

From Germaphosphene to Germaphosphetene

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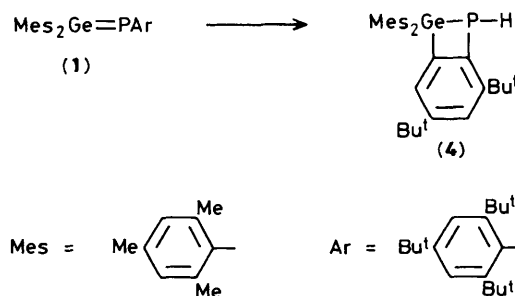
Thermolysis of the germaphosphene (1) affords nearly quantitatively the germaphosphetene (4), which is the first stable four-membered heterocycle with a Ge–P–C linkage; its structure has been determined by X-ray crystallography.

Interest in multiple bonding between the heavier Main-group elements [particularly from Group 14 (Si, Ge, Sn) and 15 (P, As)] has been very considerable during the last few years.¹

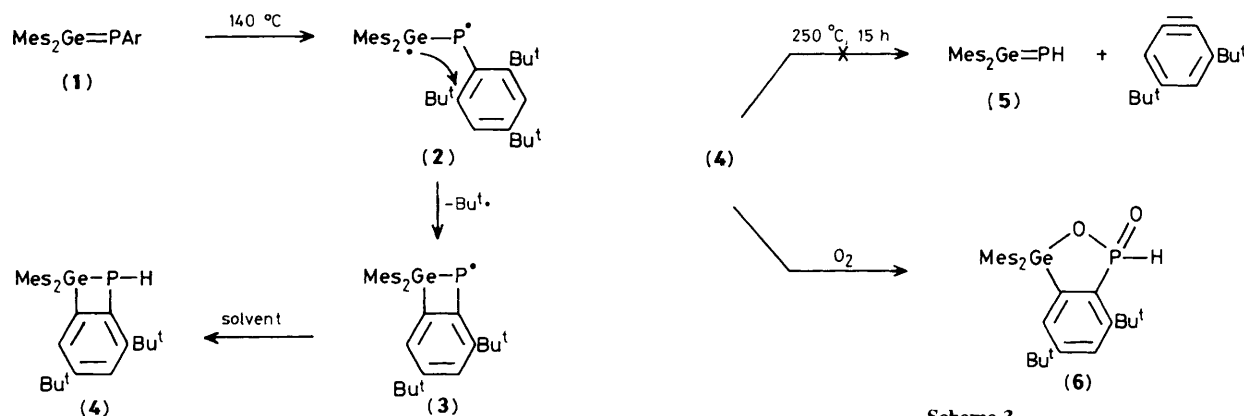
Judicious choice of sterically-demanding ligands has permitted the synthesis of stable compounds containing Si=P,² Ge=P,³ and Sn=P⁴ double bonds; the reactivity of such species is still relatively unexplored.

We now report the thermolysis of (1), leading to the first stable germaphosphetene (4).

Unlike its silaphosphene isologue² or the stannaphosphene [(Me₃Si)₂CH]₂Sn=PBu^t₃C₆H₂,⁴ the germaphosphene (1) is thermally very stable and can be recovered unchanged after heating for two days at 100 °C. A noteworthy thermochromism has been observed: (1) is yellow at –100 °C, orange



Scheme 1. Conditions: 140 °C, 40 h, C₆H₆ (–Me₂C=CH₂).



Scheme 3

at room temperature, and orange-red at +100 °C; a similar phenomenon has been observed in other double-bonded species such as $R_2N=P=P-NR_2$,⁵ $Mes_2Si=SiMes_2$,^{1a} and even $(R_3Si)_2C=C(SiR_3)_2$.⁶

Thermolysis of (1) in benzene in a sealed tube, at 140 °C, was continued until complete decoloration of the starting orange-red solution (about 40 h). Removal of the solvent under reduced pressure and crystallization of the crude product from pentane afforded white crystals of (4) (Scheme 1).

