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Molecular Structures of New Compounds with Ge = C and Sn = C Double Bonds [1]

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ABSTRACT: *Addition reactions of the diarylgermylene R_2Ge: ($R = 2$-tBu-4,5,6-Me_3C_6H) and the heteroleptic stannylene RR′Sn: ($R' = Si(SiMe_3)_3$) to the cryptodiborylcarbene $(Me_3Si)_2C(tBuB)_2C$: furnish the germaethene $(Me_3Si)_2C(tBuB)_2C{=}GeR_2$ (***8***) and the stannaethene $(Me_3Si)_2C(tBuB)_2C{=}SnRR'$ (***12***), respectively. The X-ray structure analysis of* **8** *reveals a twisting of the Ge = C double bond with torsion angles of 33 and 34°. In addition to a slight twisting of the double bond (average torsion angle = 11.9°), compound* **12** *shows a trans-bending of the substituents with bent angles of 13.2° at the tin and 9.7° at the carbon atom of the Sn = C double bond.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 554–558, 1999

INTRODUCTION

Although stable germenes (germaethenes) and stannenes (stannaethenes), which are molecules containing Ge = C and Sn = C double bonds, respectively, have been known since 1987 and have in the meantime revealed some interesting chemistry [2,3], structurally characterized members of these classes of compounds are still very rare. The germenes include the diarylgermene **1** [4a,b] and the diaminogermene **2** [5a–c]. The latter must be included in the group of donor-stabilized molecules because of its free electron pairs on the nitrogen atoms. Structurally characterized stannenes are equally rare; only for compounds **3** [6a,b] and **4** [7] have the structures been confirmed unequivocally. In addition, the molecules resulting from the reactions of nucleophilic carbenes of the Arduengo type with germanium diiodide [8], diarylstannylene [9], or tin(II) chloride [10] contain formal element–carbon double bonds. Because of their large E–C bond lengths and the characteristic bending of the substituents at the Ge or Sn atoms, they must, like the product from the reaction of a diarylstannylene with an isocyanide [11a,b], be considered as Lewis acid–base adducts rather than as double bond systems. See Scheme 1.

The successful syntheses of some new germylenes and stannylenes will broaden the category of germenes and stannenes. We now report on the formation and characterization of two novel compounds obtained by the addition of a diarylgermylene and a heteroleptic stannylene to the electrophilic cryptodiborylcarbene **7**.

RESULTS AND DISCUSSION

We recently prepared the digermene **5** that has a short Ge = Ge double bond length of 225.21(8) pm, which is indicative of a relatively strong Ge–Ge bond and almost planar environments at both germanium atoms. Compound **5** is indeed stable for unlimited

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Dedicated to Professor Alfred Schmidpeter on the occasion of his 70th birthday.

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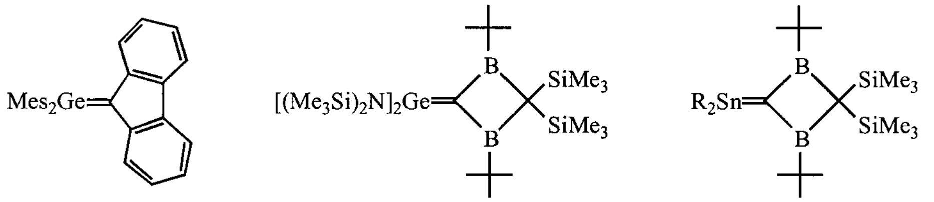
times in the solid state but dissociates into the germylene molecules **6** in solution [12]. Reaction of **6** with the cryptodiborylcarbene **7** [13a–f] in toluene at room temperature furnishes the germene **8** within a few minutes; this product can then be isolated in 62% yield. (See Scheme 2.)

