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Synthesis and Properties of the First Stable Neutral Germaaromatic Compound, 2-{2,4,6-Tris-[bis-(trimethylsilyl)methyl]phenyl}-2-germanaphthalene

Norio Nakata, Nobuhiro Takeda, and Norihiro Tokitoh*

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

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The first stable neutral germaaromatic compound, 2-germanaphthalene **1a**, was synthesized by taking advantage of an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). The molecular structure and aromaticity of **1a** were discussed on the basis of its NMR, UV−vis, and Raman spectra, X-ray crystallographic analysis, and theoretical calculations. All the ^{1}H and ^{13}C NMR chemical shifts of the 2-germanaphthalene ring of **1a** were in good agreement with the calculated values for 2-germanaphthalene and 2-phenyl-2-germanaphthalene. The patterns of UV−vis and Raman spectra of **1a** were similar to those of naphthalene, although the shift to longer wavelength (in the UV−vis spectrum) and smaller wavenumber (in the Raman spectrum) resulting from the replacement of carbon with germanium were observed. X-ray crystallographic analysis of **1a** revealed that the 2-germanaphthalene ring was almost planar and perpendicular to the benzene ring of the Tbt group. These experimental results indicate the delocalization of π-electrons in the 2-germanaphthalene ring of **1a**. Theoretical calculations (NICS(1), Λ, and ASE$_{\mathrm{isom}}$) also indicated the ring current effects and aromatic stabilization of 2-germanaphthalene. 2-Germanaphthalene **1a** reacted as a Ge−C double-bond compound (germene) with water, *t*-BuLi, mesitonitrile oxide, 2,3-dimethyl-1,3-butadiene, and some elemental chalcogens to give the corresponding adducts.

Introduction

In recent years, there has been considerable interest in the aromatic properties of germaaromatic compounds,[1] namely, Ge-containing $[4n + 2]$-π-electron ring systems, since they are heavier congeners of aromatic hydrocarbons[2] which play very important roles in organic chemistry. Although ionic germaaromatic compounds, cyclotrigermenium cations[3] and germole dianions,[4] have been successfully synthesized as stable compounds and their aromatic character has been demonstrated, the properties of neutral germaaromatic compounds have been little known. Märkl et al. reported the synthesis of 1,4-di-*tert*-butylgermabenzene,[5] the generation of which was confirmed only by the formation of its [2 + 2] dimer and the trapping reaction with diene. Furthermore, they described the spectroscopic detection of 1,4-dialkylgermabenzenes in the gas phase by VTPES (variable-temperature photoelectron spectroscopy) experiments.[6] However, no isolation of a neutral germaaromatic compound has been reported yet, probably due to its high reactivity.

Meanwhile, we have already succeeded in the synthesis and isolation of kinetically stabilized silabenzene,[7] 2-silanaphthalene,[8] and 9-silaanthracene,[9] the first examples of stable neutral silaaromatic compounds, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). With these stable systems in hand, we have revealed their molecular structures and reactivities and discussed the aromaticity of these silaaromatic compounds. The successful results in the silaaromatic systems naturally prompted us to extend this chemistry to the much heavier metallaaromatic systems of group 14 elements, i.e., germaaromatics. In preliminary contributions, we have recently reported the synthesis and structure of the first stable 2-germanaphthalene, **1a** (Chart 1), bearing a Tbt group on the germanium

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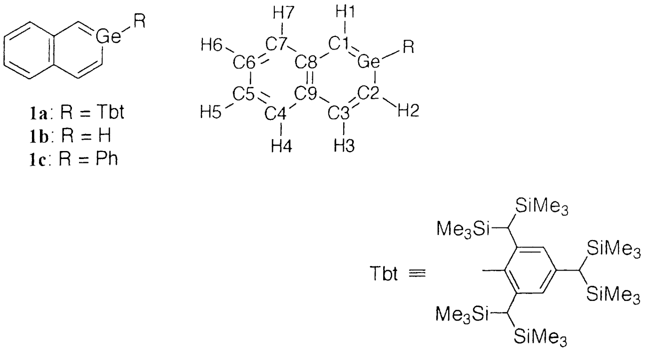
Chart 1



atom,[10] and the reactions of **1a** with elemental sulfur and selenium.[11] In addition, a kinetically stabilized germabenzene was also synthesized and its detailed properties, especially its aromatic character, were revealed.[12] Here, we wish to describe the details of the synthesis, structure, reactivity, and aromaticity of 2-germanaphthalene **1a** kinetically stabilized by the Tbt group, the first stable neutral germaaromatic compound.

Experimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. ^{1}H NMR (400 or 300 MHz), ^{13}C NMR (100 or 75 MHz), and ^{77}Se NMR (57 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM AL-400 or JEOL JNM AL-300 spectrometer at room temperature. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Flash column chromatography (FCC), short column chromatography (SCC), and preparative thin-layer chromatography (PTLC) were performed with Merck silica gel 60, Wakogel C-200, and Merck Kieselgel 60 PF254, respectively. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent $CHCl_3$). Electronic spectra were recorded on a JASCO Ubest-50 UV−vis spectrometer. Raman spectra were measured at room temperature on a Raman spectrometer consisting of a Spex 1877 Triplemate and an EG & G PARC 1421 intensified photodiode array detector. An NEC GLG 108 He−Ne laser (632.8 nm) was used for Raman excitation. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. *o*-(2-Bromoethyl)benzyl bromide[13] and trichloro{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}germane ($TbtGeCl_3$)[14] were prepared according to the reported procedures.

Theoretical Calculations. The geometries of 2-germanaphthalenes were optimized by using the Gaussian 98 program at B3LYP/6-31G(d) levels of density functional theory.[15] The GIAO-B3LYP and NICS calculations were carried out with 6-311G(3d) for Ge and 6-311G(d) for C and H. Mulliken and NPA (natural population analysis)[16] charge distributions were calculated at MP2/6-31G(d) levels. The diamagnetic susceptibility exaltations (Λ) were calculated at CSGT-HF/6-31G(d) levels. In the geometry optimization of 2-phenyl-2-germanaphthalene (**1c**), the phenyl group was fixed perpendicularly to the 2-germanaphthalene ring (transition state).

Preparation of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1,2,3,4-tetrahydro-2-germanaphthalene (2). A solution of *o*-(2-bromoethyl)benzyl bromide (1.98 g, 7.13 mmol) in THF (70 mL) and a solution of $TbtGeCl_3$ (6.71 g, 9.19 mmol) in THF (70 mL) were simultaneously added dropwise to dried magnesium (1.14 g, 46.94 mmol) and 100 mL of THF over 0.5 h, and the reaction mixture was stirred for 2 h at room temperature. To the mixture was added $LiAlH_4$ (0.37 g, 9.75 mmol) at 0 °C, and the resulting gray suspension was stirred for 1 h. After slow addition of an aqueous solution of NaOH (ca. 4 mL, 15% w/w) at 0 °C, the resulting white suspension was filtered through Celite and rinsed with hexane (ca. 100 mL). The solvents were evaporated, and the residue was purified by FCC (hexane) to give almost pure **2** (1.72 g, 33%) as a white powder. **2**: mp 187−193 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.02−0.04 (s, 54H), 1.23−1.29 (m, 2H), 1.31 (s, 1H), 1.89 (s, 2H), 2.39−2.59 (m, 2H), 2.80−2.89 (m, 1H), 3.01−3.08 (m, 1H), 4.46 (br s, 1H), 6.29 (br s, 1H), 6.41 (br s, 1H), 7.10−7.18 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 0.65 (q), 0.71 (q), 0.95 (q), 11.05 (t), 21.28 (t), 29.01 (d), 29.43 (d), 30.17 (d), 30.55 (t), 121.71 (d), 125.45 (d), 126.65 (d), 126.85 (d), 128.43 (d), 129.01 (d), 129.41 (s), 138.89 (s), 140.57 (s), 143.69 (s), 149.99 (s), 150.28 (s). Anal. Calcd for $C_{36}H_{70}GeSi_6$: C, 58.11; H, 9.48. Found: C, 58.05; H, 9.63.

