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Reaction of a Stable Phosphinocarbene with Germane- and Stannanediyls: Evidence for *C*-Phosphanylgerma- and *C*-Phosphanylstannaethene to *C*-Germyl- and *C*-Stannylphosphaalkene Rearrangements

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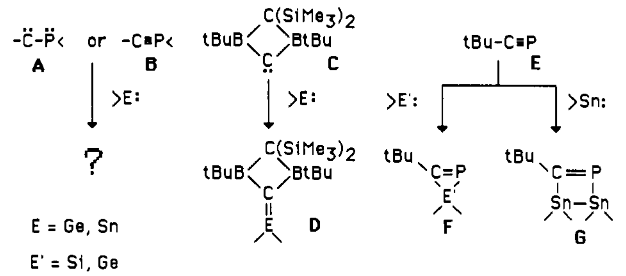
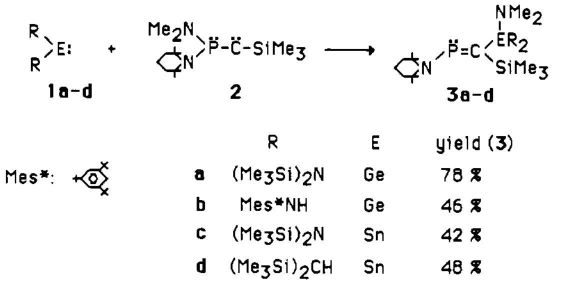
Introduction

Recently, the synthesis of stable "carbene-like" species has been reported.[1-3] We have shown that, depending on the nature of the reagents, phosphinocarbenes can react either as "classical" carbenes A or λ^5-phosphaacetylenes B.[1] The carbene C from Berndt et al.[3] reacts with germane-[4a,b] and stannanediyls[4b,c] leading to stable germa- and stannaethenes D. On the other hand, it has been demonstrated that *tert*-butyl-λ^3-phosphaacetylene (E) undergoes a 2 + 1 cycloaddition with carbenes,[5] silanediyls,[6] and germanediyls[7] affording three-membered rings containing a phosphorus–carbon double bond, F. According to Cowley et al.,[8] bis[bis(trimethylsilyl)amino]stannanediyl (**1c**)[9] does not react with E, while the isoelectronic $[(Me_3Si)_2CH]_2Sn$ (**1d**), which is in equilibrium with its dimer in solution,[10] gives rise to the corresponding phosphadistannacyclobutene G (Scheme I). Thus, a carbene–carbene coupling type reaction or cycloaddition processes can be expected from the reaction of phosphinocarbenes with germane- and stannanediyls leading to metallaethenes or λ^5-phosphacycloalkenes. Here we report the reaction of [(dimethylamino)(2,2,6,6-tetramethylpiperidino)phosphanyl](trimethylsilyl)carbene (**2**)[1d] with the germanium and tin carbene isologues **1a–d**.

Scheme I



Scheme II



	R	E	yield (3)
a	$(Me_3Si)_2N$	Ge	78 %
b	Mes*NH	Ge	46 %
c	$(Me_3Si)_2N$	Sn	42 %
d	$(Me_3Si)_2CH$	Sn	48 %

Results and Discussion

In toluene solution, germanediyls **1a**[9] and **1b**[11] or stannanediyls **1c**[9] and **1d**[10] readily react at room temperature with phosphanylcarbene **2**. According to ^{31}P NMR spectroscopy, these reactions are quantitative. After removal of the solvents, the resulting viscous orange oils were dissolved in hexane and **3a–d** crystallized at −20 °C as pale yellow crystals (Scheme II).

