Synthesis, Structural Characterization, and Photolysis of Dibenzodehydro[16]annulenes Containing E–E σ Bonds (E = Si and Ge)

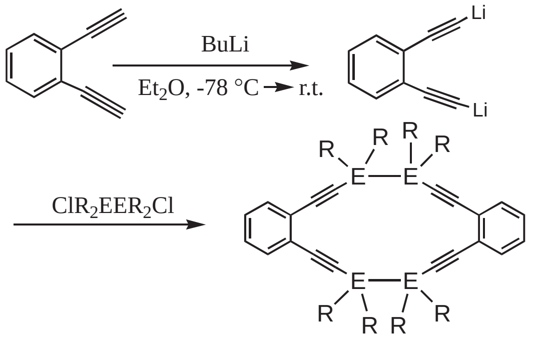
Kunio Mochida,*[1] Junichi Ohto,[1] Matsuri Masuda,[1] Masato Nanjo,[1] Hidekazu Arii,[1] and Yasuhiro Nakadaira[2]
[1]*Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588*
[2]*Department of Chemsitry, The University of Electro-Communication, Chofu, Tokyo 182-8585*

(Received October 1, 2007; CL-071085; E-mail: kunio.mochida@gakushuin.ac.jp)

Dibenzodehydro[16]annulenes containing silicon–silicon and germanium–germanium σ bonds were newly prepared, and their structures were established by spectroscopic methods and X-ray diffraction analysis. On the photolysis, these sila- and germa-cycles evolve the corresponding divalent species, silylene and germylene, respectively, and in addition, the germanes led to the ring contraction to give a fourteen-membered germacycle.

The electronic structure and properties of macrocyclic conjugated π-electron systems (annulenes) have been extensively studied and have been the subject of current interest.[1] New annulenes containing the σ bond of group 14-element catenates, which is known to be as reactive as that of the corresponding C=C π bond,[2] are interesting research targets in view of annulene, group 14-element chemistry, and new materials. While the chemistry of ethynylene polysilanes has been studied by Sakurai and co-workers,[3–5] there have been few reports on germanium analogs.[5] We wish to report herein the syntheses and their structures of 1,2,9,10-tetrametalladehydro[16]annulenes (1,1,2,2,9,9,10,10-octaalkyl-1,2,9,10-tetrametalla-5,6,13,14-dibenzocyclohexadeca-3,7,11,15-tetrayne (**1**: E = Si, R = Me; **2**: E = Ge, R = Me: **a**, R = ^{i}Pro: **b**). The photolysis of **1** and **2** led to the ring contraction accompanied by the generation of divalent species (silylenes and germylenes). The divalent species formed were identified with appropriate trapping experiments and laser flash photolysis.

Compounds **1** and **2** were obtained by the treatment of 1,2-bis(2-lithioethynyl)benzene with the corresponding 1,2-dichlorodisilane and 1,2-dichlorodigermanes, respectively (eq 1). Typically, to a solution of 1,2-diethynylbenzene (28.2 mmol) in Et_2O (40 mL) was added BuLi (27.6 mmol) in Et_2O at −70 °C under argon. The reddish orange solution was stirred for additional 1 h. To the solution, 1,1,2,2-tetramethyl-1,2-dichloro-1,2-digermane (27.2 mmol) was added, and then, the mixture was warmed to room temperature over a period of 10 h with stirring. The reaction mixture was hydrolyzed, extracted with ether, and then dried over sodium sulfate. Removal of the volatile components in vacuo gave **2a** as colorless solids in 3.0% isolated yield. At the same time, considerable amounts of unidentified cyclic and linear oligomers were also detected in the residue.



(1)

1:(E = Si, R = Me), 8.8% yield; **2a**:(E = Ge, R = Me), 3.0% yield; **2b**:(E = Ge, R = ^{i}Pr), 6.7% yield

The compound **2a**[6] was recrystallized from hexane and characterized by spectroscopic methods coupled with X-ray diffraction analysis.