Orange-red single crystals of **8** that were suitable for X-ray crystallography (Figure 1) were finally obtained from *n*-hexane after 30 days at −50°C. Compound **8** crystallizes as two independent molecules, pairs of which occupy the unit cell. The sole symmetry element in both molecules is a C_2 axis passing along the Ge = C double bond. The length of the Ge = C(1) double bond cannot be determined with high precision because of the large standard deviations. However, it is in the same range (about 180 pm) as was observed for the germenes **1** and **2**. Although the bonds are twisted with torsion angles of 33° for the first molecule and 34° for the second molecule, both atoms of the double bond have planar arrangements of their substituents (angular sums at each atom are 360°).

Like the digermene **5**, the stannylenes **9** [14] and **10** [15a,b] exist as distannenes with tin–tin double bonds in the solid state. In solution, however, they both dissociate almost completely to electron-deficient molecules. When solutions of the two stannylenes are mixed, a rapid substituent exchange occurs with formation of the heteroleptic stannylene **11**, which also exists as the heteroleptic distannene in the solid state [16]. The reaction of **11** with the cryptodiborylcarbene **7** proceeds rapidly as seen from the color change from green to light brown. Bundles of yellow crystals of **12** can be isolated from the reaction mixture with a 64% yield at −50 °C. (See Scheme 3.) The preparation of single crystals was difficult at first, but finally, red crystals of **12** (Figure 2) that were suitable for X-ray crystallography were obtained from an *n*-hexane solution after 90 days at −50°C.

In spite of the differing substitution at the tin atom, the Sn = C bond length [203.2(2) pm] is of the same size as those in the stannenes **3** [202.5(4) pm] and **4** [203.2(5) pm]. Conspicuous features are the small torsion angle of merely 12° along the Sn = C axis and the folding of the C_2B_2 ring in which the plane defined by the atoms C(1)–B(1)–C(2) and C(1)–B(2)–C(2) form an angle of 27.5°. The *trans*-bending of the substituents with angles of 13.2° at the tin atom and 9.7° at the carbon atom C(1) is unusual because most theoretical calculations for the parent