From the spectroscopic data, it was clear that **3a–d** have similar structures. The ^{31}P NMR chemical shifts (**3a**; +457 ppm; **3b**, +446 ppm; **3c**, +438 ppm; **3d**, +406 ppm) demonstrated that the phoshorus atoms were dicoordinated and that none of the expected products (germa- and stannaethenes, or three- or four-membered rings) were obtained. Moreover, in the ^{1}H NMR spectra, the dimethylamino groups always appeared as singlets, showing that they were not bound directly to phosphorus, and for **3c** and **3d**, tin satellites were observed [**3c** 2.78, $^2J(^{117}\text{SnH}) = 43.2$ Hz, $^2J(^{119}\text{SnH}) = 44.8$ Hz; **3d** 2.79, $^2J(^{117}\text{SnH}) = 43.1$ Hz, $^2J(^{119}\text{SnH}) = 44.5$ Hz], proving connectivity to the tin atom. The structure of **3c** has been clearly established by a single crystal X-ray diffraction study. The ORTEP view of the molecule is shown in Figure 1, and the pertinent metric parameters appear in Table I. The SnC(1)Si(1)PN(1) fragment is planar (the atom deviations from the least-squares plane do not exceed 0.014 (4) Å). The PC(1) bond length (1.675 Å) is in the range expected for a phosphorus–carbon double bond.[12] The N(1) atom has a pyramidal configuration, while the N(2), N(3), and N(4) atoms are trigonal-planar. Due to steric effects, the tetrahedral geometry of tin is strongly distorted (bond angles range from 103.5 to 121.3°).

Since we have already shown that phosphinocarbenes react with isonitriles to give the corresponding ketene imines,[1b,d] it is reasonable to rationalize the formation of **3a–d** via the primary formation of germa- or stannaethenes **4**, which result from a carbene–carbene coupling type reaction. A subsequent 1,3-shift of the dimethylamino group from phosphorus to germanium or

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(1) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621. (c) Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853. (d) Gillette, G.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1429. (e) Horchler v. Locquenghien, K.; Baceiredo, A.; Boese, R.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 5062. (f) Dixon, D. A.; Dobbs, K. D.; Arduengo, A. J.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8782. (g) Regitz, M. *Angew Chem., Int. Ed. Engl.* **1991**, *30*, 674.

(2) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(3) Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 826.

(4) (a) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798. (b) Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure Appl. Chem.* **1987**, *57*, 1011. (c) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546.

(5) (a) Wagner, O.; Ehle, M.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 225. (b) Memmesheimer, H.; Al-Dulayymi, J. R.; Baird, M. S.; Wettling, T.; Regitz, M. *Synlett* **1991**, 443.

(6) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 776.

(7) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 753.

(8) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 838.

(9) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Riviere, P.; Riviere-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

(10) (a) Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (c) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Fjelberg, T.; Haaland, A.; Schilling, B. E. R. *Ibid.* **1986**, 2387.

(11) Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, *1587*.

(12) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; p 157.

0020-1669/92/1331-3493$03.00/0

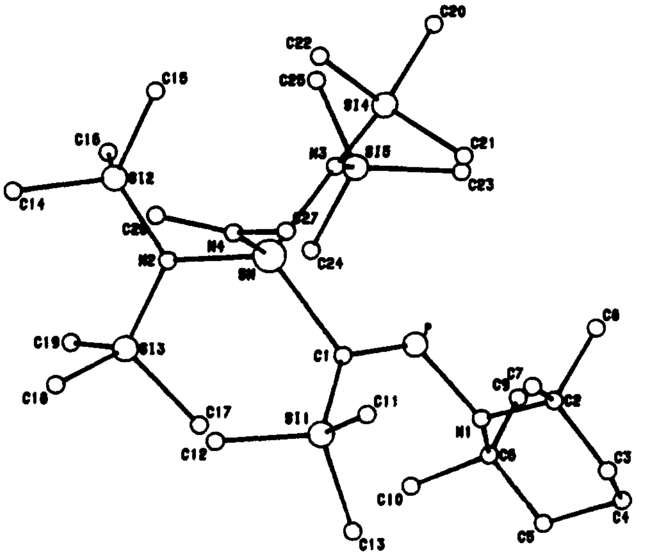
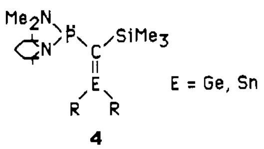


Figure 1. Molecular drawing of 3c.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 3c

