic diffractometer employing Cu-K_α radiation. The space group was deduced from systematic absences and intensity statistics. The structure of (**3**) was determined by direct methods. Similarity in morphology, cell dimensions, and the common space group indicated close correspondence between the two molecular structures and their crystal packing. For (**2**), the positions of P, S(1), Si(1), and Si(2) of (**3**) were accordingly used to phase difference Fourier syntheses from which the remaining atoms of (**2**) were located. Both structures were refined by blocked-matrix least-squares methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. H atoms were included at geometrically constrained positions (C–H 1.08 Å) based on those found in difference maps, with fixed isotropic thermal parameters equal to those of their parent atoms. Final R factors were R = 0.061, R_w = 0.064 for (**2**) (1209 unique reflexions) and R = 0.045, R_w = 0.047 for (**3**) (1269 unique reflexions). Since the space group is non-centrosymmetric and anomalous dispersion corrections were applied to the S, P, and Si scattering factors, it was necessary to test the absolute configurations of the crystals chosen for analysis. Significance tests based on Hamilton's R-ratio indicated that the crystals of (**2**) and (**3**) chosen had opposite chirality. The deposited fractional co-ordinates reflect this difference. Enantiomers of (**2**) and (**3**) with the same chirality are illustrated in the Figures to emphasize the similarity between the molecular structures.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.