Dibenzodehydro[1]annulenes, **1**[7] and **2b**,[8] were prepared similarly by the reaction of 1,2-(diethynyllithio)benzene with 1,1,2,2-tetramethyl-1,2-dichloro-1,2-disilane and 1,1,2,2-tetraisopropyl-1,2-dichloro-1,2-digermane in 9.0 and 7.0% isolated yields, respectively. Figure 1 shows molecular structures of **1** and **2a** determined by X-ray crystallography. Compounds, **1** and **2a**, have chair-like geometries where the aromatic rings adopt anti-configuration each other as shown.

The average bond distances of C(sp)–C(sp), Si–C(sp), and Si–Si of **1** are 1.23, 1.84, and 2.35 Å, respectively. These bond distances obtained are normal for cyclic organosilicon compounds having ethynylene units.[9] In sixteen-membered silacycle **1**, the averages of C(sp)–Si–Si and C(sp)–C(sp)–Si bond angles are 108.2 and 175.1°, respectively. On the other hand, in germanium compound **2a**, the average bond distances of C(sp)–C(sp), Ge–C(sp), and Ge–Ge are 1.21, 1.92, and 2.42 Å, respectively. The averages of C(sp)–Ge–Ge and C(sp)–C(sp)–Ge bond angles are 106.3 and 171.3°, respectively.

These sixteen-membered ring compounds **1** and **2a** show UV maxima (λ_{max}) at 258 nm (ε: $8.0 \times 10^4\,M^{-1}\,cm^{-1}$) and 254 nm ($\varepsilon$: $8.0 \times 10^4\,M^{-1}\,cm^{-1}$), respectively.[10] In comparison with that of **3** (λ_{max} 241 nm, $\varepsilon = 9.0 \times 10^4\,M^{-1}\,cm^{-1}$), the large bathochromic shift observed indicates appreciable electronic interaction between these ethynylene units through the σ (metal–metal) bonds. Interestingly, the σ (metal–metal) and the vertical

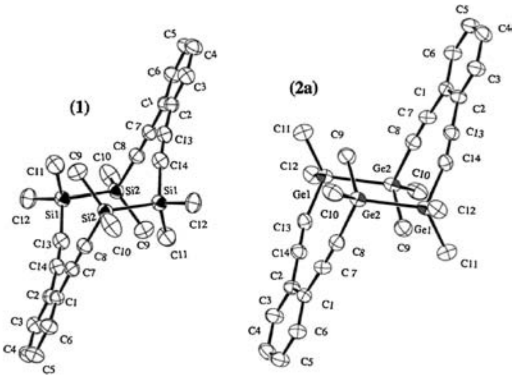
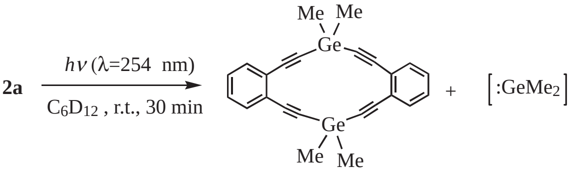


Figure 1. Molecular structures of **1** and **2a**.

π (C=C) orbitals are well located for σ–π conjugation albeit in solids as shown in the figure. Theses results may be due to σ (metal–metal)–π (C–C) conjugation interaction in contrast with that of 1,2-diethynylbenzene.

