promising new source for bioactive compounds. It would be interesting if the ability of the intracellular symbionts to produce some antimicrobial substances is one of the defense mechanisms of the insects which lack immunological defensive systems.

Acknowledgment. We are grateful to Dr. T. Nakagawa (Ueno Fine Chemical Industries, Ltd.) for MIC studies, to Dr. T. Iwashita and K. Mizukawa (SUNBOR) for NMR measurements, and to Dr. I. Kubota (Suntory Institute for Biomedical Research) for amino acid analyses. Financial assistance via the Special Coordination Fund from the Science and Technology Agency of the Japanese government is gratefully acknowledged.

Supplementary Material Available: Positive and negative EI-MS and proposed fragmentation mechanisms of some predominant ions (1 page). Ordering information is given on any current masthead page.

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The First Stable Germene: A Compound with a Germanium-Carbon Double Bond

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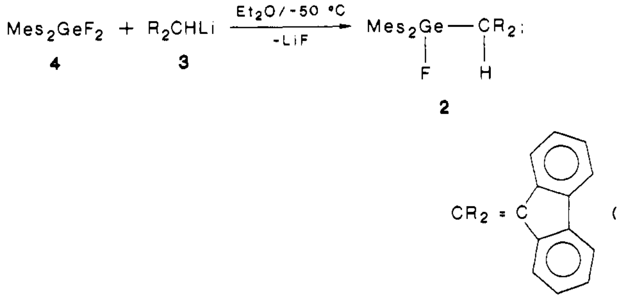
There is now a great deal of interest in group 13, 14, and 15 elements in low coordination states.[1] Since 1981, several new compounds of the type $M{=}M'$ (M and M′: group 13, 14, and 15 elements) with pπ–pπ bonds have been reported. In organogermanium chemistry, the first stable derivatives with a sp^2-hybridized germanium have only been prepared very recently: they are the digermenes $R_2Ge{=}GeR_2$[2] (R = bis(trimethylsilyl)methyl,[2a] 2,6-dimethylphenyl,[2b] 2,6-diethylphenyl[2c]), the germaphosphene $R_2Ge{=}PR'$[3a] (R = mesityl, R′ = 2,4,6-tri-*tert*-butylphenyl), and the germaimines $R_2Ge{=}NR'$[3b] (R = $(Me_3Si)_2N$, R′ = $N{=}C(R'')(R''')$). Germenes $R_2Ge{=}CR_2'$ have long been speculated as reactive intermediates and could only be characterized by trapping reactions.[1c,d,4,5]

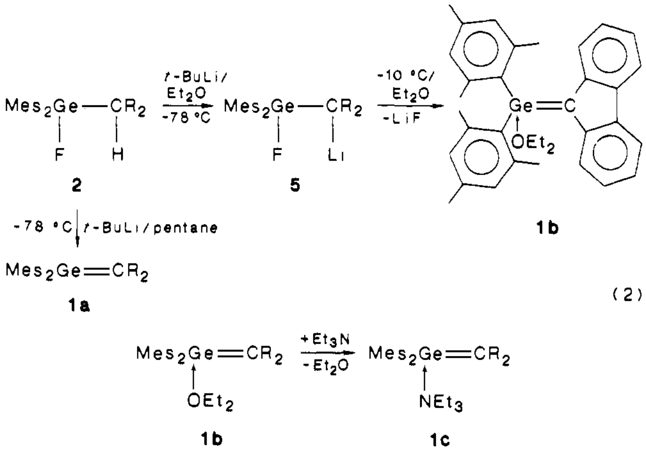
In the present paper we describe the synthesis and some reactions of the first stable compound with a germanium–carbon double bond, the germene **1**. The highly air-sensitive **1** is stabilized owing to large steric hindrance around the double bond and high mesomeric effects; it has been isolated as adducts (**1b**, **1c**, **1d**) with bases and characterized by its physicochemical data and its expected trend in chemical reactivity.

The first step in the synthesis of **1** involves the preliminary preparation of organofluorogermane **2**[6] by addition of the fluorenyllithium **3** (prepared by reacting *n*-butyllithium (1.6 M in hexane) with fluorene) to dimesityldifluorogermane **4**[3]) (eq 1).