The structure of (4) follows from its n.m.r., i.r., and mass spectroscopic data† and also from an X-ray structure determination. The X-ray analysis‡ shows an essentially planar four-membered heterocycle (torsion angles <5°), with classical Ge-C (1.962 Å), Ge-P (2.354 Å), and P-C (1.856 Å) bond lengths. The C-C bond of the four-membered heterocycle (1.391 Å) has a length typical for a C-C bond in a phenyl

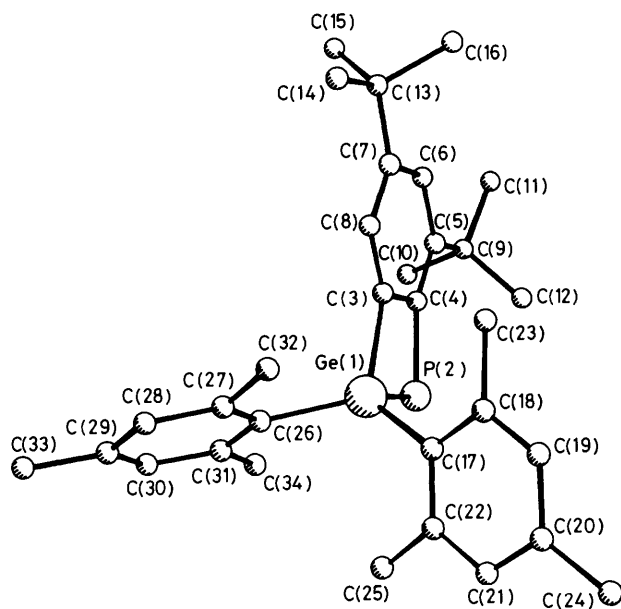


Figure 1. Molecular structure of one of two crystallographically independent molecules of (4). Principal distances (Å), angles (°) and torsion angles (°) for both molecules which have very similar data are: Ge-P: 2.354(3)/2.369(3), Ge-C(3): 1.962(9)/1.953(8), Ge-C(17): 1.975(7)/1.991(10), Ge-C(26): 1.976(9)/1.991(9), P-C(4): 1.856(10)/1.856(3), C(4)-C(3): 1.391(11)/1.392(12), C(4)-C(5): 1.408(12)/1.407(13), C(3)-C(8): 1.377(14)/1.376(10), C(3)-Ge-P: 75.0(0.3)/74.9(0.3), Ge-P-C(4): 75.6(0.3)/75.2(0.3), P-C(4)-C(3): 108.2(0.6)/108.5(0.6), C(4)-C(3)-Ge: 100.9(0.7)/101.3(0.5), C(17)-Ge-C(26): 111.9(0.3)/112.6(0.4), C(3)-Ge-C(17): 119.9(0.4)/119.3(0.4), C(26)-Ge-P: 121.8(0.3)/121.0(0.3), C(8)-C(3)-Ge: 136.8(0.6)/136.0(0.7), C(5)-C(4)-P: 131.4(0.6)/131.2(0.6), C(17)-Ge-P: 109.8(0.3)/111.1(0.3), C(3)-C(4)-C(5): 120.9(0.9)/120.2(0.7), C(8)-C(3)-C(4): 122.3(0.8)/122.6(0.8), C(3)-Ge-P-C(4): 3/1, P-Ge-C(3)-C(4): -4/-2, Ge-C(3)-C(8): 180/-178, Ge-C(3)-C(4)-C(5): -179/180.

group. The Ge-P-C (75.6°) and P-Ge-C (75.0°) angles are very small.

The formation of (4) may be explained by a radical process involving the preliminary formation of (3) by intramolecular radical aromatic substitution in the biradical (2) formed at 140 °C, followed by an abstraction of hydrogen from the solvent (C_6H_6) (Scheme 2).

