Synthesis and Structure of a Phosphagermirene

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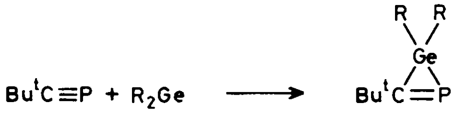
The first phosphagermirene has been prepared *via* the reaction of the phospha-alkyne $Bu^tC{\equiv}P$ with the germylene $\{(Me_3Si)_2CH\}_2Ge$.

Recently it has been demonstrated that phospha-alkynes ($RC{\equiv}P$) will add carbene[1] and silylene[2] moieties to afford phosphirenes and phosphasilirenes, respectively. However, structural information is only available for the $W(CO)_5$ adducts of these interesting compounds. We report (i) synthesis of the first phosphagermirene, and (ii) the first *X*-ray structural data for this type of ring system.

In a typical reaction, GeR_2 [R = $(Me_3Si)_2CH$][3] (1.0 mmol) in n-hexane (50 ml) was treated with $Bu^tC{\equiv}P$[4] (1.5 mmol) in 1,2-dimethoxyethane at 25 °C. The colour of the mixture changed immediately from orange to yellow. The solvent and excess of $Bu^tC{\equiv}P$ were removed by evacuation and the residue was recrystallised from toluene to afford an 80% yield of yellow, crystalline 2,2-di[bis(trimethylsilyl)methyl]3-t-butylphosphagermirene (**1**) (m.p. 89—91 °C).

The ^{31}P n.m.r. chemical shift for (**1**)† falls in the region expected for P=C.[5] Moreover, integration of the ^1H n.m.r. signals reveals (a) a 2 : 1 ratio of $(Me_3Si)_2CH$ and Bu^t groups, and (b) that there are two environments for the Me_3Si groups.

The structure of (**1**) was confirmed by *X*-ray analysis (Figure 1).‡ Note that there are two independent molecules per



(**1**)

R = $(Me_3Si)_2CH$

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† N.m.r. spectra recorded at ambient temperature relative to 85% H_3PO_4 (^{31}P) or Me_4Si (^1H and ^{13}C): $^{31}P\{^1H\}$ n.m.r. (n-hexane; 121.5 MHz) δ +315(s); ^1H n.m.r. (C_6D_6; 300 MHz) δ 1.43 (s, 9H, Bu^t), 1.2 (s, 18H, Me_3Si), and 1.7 (s, 18H, Me_3Si); $^{13}C\{^1H\}$ n.m.r. (C_6D_6; 75.4 MHz) δ 3.0 (s, Me_3Si), 3.4 (s, Me_3Si), 10.88 [s, $CH(SiMe_3)_2$], 31.73 [d, $^3J_{PC}$ 7.5 Hz, $C(CH_3)_3$], and 44.24 [d, $^2J_{PC}$ 1.5 Hz, $C(CH_3)_3$].

‡ *Crystal data* for (**1**): $C_{19}H_{47}GePSi_4$, $M = 491.49$, monoclinic, $P2_1/n$ (No. 14), $a = 23.074(5)$, $b = 12.548(3)$, $c = 23.235(5)$ Å, $\beta = 118.74(2)°$, $U = 5897.9$ Å^3, $Z = 8$, $D_c = 1.107$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 12.4$ cm^{-1}; 7693 unique reflections measured with an Enraf-Nonius CAD-4 diffractometer over the range $3.0 \leqslant 2\theta \leqslant 45.0°$ ($\theta/2\theta$ scan mode). Anisotropic decay and empirical absorption corrections were made. The structure was solved by direct methods and refined (difference Fourier; full matrix least-squares) using 4050 reflections with $I > 3.0\sigma(I)$. The final residuals were $R = 0.0515$ and $R_w = 0.0617$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

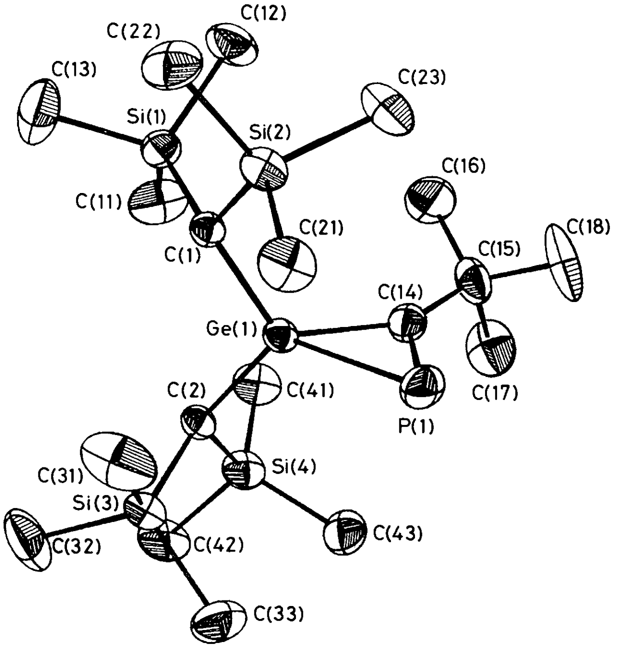

Figure 1. View (ORTEP) of (**1**) showing the atom numbering scheme for molecule 1. Important lengths (Å) and angles (°): molecule 1, Ge(1)–P(1) 2.298(4), Ge(1)–C(14) 1.932(11), P(1)–C(14) 1.661(11), P(1)–Ge(1)–C(14) 45.2(3), Ge(1)–P(1)–C(14) 55.7(4), Ge(1)–C(14)–P(1) 79.1(5); molecule 2, Ge(2)–P(2) 2.291(4), Ge(2)–C(24) 1.928(11), P(2)–C(24) 1.678(11), P(2)–Ge(2)–C(24) 45.9(3), Ge(2)–P(2)–C(24) 55.6(4), Ge(2)–C(24)–P(2) 78.6(4).

asymmetric unit. The average phosphorus–carbon bond distance [1.669(11) Å] is indicative of a bond order of two[5]; hence (**1**) may be considered to be isolobal[6] with cyclopropene. The P–Ge distance [average 2.294(4) Å] is similar to those observed in the diphosphagermirane, $Et_2Ge(PBu^t)_2$ [2.301(2) and 2.300(2) Å].[7] There are, however, significant differences in the intra-ring angles, the largest being P–C–Ge [average 78.8(5)°]. Finally, it is clear from the structure that the Me_3Si group non-equivalence results from diastereotopy.

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