Preparation of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-germanaphthalene (3). A mixture of **2** (0.76 g, 1.02 mmol), *N*-bromosuccinimide (NBS; 4.43 g, 7.13 mmol), and a catalytic amount of benzoyl peroxide was dissolved in benzene (25 mL), and the solution was refluxed for 2 h. After removal of the solvent in vacuo and addition of THF (20 mL), $LiAlH_4$ (0.15 g, 3.98 mmol) was added to the mixture at 0 °C. The gray suspension was stirred for 1 h, and an aqueous solution of NaOH (ca. 0.5 mL, 15% w/w) was slowly added to the mixture at 0 °C. The resulting white suspension was filtered through Celite and rinsed with hexane (ca. 15 mL). After evaporation of the solvents, the residue was purified by FCC (hexane) to give an inseparable mixture of **3a** and **3b** (ca. 1:1 ratio, which was determined by NMR). This mixture was dissolved in THF (15 mL) and cooled to −78 °C, and then *t*-BuLi (0.49 M in hexane/pentane, 2.3 mL, 1.13 mmol) was added to it. After the solution was stirred for 30 min, an excess amount of a saturated aqueous solution of NH_4Cl was added. The solvents were evaporated, and inorganic salts were removed by SCC (hexane). Reprecipitation from $CHCl_3/CH_3CN$ gave pure **3a** (0.47 g, 62% from **2**) as a white powder. **3a**: mp 123−126 °C; ^{1}H NMR ($CDCl_3$) δ −0.06 (s, 18H), 0.05 (s, 36H), 1.31 (s, 1H), 2.07 (br s, 1H), 2.12 (br s, 1H), 2.55 (dd, J = 15.5, 3.6 Hz, 1H), 2.70 (dd, J = 15.5, 3.6 Hz, 1H), 4.96 (dd, J = 3.6, 3.6 Hz, 1H), 6.28 (br s, 1H), 6.40 (br s, 1H), 6.53 (d, J = 12.8 Hz, 1H), 7.08−7.13 (m, 4H), 7.23 (d, J = 12.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.36 (q), 0.62 (q), 0.71 (q), 0.95 (q), 18.22

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(t), 28.92 (d), 29.23 (d), 30.23 (d), 121.71 (d), 125.94 (d), 126.60 (d), 127.50 (d), 128.15 (d), 128.35 (s), 131.16 (d), 132.08 (d), 135.14 (s), 135.24 (s), 143.92 (s), 144.21 (d), 150.41 (s), 150.59 (s). Anal. Calcd for $C_{36}H_{68}GeSi_6$: C, 58.27; H, 9.24. Found: C, 58.16; H, 9.37.

Preparation of 2-Bromo-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-germanaphthalene (4). A mixture of **3a** (0.37 g, 0.50 mmol), NBS (90 mg, 0.51 mmol), and a catalytic amount of benzoyl peroxide was dissolved in benzene (20 mL), and the mixture was refluxed for 2 h. The solvent was evaporated, and hexane (10 mL) was added. Filtration of the mixture followed by removal of the solvent in vacuo afforded almost pure **4** (0.41 g, 99%) as a white powder. **4**: mp 174−177 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.05 (s, 9H), 0.01 (s, 9H), 0.03 (s, 18H), 0.06 (s, 9H), 0.10 (s, 9H), 1.32 (s, 1H), 2.14 (br s, 1H), 2.17 (br s, 1H), 2.95 (d, J = 15.2 Hz, 1H), 3.13 (d, J = 15.2 Hz, 1H), 6.28 (br s, 1H), 6.41 (br s, 1H), 6.65 (d, J = 12.8 Hz, 1H), 7.10−7.15 (m, 4H), 7.19 (d, J = 12.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 74.8 MHz) δ 0.39 (q), 0.46 (q), 0.68 (q), 0.71 (q), 0.89 (q), 1.12 (q), 28.92 (d), 29.29 (d), 29.41 (t), 30.58 (d), 122.15 (d), 126.56 (d), 127.03 (d), 127.70 (s), 127.84 (d), 131.01 (d), 131.47 (d), 131.75 (d), 134.04 (s), 134.22 (s), 143.43 (d), 146.11 (s), 150.65 (s), 151.12 (s). Anal. Calcd for $C_{36}H_{67}BrGeSi_6$: C, 52.67; H, 8.23. Found: C, 52.64; H, 8.47.