(1)

1 was formed by dehydrofluorination of **2** with *tert*-butyllithium: 1 equiv of *t*-BuLi was added to **2** in ethereal solution at −78 °C under nitrogen. A yellow-orange color due to **5** developed immediately. Elimination of LiF occurred at −10 °C to give **1b**,[7] which crystallizes on cooling (eq 2).



(2)

The "free" germene **1a**[7] can be obtained by reacting *tert*-butyllithium with **2** in pentane, but attempts to isolate it in pure form failed because of the presence of unreacted starting material **2** and the formation of hydrogermane **10** as a byproduct. **1a** was characterized in situ as **1b** by quenching with methanol to give **7** (see Scheme I).

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(6) **2**: white crystals, mp 64–65 °C; ^{1}H NMR (C_6D_6) δ 2.03 (s, 6 H, *p*-Me), 2.15 (d, $^5J_{HF}$ = 1.0 Hz, 12 H, *o*-Me), 4.86 (d, $^3J_{HF}$ = 4.4 Hz, 1 H, CH), 6.63 (s, 4 H, aromatic Mes), 6.80–7.86 (m, 8 H, CR_2); ^{19}F NMR −99 (reference CF_3COOH). Anal. Calcd for $C_{31}H_{31}GeF$: C, 75.19; H, 6.31. Found: C, 75.32; H, 6.45.

(7) **1a** ^{1}H NMR (C_6D_6) δ 2.06 (s, 6 H, *p*-Me), 2.20 (s, 12 H, *o*-Me), 6.63 (s, 4 H, aromatic Mes), 6.80–7.96 (m, 8 H, CR_2). **1b**: orange crystals, mp 85–86 °C; ^{1}H NMR (C_6D_6) δ 0.70–1.26 (m, 6 H, OCH_2CH_3), 1.80 (s, 6 H, *p*-Me), 2.30 (s, 12 H, *o*-Me), 2.76–3.43 (m, 4 H, OCH_2CH_3), 6.63 (s, 4 H, aromatic Mes), 6.76–7.90 (m. 8 H, CR_2); mass spectrum (EI), *m/e* (relative intensity) 476 (M, 20), 312 (Mes_2Ge, 100). Anal. Calcd for $C_{35}H_{40}GeO$: C, 76.53; H, 7.34. Found: C, 76.14; H, 7.01. **1c**: orange crystals, mp 74–75 °C; ^{1}H NMR (C_6D_6) δ 0.60–1.06 (m, 6 H, NCH_2CH_3), 1.96 (s, 6 H, *p*-Me), 2.33 (s, 12 H, *o*-Me), 2.26–2.80 (m, 4 H, NCH_2CH_3), 6.63 (s, 4 H, aromatic Mes), 6.76–7.90 (m, 8 H, CR_2); mass spectrum (EI), *m/e* (relative intensity) 476 (M, 20), 312 (Mes_2Ge, 100). Anal. Calcd for $C_{37}H_{45}GeN$: C, 77.10; H, 7.87. Found: C, 76.88; H, 7.62. **1d**: orange crystals, mp 78–80 °C; ^{1}H NMR (C_6D_6) δ 1.42–1.69 (m, 4 H, CCH_2), 2.30 (s, 6 H, *p*-Me), 2.63 (s, 12 H, *o*-Me), 3.51–3.78 (m, 4 H, OCH_2), 6.90 (s, 4 H, aromatic Mes), 7.10–8.15 (m, 8 H, CR_2); mass spectrum (EI), *m/e* (relative intensity) 476 (M, 20), 312 (Mes_2Ge, 100). Anal. Calcd for $C_{35}H_{38}GeO$: C, 76.81; H, 7.00. Found: C, 77.17; H, 6.88.