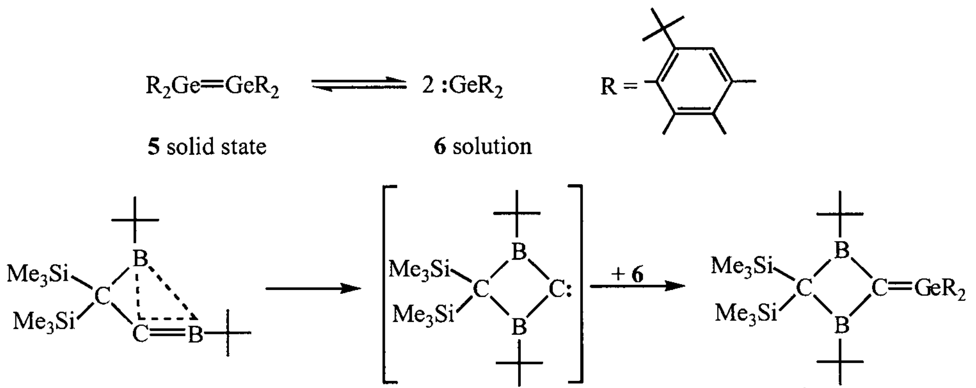


1 Mes = 2,4,6-$Me_3C_6H_2$

2

3 R = $CH(SiMe_3)_2$
4 R = 2-*t*Bu-4,5,6-Me_3C_6H

SCHEME 1



7a **7b** **8**

SCHEME 2

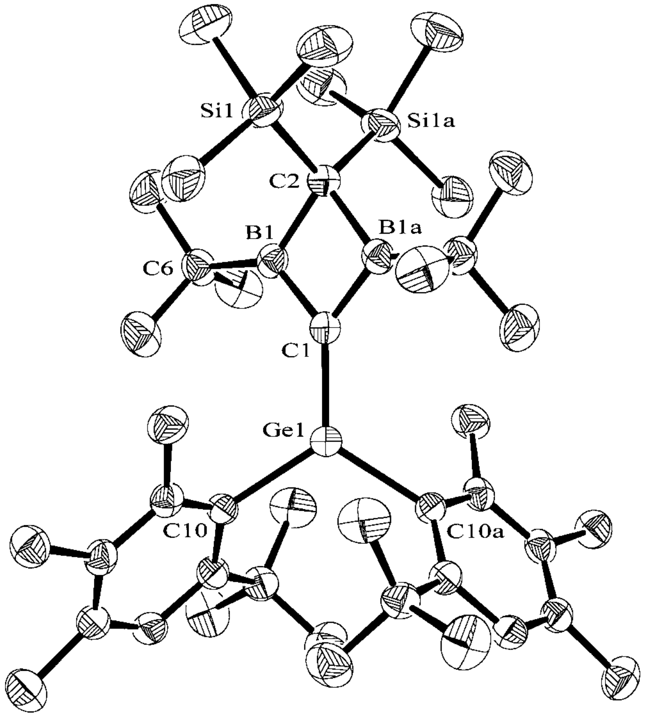


FIGURE 1 Molecular structure of **8** in the crystal (hydrogen atoms omitted, ellipsoids represent the 50% probability level). Only one of the two independent molecules is shown. Selected bond lengths (pm) and angles (deg) for molecule 1 and molecule 2 are as follows. Ge–C(1): 184.5(10), 177.3(14); Ge–C(10): 201.5(3), 201.2(3); B(1)–C(1): 152.6(10), 155.6(13); B(1)–C(2): 163.8(11), 165.0(15); C(1)–Ge–C(10): 122.9(1), 123.8(1); C(10)–Ge–C(10)*: 114.1(2), 112.5(3); B(1)–C(1)–Ge: 137.4(4), 137.6(5); B(1)–C(1)–B(1)*: 85.1(8), 84.7(10); B(1)–C(2)–B(1)*: 78.2(7), 78.9(9).

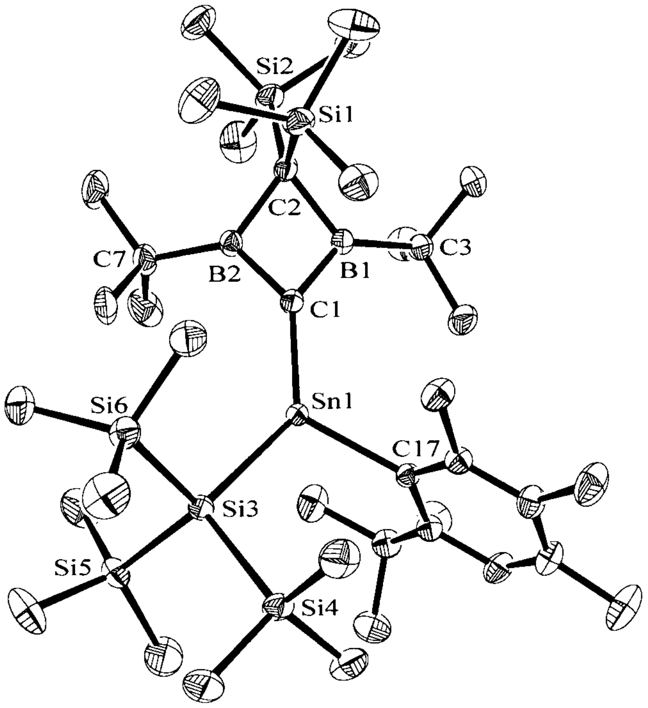
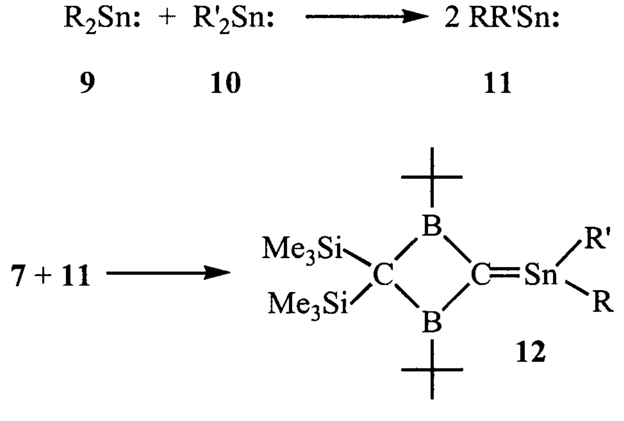