Sn–N(2)	2.070 (2)	N(1)–P–C(1)	113.5 (2)
Sn–N(3)	2.080 (2)	Sn–C(1)–P	105.5 (2)
Sn–N(4)	2.013 (3)	Sn–C(1)–Si(1)	122.6 (2)
Sn–C(1)	2.184 (3)	P–C(1)–Si(1)	131.9 (3)
P–N(1)	1.734 (3)	N(2)–Sn–N(3)	106.9 (1)
P–C(1)	1.675 (3)	N(2)–Sn–N(4)	103.6 (2)
C(1)–Si(1)	1.883 (4)	N(2)–Sn–C(1)	121.3 (2)
		N(3)–Sn–N(4)	112.2 (2)
		N(3)–Sn–C(1)	109.2 (1)
		N(4)–Sn–C(1)	103.5 (1)

tin produces **3a–d**. These two reactions are highly chemioselective since we only observed the migration of the smallest phosphorus substituent.



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These results demonstrate, once more, the carbene behavior of phosphinocarbenes and show the reluctance of germanium and tin to be doubly-bonded. Moreover, it is of interest to note that although **2** is thermally very stable, it is quite reactive even with bulky reagents such as **1a–d**.

Experimental Section

All experiments were performed in an atmosphere of dry nitrogen. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Gemini 200 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Melting points are uncorrected.

Preparation of 3a. A toluene solution (5 mL) of phosphinocarbene **2** (0.9 g, 3 mmol) was added dropwise at −30 °C to a toluene solution (5 mL) of bis[bis(trimethylsilyl)amino]germanediyl (**1a**) (1.06 g, 2.7 mmol). The mixture was warmed to room temperature and stirred for 0.5 h. Quantitative formation of **3a** was indicated by ^{31}P NMR spectroscopy. After removal of the solvent, the residue was dissolved in hexane (1.5 mL), and **3a** crystallized at −20 °C as pale yellow crystals (1.46 g, 78% yield). Mp: 132–133 °C. ^1H NMR (C_6D_6): δ 0.45 (br s, 36 H, CH_3SiN), 0.50 (s, 9 H, CH_3SiC), 1.25–1.50 (m, 18 H, CH_3C and CH_2), 2.61 (s, 6 H, CH_3N). ^{13}C NMR (C_6D_6): δ 6.68 (d, J_{PC} = 2.2 Hz, CH_3SiC), 7.73 (d, J_{PC} = 3.5 Hz, CH_3SiN), 18.15 (s, NCC*C*), 27.00 and 37.02 (br s, *C*H$_3$C), 41.61 (s, NC*C*), 42.11 (s, CH_3N), 56.20 (d, J_{PC} = 5.2 Hz, NC), 196.49 (d, J_{PC} = 106.6 Hz, P=C). Anal. Calcd for $C_{27}H_{69}GeN_4PSi_5$: C, 46.74; H, 10.02; N, 8.07. Found: C, 46.58; H, 10.08; N, 8.14.

Preparation of 3b. Using the same experimental procedure as above, except that the toluene solution (5 mL) of carbene **2** (0.60 g, 2 mmol) was added to a toluene solution (10 mL) of bis[(2,4,6-tri-*tert*-butylphenyl)amino]germanediyl (1.01 g, 1.7 mmol) at room temperature, **3b** was obtained as pale yellow crystals (0.70 g, 46% yield). Mp: 125–128 °C. ^1H NMR (C_6D_6): δ 0.32 (s, 9 H, CH_3Si), 1.19 (s, 12 H, $(CH_3)_2C$), 1.20–1.38 (m, 6 H, CH_2), 1.40 (s, 18 H, *p*-tBu), 1.69 (s, 36 H, *o*-tBu), 2.40 (s, 6 H, CH_3N). ^{13}C NMR (C_6D_6): δ 5.00 (d, J_{PC} = 2.7 Hz, CH_3Si), 17.87 (s, NCC*C*), 31.24 (br s, $(CH_3)C$), 31.92 (s, *p*-$(CH_3)_3C$), 33.12 (s, *o*-$(CH_3)_3C$), 34.42 (s, *p*-$(CH_3)_3C$), 37.01 (s, *o*-$(CH_3)_3C$), 41.33 (s, NC*C*), 42.07 (d, J_{PC} = 2.6 Hz, CH_3N), 55.52 (d, J_{PC} = 4.5 Hz, NC), 122.71, 141.86, 143.38, and 143.95 (s, C_{aro}), 188.14 (d, J_{PC} = 102.7 Hz, P=C). Anal. Calcd for $C_{51}H_{93}GeN_4PSi$: C, 68.52; H, 10.49; N, 6.27. Found: C, 68.61; H, 10.38; N, 6.18.