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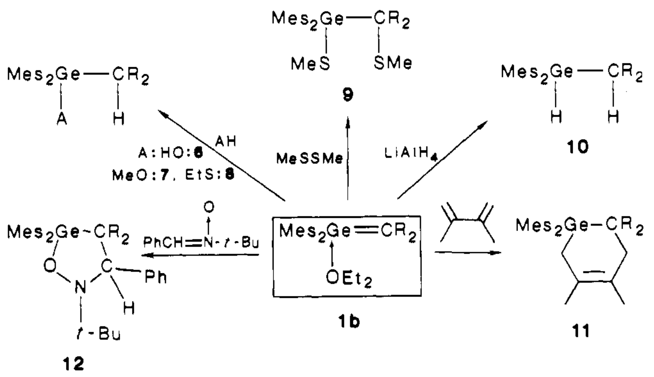
1a forms a very stable adduct **1b**[7] with a weak Lewis base such as diethyl ether. Addition of a stoichiometric amount of triethylamine to **1b** gives adduct **1c**[7] (eq 2). When addition of *t*-BuLi to **2** is carried out in THF, adduct **1d** (THF·Mes$_2$Ge=CR$_2$) was quantitatively obtained; **1d** was spectroscopically[7] and chemically (addition of methanol leading to **7**) characterized. All these adducts which are very thermally stable (no decomposition occurred after heating **1b** in a sealed tube at 85 °C for 15 h) are highly air-sensitive and present thermochromism: crystals of **1b**, **1c** and **1d** are yellow at −100 °C, orange at room temperature, and orange-red at 80 °C.

When the double bond is markedly polarized, the metal has a strong electrophilic character; therefore, it is easily complexed by Lewis bases such as ether oxides or amines, like in silenes[8] and silaimines.[9] Such complexation has not been observed in symmetric molecules $\rangle M{=}M\langle$ (M = Si,[1a,b] Ge,[2] Sn[10]) or in metallaphosphenes $\rangle M{=}P-$ (M = Si,[11] Ge,[3a] Sn[12]) where metal 14 is bound to phosphorus, a less negative atom than carbon or nitrogen.[13]

Germene **1** is stabilized owing to bulky groups on germanium and probably high mesomeric effects between the germanium–carbon double bond and the fluorenyl group. Such a group has already allowed the stabilization of phosphaalkenes $-P{=}C\langle$[14] and of a boraalkene $-B{=}C\langle$.[15]

The structure of **1b** was corroborated by its chemical behavior. A preliminary investigation reveals that **1b** is highly reactive; reactions proceed probably via the free germene **1a**, which is formed by previous dissociation of the adduct. Protic reagents (water, methanol, ethylthiol) and dimethyl disulfide add quantitatively on the Ge=C double bond of **1** to form respectively **6**, **7**, **8**, and **9**;[16] lithium aluminum hydride reduces **1b** to **10**.[16] 1,3-Cycloaddition has been observed with *N*-(*tert*-butyl)-α-phenylnitrone[16] and 1,4-cycloaddition with 2,3-dimethylbutadiene;[16] in the last case, the ene reaction has not been observed (Scheme I).

Scheme I



All these reactions are nearly quantitative and occur at room temperature. They demonstrate the existence of a true double bond between germanium and carbon. **1** is the first stable germene whereas some silenes have already been isolated.[1b,c,8] The stabilization of **1** seems to confirm recent calculations[17] that have predicted close π-bond energies for germenes and silenes.