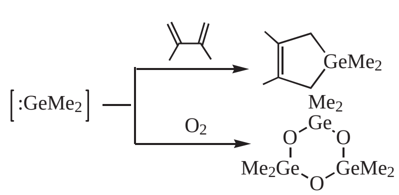
Preliminary examination of thermal and photochemical properties of **1** and **2a** revealed that both were stable on prolonged heating at 150 °C, but silacycle **1** was labile on UV irradiation, and in fact the irradiation of **1** with 110-W medium-pressure Hg arc lamp at room temperature for 30 min under argon in cyclohexane (ca. 0.05 M) gave unidentified complex mixtures (81% conversion yield), whereas in similar photolysis of **1** in the presence of 2,3-dimethylbuta-1,3-diene, only a small amount of 1,1,3,4-tetramethyl-1-silacyclopenta-3-ene[11] was formed and detected with GC and GC-MS spectra (>10% yield) along with complex reaction mixture. So, the laser flash photolysis[12] of **1** was attempted to clarify the mechanism of silylene generation, but any clear transient signal was not observed around 420–430 nm being assigned to that due to the silylene.[13]

On the other hand, similar irradiation of **2a** in cyclohexane with the Hg arc lamp underwent the ring contraction to give fourteen-membered germacycle **3**[14] (20% yield) together with a small amount of unreacted **2a** (85% conversion yield). The formation of **3** is indicative of the generation of dimethylgermylene during the photolysis. Actually, dimethylgermylene generated was trapped with 2,3-dimethylbuta-1.3-diene, a germylene-trapping reagent, to give 1,1,3,4-tetramethyl-1-germacyclopenta-3-ene[15] in low yields (ca. 30% yield). At the same time, the germylene reacted with the dissolved oxygen to form 1,3,5-trioxacyclohexatrigermane (ca. 10% yield)[16] Accord with those results obtained, laser flash photolysis of **2a** in cyclohexane gave a weak transient absorption around 420–430 nm and is reasonably assigned to that of the germylene from the comparison of its spectral characteristics reported.[17]



3

(2)



(3)

In summary, we have newly prepared dibenzodehydro[16]annulenes **1** and **2** containing E–E σ bonds (E = Si and Ge). The electronic perturbation to the annulene due to the σ–π conjugation is not large but significant. The UV photolysis of the silicon and germanium compounds led ineffectively to the ring contraction with the formation of silylenes and germylenes, respectively.

We thank Prof. M. Wakasa and Mr. M. Gohdo of Saitama University for measuring laser flash photolysis of **1** and **2a**.

References and Notes

1 For recent reviews of annulene chemistry, see: a) R. Faust, *Angew. Chem., Int. Ed.* **1998**, *37*, 2825. b) F. Diederich, L. Gobbi, *Top Curr. Chem.* **1999**, *201*, 43. c) U. H. F. Bunz, *Top. Curr. Chem.* **1999**, *201*, 131. d) U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, *28*, 107. e) W. J. Youngs, C. A. Tessier, J. D. Bradshaw, *Chem. Rev.* **1999**, *99*, 3153. f) F. Diederich, *Chem. Commun.* **2001**, 219. g) J. A. Marsden, G. J. Palmer, M. M. Haley, *Eur. J. Org. Chem.* **2003**, 2355.

2 a) H. Sakurai, *Kagaku no Ryouiki* **1975**, *29-1*, 36. b) M. Kira, in *Synthesis and Application of Organosilicon Compound*, ed. by H. Sakurai, CMC, Tokyo, **1989**, Chap. 2.

3 H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, C. Kabuto, *J. Am. Chem. Soc.* **1983**, *105*, 3359.

4 H. Sakurai, S. Hoshi, A. Kamiya, A. Hosomi, C. Kabuto, *Chem. Lett.* **1986**, 1781.

5 H. Sakurai, *Advances in Inorganic Chemistry*, **2000**, Vol. 50, p. 359.

6 **2a**: mp 230 °C; ^{1}H NMR (C_6D_6) δ 0.71 (s, 24H), 6.72–6.75 (m, 4H), 7.40–7.43 (m, 4H); DI-MS (*m/z*, %) 660 (M^+), 645 ($M^+ - Me$). Crystal data for **2a**: $C_{28}H_{32}Ge_4$, $M_r = 658.90$, monoclinic, space group $P2_1/c$ (#14), $a = 10.4100(10)$, $b = 12.1290(13)$, $c = 13.3280(12)$ Å, $\beta = 121.111(6)°$, $V = 1440.8(2)$ Å^3, $T = 120$ K, $Z = 2$, $D_{calcd} = 1.519$ g/cm^3, $R_1 = 0.0516$ ($I > 2.0\sigma(I)$), $wR_2 = 0.1589$ (all data). Ref. 18.