Synthesis of 2-Germanaphthalene 1a. In a glovebox filled with argon, **4** (54.6 mg, 0.067 mmol) was dissolved in THF (1 mL, dried over K mirror and distilled by trap-to-trap method), and lithium diisopropylamide (LDA) (2.0 M in heptane/THF/ethylbenzene, 41 μL, 0.082 mmol) was added to the solution. The solvents were removed under reduced pressure, and hexane (3.5 mL) was added to the residue. The mixture was left for 10 h, and the generated precipitates were removed by decantation. Removal of the solvent in vacuo afforded almost pure 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-germanaphthalene (**1a**; 49.1 mg, 98%). **1a**: mp 143−145 °C dec; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.13 (s, 36H), 0.20 (s, 18H), 1.52 (s, 1H), 2.38 (br s, 1H), 2.48 (br s, 1H), 6.64 (br s, 1H), 6.75 (br s, 1H), 7.03 (dd, J = 6.8, 8.0 Hz, 1H), 7.20 (dd, J = 6.8, 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.85 (dd, J = 12.1, 1.7 Hz, 1H), 8.24 (d, J = 1.7 Hz, 1H), 8.55 (d, J = 12.1 Hz, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ 0.93 (q), 1.19 (q), 31.40 (d), 36.37 (d), 36.82 (d), 120.75 (d), 121.84 (d), 126.26 (d), 126.41 (d), 127.69 (d), 128.12 (s), 128.40 (d), 130.45 (d), 131.75 (s), 133.71 (d), 145.15 (s), 145.89 (d), 146.66 (s), 150.01 (s), 150.07 (s); UV−vis (hexane; λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)) 269 (2×10^4), 335 (1×10^4), 386 (2×10^3); HRMS (FAB) found m/z 740.2983 ($[M]^+$), calcd for $C_{36}H_{66}GeSi_6$ 740.2962. Although we tried the elemental analysis several times, the results agreed not with the composition of **1a** but that of hydrolyzed product **5** due to the high moisture sensitivity of **1a**.

Reaction of 1a with Water. To a solution of **1a** (25.1 mg, 0.035 mmol) in THF (0.5 mL) was added water (0.5 mL) at room temperature, and the solution was stirred for 30 min. After the solvent was removed under reduced pressure, purification by PTLC ($CHCl_3$) afforded 2-hydroxy-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-germanaphthalene (**5**) as a white powder (26.5 mg, 99%). **5**: mp 165−167 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.06 (s, 18H), 0.02−0.07 (s, 36H), 1.24 (s, 1H), 1.30 (s, 1H), 2.18 (br s, 1H), 2.24 (br s, 1H), 2.67 (d, J = 15.2 Hz, 1H), 2.79 (d, J = 15.2 Hz, 1H), 6.26 (br s, 1H), 6.39 (br s, 1H), 6.54 (d, J = 12.8 Hz, 1H), 7.08−7.13 (m, 4H), 7.24 (d, J = 12.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 74.8 MHz) δ 0.41 (q), 0.68 (q), 0.99 (q), 26.01 (t), 28.52 (d), 28.82 (d), 30.39 (d), 122.02 (d), 126.11 (d), 126.89 (d), 127.51 (d), 128.67 (s), 131.25 (d), 131.43 (d), 132.27 (d), 134.46 (s), 135.22 (s), 144.74 (d), 145.12 (s), 150.34 (s), 150.67 (s). Anal. Calcd for $C_{36}H_{68}GeOSi_6$: C, 57.04; H, 9.04. Found: C, 57.05; H, 9.25.