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[16] **6**: white crystals, mp 72–73 °C; ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, *p*-Me), 2.20 (s, 12 H, *o*-Me), 4.75 (s, 1 H, *H*CR$_2$), 6.65 (s, 4 H, aromatic Mes), 6.85–7.80 (m, 8 H, CR$_2$); IR (Nujol) ν(GeOH) 3420 cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 494 (M, 5), 429 (Mes$_2$GeOH, 100). Anal. Calcd for $C_{31}H_{32}GeO$: C, 75.49; H, 6.54. Found: C, 75.36; H, 6.30. **7**: white crystals, mp 55–57 °C; ^{1}H NMR (C_6D_6) δ 2.08 (s, 6 H, *p*-Me), 2.56 (s, 12 H, *o*-Me), 3.35 (s, 3 H, MeO), 4.90 (s, 1 H, *H*CR$_2$), 6.70 (s, 4 H, aromatic Mes), 7.03–7.93 (m, 8 H, CR$_2$). Anal. Calcd for $C_{32}H_{34}GeO$: C, 75.77; H, 6.76. Found: C, 75.66; H, 6.87. **8**: yellow-green crystals, mp 135–136 °C dec. ^{1}H NMR (C_6D_6) δ 1.00 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 1.60 (q, $^3J_{HH}$ = 7.0 Hz, 2 H, CH$_2$), 2.05 (s, 6 H, *p*-Me), 2.66 (s, 12 H, *o*-Me), 4.88 (s, 1 H, *H*CR$_2$), 6.62 (s, 4 H, aromatic Mes), 7.00–7.93 (m, 8 H, CR$_2$). Anal. Calcd for $C_{33}H_{36}GeS$: C, 73.77; H, 6.75. Found: C, 74.09; H, 7.02. **9**: white crystals, mp 184–186 °C; ^{1}H NMR (C_6D_6) δ 1.00 (s, 3 H, GeSMe), 1.55 (s, 3 H, CSMe), 2.00 (s, 6 H, *p*-Me), 2.10 (s, 12 H, *o*-Me), 6.53 (s, 1 H, aromatic Mes), 6.93–8.03 (m, 8 H, CR$_2$). Anal. Calcd for $C_{33}H_{36}GeS_2$: C, 69.61; H, 6.37. Found: C, 69.98; H, 6.66. **10**: white crystals, mp 110–111 °C; ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, *p*-Me), 2.20 (s, 12 H, *o*-Me), 4.80 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, *H*CR$_2$), 5.20 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, GeH), 6.73 (s, 4 H, aromatic Mes), 6.93–7.93 (m, 8 H, CR$_2$); IR (Nujol) ν(Ge-H) 2070 and 2095 cm^{-1} (two bands, probably due to a Fermi resonance with band at 1040 cm^{-1}). Anal. Calcd for $C_{31}H_{32}Ge$: C, 78.03; H, 6.76. Found: C, 77.74; H, 7.04. **11**: white crystals, mp 123–124 °C; ^{1}H NMR (C_6D_6) δ 1.38 (s, 3 H, Me), 1.83 (s, 3 H, Me), 1.95 (s, 12 H, *o*-Me), 2.06 (s, 6 H, *p*-Me), 2.48 (s, 2 H, CH$_2$), 2.55 (s, 2 H, CH$_2$), 6.68 (s, 4 H, aromatic Mes), 7.05–7.91 (m, 8 H, CR$_2$). Anal. Calcd for $C_{37}H_{40}Ge$: C, 79.74; H, 7.23. Found: C, 79.50; H, 7.33. **12**: white crystals, mp 220–222 °C; ^{1}H NMR (C_6D_6) δ 1.80 (s, 3 H, *p*-Me), 1.86 (s, 3 H, *p*-Me), 1.93 (s, 6 H, *o*-Me), 2.01 (s, 6 H, *o*-Me), 4.73 (s, 1 H, CH), 6.38 (s, 4 H, aromatic Mes), 6.56–7.50 (m, 13 H, Ph and CR$_2$); mass spectrum (EI), *m/e* (relative intensity) 653 (M, 30), 638 (M-15, 5), 596 (M-*t*-Bu, 5), 566 (M-*t*-Bu-2Me, 5), 476 (**1a**, 100). Anal. Calcd for $C_{42}H_{45}GeNO$: C, 77.32; H, 6.95. Found: C, 77.50; H, 7.22.

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Tandem Flowing Afterglow–Selected Ion Flow Tube and Its Application to the Thermal Energy Reactions of $^{18}O^-$

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Since its development by Ferguson, Fehsenfeld, and Schmeltekopf[1] in 1963, the flowing afterglow (FA) has proven to be a valuable technique for studying the kinetics, thermochemistry, and detailed dynamics of gas-phase ion–molecule reactions. The capabilities of this method were greatly extended by Adams and Smith[2] in 1976 by their development of the selected ion flow tube (SIFT); in the last decade several research groups have applied this technique to a variety of important chemical problems. We wish to report the design and construction of a tandem FA–SIFT instrument with considerably enhanced sensitivity, resolution, and chemical versatility. With this instrument we have generated $^{18}O^-$ from isotopically unenriched precursors and studied its chemistry with a variety of reagents. These studies provide the first thermal energy rate constants for these processes and reveal several previously hidden reactions; in particular, it is found that isotope exchange competes with associative detachment in the reactions of O^- with CO and SO_2.

The new tandem FA–SIFT system is shown schematically in Figure 1. Ions are generated in the flowing afterglow source and extracted and focused into the SIFT quadrupole mass filter; the mass-selected ions are refocused and injected into the flow-drift tube where neutral reagents are added to carry out ion chemistry. The ionic reactants and products are detected with a quadrupole mass filter coupled with an electron multiplier. For this study the drift capability[3] was not employed.

With this instrument we have generated unexpectedly large

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