From Germaphosphene to Germaphosphetene

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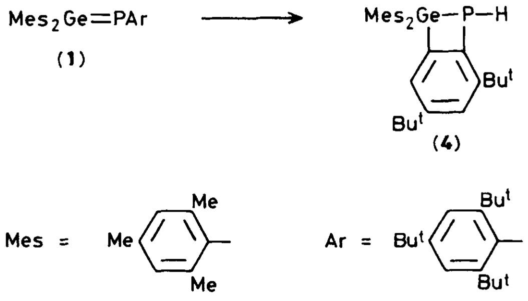
Thermolysis of the germaphosphene (**1**) affords nearly quantitatively the germaphosphetene (**4**), which is the first stable four-membered heterocycle with a Ge–P–C linkage; its structure has been determined by *X*-ray crystallography.

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]

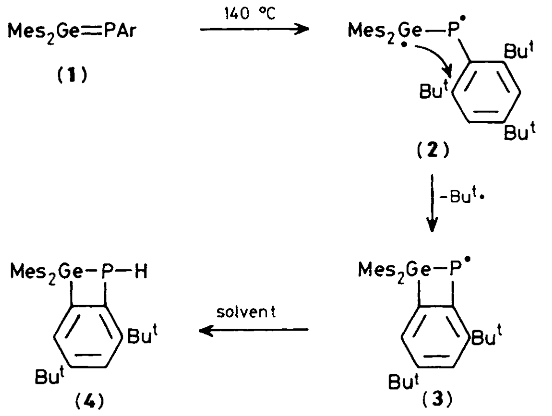
Judicious choice of sterically-demanding ligands has permitted the synthesis of stable compounds containing Si=P,[2] Ge=P,[3] and Sn=P[4] double bonds; the reactivity of such species is still relatively unexplored.

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

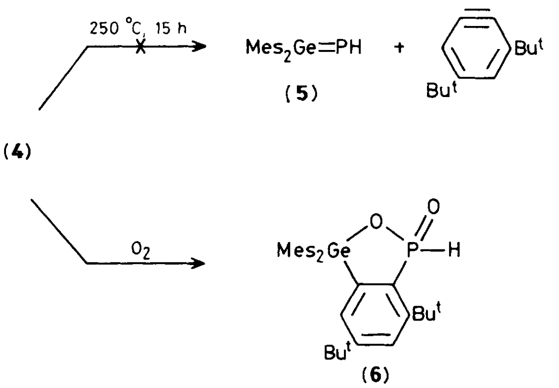
Unlike its silaphosphene isologue[2] or the stannaphosphene $[(Me_3Si)_2CH]_2Sn{=}PBu^t{}_3C_6H_2$,[4] the germaphosphene (**1**) is thermally very stable and can be recovered unchanged after heating for two days at 100 °C. A noteworthy thermochromism has been observed: (**1**) is yellow at −100 °C, orange



Scheme 1. *Conditions:* 140 °C, 40 h, C_6H_6 ($-Me_2C{=}CH_2$).



Scheme 2



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

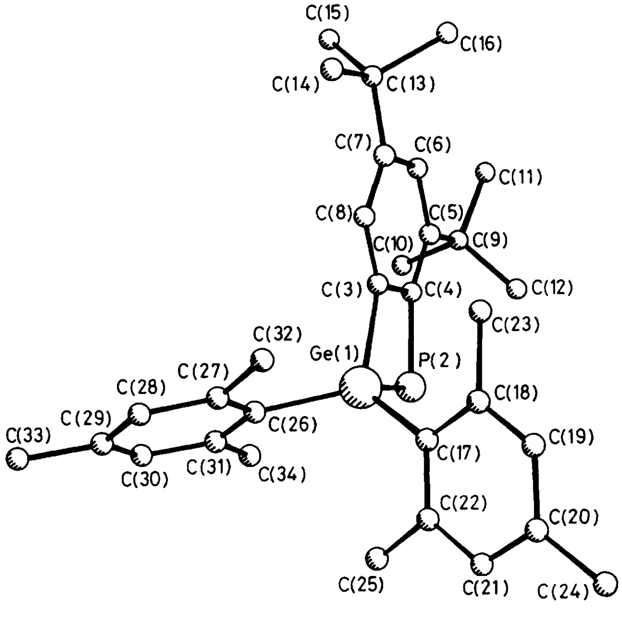


Figure 1. Molecular structure of one of two crystallographically independent molecules of (**4**). Principal distances (Å), angles (°) and torsion angles (°) for both molecules which have very similar data are: Ge–P: 2.354(3)/2.369(3), Ge–C(3): 1.962(9)/1.953(8), Ge–C(17): 1.975(7)/1.991(10), Ge–C(26): 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)–C(7): 180/–178, Ge–C(3)–C(4)–C(5): –179/180.

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]

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† (**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. ν(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. ν(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; $\alpha = 110.23(7)$, $\beta = 91.70(7)$, $\gamma = 90.61(6)$°; $U = 3005$ Å^3, $D_C = 1.17$ g/cm^3 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 $P2_1$ four-circle diffractometer, with Mo-K_α radiation, $\lambda = 0.71069$ Å, to $2\theta = 55°$. 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 $R_2\overline{M-P(Ph)CH_2C}H_2$ (M = Si,[8] Ge[9]), 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-digermacyclobutenes[10] and germacyclopropenes[11] which are stable whereas 1,2-digermacyclobutanes and germacyclopropanes have never been isolated. In phosphorus chemistry some diphosphetenes have been described[12] 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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