Preparation of 3c. Using the same experimental procedure as above, except that the toluene solution (7 mL) of carbene **2** (1.53 g, 5.1 mmol) was added to an ice-cooled hexane solution (5 mL) of bis[bis(trimethylsilyl)amino]stannanediyl (**1c**) (2.20 g, 5.0 mmol), **3c** was obtained as pale yellow crystals (1.55 g, 42% yield). Mp: 123–124 °C. ^1H NMR (C_6D_6): δ 0.09 (s, 9 H, CH_3SiC), 0.49 (s, 36 H, CH_3SiN), 1.38 (s, 12 H, CH_3C), 1.35–1.44 (m, 6 H, CH_2), 2.78 (s, 6 H, CH_3N). ^{13}C NMR (C_6D_6): δ 5.11 (d, J_{PC} = 3.2 Hz, *C*H$_3$SiC), 7.03 (d, J_{PC} = 2.9 Hz, CH_3SiN), 18.05 (s, NCC*C*), 32.07 (br s, *C*H$_3$C), 41.64 (s, CH_3N), 43.75 (s, NC*C*), 55.98 (d, J_{PC} = 4.4 Hz, NC), 201.70 (d, J_{PC} = 106.0 Hz, P=C). Anal. Calcd for $C_{27}H_{69}N_4PSi_5Sn$: C, 43.83; H, 9.40; N, 7.60. Found: C, 43.64; H, 9.58; N, 7.57.

Preparation of 3d. Using the same experimental procedure as above, **3d** was obtained as pale yellow crystals (48% yield). Mp: 106–108 °C. ^1H NMR (C_6D_6): δ 0.11 (s, 9 H, CH_3Si), 0.24 (s, 36 H, CH_3Si), 1.35–1.46 (m, 18 H, CH_3C and CH_2), 2.79 (s, 6 H, CH_3N). ^{13}C NMR (C_6D_6): δ 4.94 (s, *C*H$_3$SiCH), 5.11 (s, *C*H$_3$SiCP), 18.12 (s, NCC*C*), 31.95 (br s, *C*H$_3$C), 32.04 (s, SnCH), 41.71 (s, NC*C*), 45.21 (s, CH_3N), 55.50 (d, J_{PC} = 3.5 Hz, NC), 203.00 (d, J_{PC} = 98.1 Hz, P=C). Anal. Calcd for $C_{29}H_{71}N_2PSi_5Sn$: C, 47.20; H, 9.70; N, 3.80. Found: C, 47.34; H, 9.55; N, 3.73.

Solid-State Structure of 3c. Selected bond distances and angles are reported in Table I. Crystal data: $C_{27}H_{69}N_4PSi_5Sn$, M = 740.0, monoclinic, space group $P2_1/n$, a = 15.372 (6) Å, b = 16.471 (7) Å, c = 15.733 (5) Å, β = 94.12 (3)°, V = 3973.2 Å^3, Z = 4, D_c = 1.24 g cm^{-3}, μ = 8.5 cm^{-1}, $F(000)$ = 1576. Crystallographic measurements were made at −90 °C, using the Enraf-Nonius CAD-4 diffractometer, operating in the $\omega/2\theta$ scan mode (the ratio of the scanning rates ω/θ = 1.2). The intensity data were collected within the range $1 \leq \theta \leq 21°$ using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensities of 3991 unique reflections were measured. The structure was solved by heavy-atom methods and refined by full-matrix least squares in the anisotropic approximation (343 variables, weighting scheme $w = 1/[\sigma^2(|F_o|) + 0.0016|F_o|^2]$). In the refinement, 3543 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were located in the difference Fourier maps and included in the final refinements with the fixed positional and thermal parameters. Convergence was obtained at R = 0.035 and R_w = 0.054. Corrections for the Lorentz and polarization effects, but not for absorption, were applied.

Supplementary Material Available: Complete listing of bond distances and angles, torsional angles, positional parameters, and general anisotropic displacement parameters expressions (10 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.