7 **1**: mp 205–206 °C; ^{1}H NMR (C_6D_6) δ 0.41 (s, 24H), 6.66–6.69 (m, 4H), 7.32–7.39 (m, 4H); ^{29}Si NMR (C_6D_6) δ −37.5(s); DI-MS (*m/z*, %) 240 (M^+), 225 ($M^+ - Me$). Crystal data for **1**: $C_{28}H_{32}Si_4$, $M_r = 240.9$, monoclinic, space group $C2/c$ (#15), $a = 18.5630(14)$, $b = 8.4760(3)$, $c = 20.6090(13)$ Å, $\beta = 114.898(3)°$, $V = 2941.2(3)$ Å^3, $T = 200$ K, $Z = 4$, $D_{calcd} = 1.086$ Mg/m^3, $R_1 = 0.0416$ ($I > 2.0\sigma(I)$), $wR_2 = 0.1546$ (all data). ref 18.

8 **2b**: mp 225–226 °C; ^{1}H NMR (C_6D_6) δ 1.42 (d, $J = 6.9$ Hz, 24H), 1.44 (d, $J = 6.9$ Hz, 24H), 1.74 (sep, 8H), 6.74–6.77 (m, 4H), 7.39–7.42 (m, 4H); DI-MS (*m/z*, %) 883 (M^+), 840 ($M^+ - {}^i$Pr). Crystal data for **2b**: $C_{44}H_{64}Ge_4$, $M_r = 883.31$, triclinic, space group $P\bar{1}$ (#2), $a = 8.8790(6)$, $b = 10.3440(9)$, $c = 13.0790(12)$ Å, $\alpha = 106.735°$, $\beta = 98.573(5)°$, $\gamma = 98.585(6)°$, $V = 1113.83(16)$ Å^3, $T = 200$ K, $Z = 1$, $D_{calcd} = 1.317$ Mg/m^3, $R_1 = 0.0353$ ($I > 2.0\sigma(I)$), $wR_2 = 0.0911$ (all data). ref 18.

9 K. Negishi, M. Unno, H. Matsumoto, *Chem. Lett.* **2004**, *33*, 430.

10 Measured in cyclohexane.

11 Y. Nakadaira, *Kagaku no Ryoiki*, **1975**, *29*, 39.

12 Nanosecond transient absorption spectra measurements were performed on degassed solutions of **1** and **2a** (ca. 10^{-4} M) in cyclohexane at 293 K using the fourth-harmonic pulse of Nd:YAG laser as the exciting light source ($\lambda = 266$ nm). M. Wakasa, *J. Phys. Chem. B* **2007**, *111*, 9434.

13 H. Shizuka, H. Tanaka, K. Tonokura, K. Murata, H. Harutsuka, J. Ohshita, M. Ishikawa, *Chem. Phys. Lett.* **1988**, *143*, 225.

14 **3**: mp 225–230 °C; ^{1}H NMR ($CDCl_3$) δ 0.70 (s, 12H), 7.21–7.24 (m, 4H), 7.42–7.45 (m, 4H); DI-MS (*m/z*, %) 454 (M^+), 439 ($M^+ - Me$).

15 M. Schriewer, W. P. Neumann, *J. Am. Chem. Soc.* **1983**, *105*, 897.

16 K. Mochida, S. Tokura, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1642.

17 K. Mochida, I. Yoneda, M. Wakasa, *J. Organomet. Chem.* **1990**, *399*, 53.

18 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp//journals/chem-lett/.

Published on the web (Advance View) November 27, 2007; doi:10.1246/cl.2008.20