FIGURE 2 Molecular structure of **12** in the crystal (hydrogen atoms omitted, ellipsoids represent the 50% probability level). Selected bond lengths (pm) and angles (deg) are as follows: Sn–C(1), 203.2(2); Sn–C(17), 217.7(2); Sn–Si(3), 262.21(6); C(1)–B(1), 152.3(3); C(1)–B(2), 152.3(3); B(1)–C(2), 163.0(3); B(2)–C(2), 163.0(3); C(1)–Sn–C(17), 120.01(7); C(1)–Sn–Si(3), 132.31(6); C(17)–Sn–Si(3), 105.36(5); B(1)–C(1)–Sn, 139.2(1); B(2)–C(1)–Sn, 137.9(1); B(2)–C(1)–B(1), 81.0(1); B(1)–C(2)–B(2), 70.7(1); Si(1)–C(2)–Si(2), 112.5(1).



R = 2-*t*Bu-4,5,6-Me$_3$C$_6$H, R' = Si(SiMe$_3$)$_3$

SCHEME 3

compound H$_2$Sn=CH$_2$ predict a planar molecule with a C_{2h} symmetry in the minimum [17–19].

EXPERIMENTAL

All manipulations were performed in oven-dried glassware under an atmosphere of dry argon. The ^{1}H, ^{13}C{^{1}H}, and ^{119}Sn NMR spectra were obtained on a Bruker AM 300 spectrometer using C$_6$D$_6$ as solvent. UV/Vis spectra were taken on a ComSpec spectrometer with fiber optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

Formation of the Germene 8

At room temperature, the cryptodiborylcarbene **7** (0.15 g, 0.48 mmol) was added with a syringe to a solution of the germylene **6** (0.20 g, 0.47 mmol) in toluene (25 mL) over a period of 20 minutes with stirring. During this time the color of the solution changed from orange to yellow. The solvent was distilled off, and the oily residue was redissolved in 10 mL of *n*-hexane. Cooling of the solution for 30 days at −50°C afforded 0.21 g (62% yield) of orange-yellow crystals of **8** (m.p. 205°C). Anal. Calcd. for $C_{42}H_{74}B_2GeSi_2$: C, 69.16; H, 10.23. Found: C, 68.58; H, 10.07. ^{1}H NMR: δ 0.56 (s, 18 H), 1.01 (s, 18 H), 1.33 (s, 18 H), 1.90 (s, 6 H), 1.96 (s, 6 H), 2.99 (s, 6 H), 7.06 (s, 2 H). ^{13}C NMR: δ 6.22 (C_p), 15.75 (C_p), 20.98 (C_p), 25.73 (C_p), 28.14 (C_q), 30.62 (C_p), 33.69 (C_p), 37.48 (C_q), 37.86 (C_q), 127.12, 134.58, 138.70, 140.62, 142.17, 150.50, 151.67 (C_p and C_q refer to primary and quaternary carbon atoms). UV/Vis: $\lambda_{max}(\varepsilon)$ 404 (2150).