A similar aromatic substitution involving a silylated radical has been described recently by Ishikawa in the thermolysis of disilacyclopropanes.⁷

† (4): m.p. 128–130 °C; n.m.r. data: 1H (C_6D_6 , int. $SiMe_4$) δ 1.32 (s, 9H, Bu^t), 1.57 (s, 9H, Bu^t), 2.12 (s, 3H, *p*-Me), 2.13 (s, 3H, *p*-Me), 2.47 (s, 6H, *o*-Me), 2.63 (s, 6H, *o*-Me), 5.12 [d, $^1J(PH)$ 165.0 Hz, 1H, PH], 6.73 (broad s, 4H, ArH, Mes), 7.60 [d, $^4J(PH)$: 2.0 Hz, 2H, ArH, Ar]; ^{31}P (C_6D_6 , 85% H_3PO_4 (δ -70.5 p.p.m. [$^1J(PH)$ 165.0 Hz]; i.r. $\nu(PH)$: 2250 cm^{-1} ; mass spectrum (electron impact, 70 eV): m/z (^{74}Ge): 532.

(6): m.p. 71–73 °C; n.m.r. data: 1H (C_6D_6) δ 1.27 (s, 9H, Bu^t), 1.80 (s, 9H, Bu^t), 2.08 (s, 3H, *p*-Me), 2.12 (s, 3H, *p*-Me), 2.42 (s, 6H, *o*-Me), 2.53 (s, 6H, *o*-Me), 6.65 (s, 2H, ArH, Mes), 6.70 (s, 2H, ArH, Mes), 7.70–7.97 (m, 2H, ArH, Ar), 8.28 [d, $^1J(PH)$: 566 Hz, 1H, PH]; ^{31}P (C_6D_6) +23.0 p.p.m., $^1J(PH)$: 566 Hz; i.r. $\nu(PH)$: 2350 cm^{-1} .

‡ *Crystal data*: (4): crystal dimensions: 0.4 × 0.4 × 0.2 mm, $C_{32}H_{43}GeP$, $M = 530.22$, triclinic, space group $P\bar{1}$, $a = 10.950(9)$, $b = 16.921(12)$, $c = 17.299(17)$ Å; $\alpha = 110.23(7)$, $\beta = 91.70(7)$, $\gamma = 90.61(6)^\circ$; $U = 3005$ Å³, $D_c = 1.17$ g/cm³ for $Z = 4$ (2 independent molecules in the asymmetric unit), 13 815 independent reflections, 5568 'observed,' with $I > 2.5 \sigma(I)$. Data were collected on a Syntex P_2 four-circle diffractometer, with $Mo-K\alpha$ radiation, $\lambda = 0.71069$ Å, to $2\theta = 55^\circ$. A standard reflection measured every 50 reflections showed slow decomposition of the crystal, necessitating a correction of intensity varying between 1.0 (beginning) and 1.25 (end). This can explain the moderate quality of the results. Empirical absorption correction used the Syntex programme (1976).¹⁴ The structure was solved by direct methods (MULTAN 80).¹⁵ Heavy atoms were revealed by Fourier transform. Parameters were refined using least squares (SHELX 76).¹⁶ H in computed position (1.08 Å from carbon). $R = 0.086$, $R_w = 0.080$, $w = 3.3197/[\sigma^2(F) + 0.00097 F^2]$. 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.

Compound (4) is the first stable four-membered heterocycle with the M-P-C linkage (M = Si, Ge); the only known heterocycles of this type, the sila- and germa-phosphetanes $R_2M-P(Ph)CH_2CH_2$ (M = Si,⁸ Ge⁹), are actually in equilibrium with their dimer.

Compound (4) is thermally very stable; it is recovered unchanged after heating at 250 °C for 15 h, and does not give the expected germaphosphene (5) according to the classical decomposition of four-membered organometallic heterocycles. This high stability can be explained by the presence of the aromatic carbon-carbon bond. Such a phenomenon has been observed for example in 1,2-digermacyclobutenes¹⁰ and germacycloprenes¹¹ which are stable whereas 1,2-digermacyclobutanes and germacycloprenes have never been isolated. In phosphorus chemistry some diphosphetenes have been described¹² but diphosphetanes are rare.¹³

The X-ray structure displays no steric hindrance round the phosphorus atom, which is easily approachable. So (4) reacts, for example with oxygen, to afford quantitatively the phosphinate (6) (Scheme 3).†

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