2-tert-Butyl-4,5,6-trimethylphenyltris-(trimethylsilyl)silylstannylene **11**

A solution of the stannylene **10** (0.43 g, 0.70 mmol) in 50 mL of *n*-hexane was added to the diarylstannylene **9** (0.33 g, 0.70 mmol). The color of the solution changed immediately to blue-green. The solution was stirred for 30 minutes at room temperature, concentrated to a volume of 15 mL and cooled at −18°C for 2 days to furnish 0.29 g (76% yield) of brown-violet crystals of $(\mathbf{11})_2$ (m.p. 115–120°C). Anal. Calcd. for $C_{44}H_{92}Si_8Sn_2$ $(\mathbf{11})_2$. C, 48.79; H, 8.56. Found: C, 48.58; H, 8.59. Spectroscopic data for **11** in solution: ^{1}H NMR: δ 0.37 (s, 27 H), 1.49 (s, 9 H), 1.75 (s, 3 H), 2.13 (s, 3 H), 2.15 (s, 3 H), 7.22 (s, 1 H). ^{13}C NMR: δ 3.91 (C_p), 15.63 (C_p), 21.15 (C_p), 31.62 (C_q), 33.58 (C_p), 38.28 (C_p), 129.27, 132.75, 135.04, 139.39, 153.18, 159.34. ^{119}Sn NMR: δ 1506. UV/Vis (*n*-hexane): λ_{max} (ε) 368 (1960), 643 (3920).

Formation of the Stannene **12**

To a solution of **11** (0.10 g, 0.18 mmol) in 20 mL of benzene was added the cryptocarbene **7** (0.06 g, 0.19 mmol) via a syringe over a period of 30 minutes with stirring. During this time the color of the solution changed from grass-green to brown-yellow. Benzene was distilled off, and the residue was redissolved in 10 mL of *n*-hexane. Cooling of the solution for 90 days at −50°C afforded 0.10 g (64% yield) of yellow crystals of **12** (m.p. 112–115°C, dec.).^{1}H NMR: δ 0.11 (s, 27 H), 0.24 (s, 18 H), 0.26 (s, 18 H), 0.47 (s, 3 H), 1.13 (s, 3 H), 1.21 (s, 3 H), 1.27 (s, 9 H), 7.04 (s, 1 H). ^{13}C NMR: δ 0.04, 1.31, 3.74, 6.60, 21.10, 29.57, 31.63, 31.99, 32.60, 33.60, 129.20, 133.77, 137.39, 138.01, 151.27, 152.43.

Crystallographic Analyses

Crystal and numerical data of the structure determinations are given in Table 1. Data were collected on a Siemens STOE AED 2 (**8**) or STOE IPDS (**12**) diffractometer using graphite monochromated No Kα radiation. The structures were solved by direct phase determination and refined by full-matrix least squares techniques against F^2 with the SHELX 93 program system [20]. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically [21].

TABLE 1 Crystallographic Data for **8** and **12**

	8	**12**
Empirical formula	$C_{42}H_{74}B_2GeSi_2$	$C_{38}H_{91}B_2Si_6Sn$
fw	729.40	856.96
a (pm)	2232.8(17)	1390.36(9)
b (pm)	1360.9(5)	956.71(4)
c (pm)	1834.8(8)	3760.6(3)
β (deg)	126.28(4)	92.146(8)
V ($\times 10^6$ pm^3)	4494	4998.7
Z	4	4
D_{calcd} (g cm^{-3})	1.078	1.139
Crystal size (mm^3)	0.76 × 0.49 × 0.42	0.50 × 0.44 × 0.33
Crystal system	Monoclinic	Monoclinic
Temp (K)	296(2)	193(2)
Space group	*C*2	$P2_1/n$
Data collection mode	ω-scan	–
2θmax (deg)	48	52
No. of refls measd	3679	35125
No. of unique refls	3677	9706
Parameters	403	424
R [$I > 2\sigma(I)$]	0.0501	0.0289
wR2 (all data)	0.1385	0.0762

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[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-115 097 (**8**) and -115 098 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: [internat.] +44-1223/336-093; e-mail: *deposit@ccdc.cam .ac.uk*).