Reaction of 1a with *t*-BuLi. To a solution of **1a** (53.6 mg, 0.072 mmol) in hexane (0.5 mL) was added *t*-BuLi (0.49 N in pentane/hexane, 0.15 mL, 0.074 mmol) at room temperature, and the solution was stirred for 30 min. After quenching with a saturated aqueous solution of NH_4Cl, the organic layer was separated and the aqueous layer was extracted with hexane several times. The combined organic layer was dried over $MgSO_4$, and the removal of the solvents in vacuo followed by purification with PTLC (hexane) afforded 2-*tert*-butyl-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-germanaphthalene (**6**; 29.7 mg, 52%) as colorless crystals. **6**: mp 223−225 °C; ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 18H), 0.03 (s, 18H), 0.09 (s, 9H), 0.11 (s, 9H), 1.08 (s, 9H), 1.27 (s, 1H), 2.02 (br s, 1H), 2.09 (br s, 1H), 2.68 (d, J = 15.3 Hz, 1H), 2.77 (d, J = 15.3 Hz, 1H), 6.23 (br s, 1H), 6.35 (br s, 1H), 6.55 (d, J = 13.2 Hz, 1H), 6.98−7.07 (m, 4H), 7.12 (d, J = 13.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 74.8 MHz) δ 0.79 (q), 0.91 (q), 1.42 (q), 1.57 (q), 1.67 (q), 1.97 (q), 21.68 (t), 25.97 (s), 28.79 (d), 28.95 (d), 29.96 (d), 30.41 (q), 122.39 (d), 125.58 (d), 126.97 (d), 127.55 (d), 129.85 (s), 130.45 (d), 131.98 (d), 132.90 (d), 135.43 (s), 136.13 (s), 142.33 (d), 143.40 (s), 151.38 (s), 151.72 (s). Anal. Calcd for $C_{40}H_{76}GeSi_6$: C, 60.19; H, 9.60. Found: C, 60.25; H, 9.72.

Reaction of 1a with Mesitonitrile Oxide. To a solution of **1a** (46.7 mg, 0.063 mmol) in THF (1 mL) was added mesitonitrile oxide (34.6 mg, 0.215 mmol) at room temperature, and the solution was stirred for 10 h. After the solvent was evaporated, purification of the residue by GPLC ($CHCl_3$) afforded 4,10b-dihydro-1-mesityl-4-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[2]benzogermino[1,2-*d*][1,2,5]oxazagermole (**7**; 35.9 mg, 86%) as a white powder. **7**: mp 245−249 °C dec; ^{1}H NMR ($CDCl_3$) δ −0.09 (s, 18H), 0.01 (s, 18H), 0.05 (s, 18H), 1.35 (s, 3H), 1.58 (s, 1H), 1.75 (br s, 1H), 1.77 (br s, 1H), 2.20 (s, 3H), 2.24 (s, 3H), 3.93 (s, 1H), 6.37 (br s, 1H), 6.48−6.52 (m, 2H), 6.55 (s, 2H), 6.83 (s, 1H), 6.91 (dd, J = 6.9, 6.9 Hz, 1H), 7.11−7.21 (m, 2H), 7.39 (d, J = 13.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.23 (q), 0.65 (q), 0.67 (q), 1.01 (q), 18.65 (q), 19.74 (q), 21.02 (q), 30.06 (d×2), 30.65 (d), 41.59 (d), 121.87 (d), 126.78 (d), 126.80 (d), 127.40 (d), 127.55 (s), 127.69 (d), 127.84 (d), 127.98 (d), 129.21 (s), 130.13 (s), 132.39 (d), 134.28 (s), 135.09 (d), 135.33 (s), 137.54 (s), 138.31 (s), 146.07 (s), 146.55 (d), 150.04 (s), 150.26 (s), 160.08 (s). Anal. Calcd for $C_{46}H_{77}GeNOSi_6$: C, 61.31; H, 8.61; N, 1.55. Found: C, 61.39; H, 8.74; N, 1.35.

Reaction of 1a with 2,3-Dimethyl-1,3-butadiene. In a glovebox filled with argon, **1a** (35.1 mg, 0.052 mmol) was dissolved in C_6D_6 (0.5 mL) and the solution was put into a 5 mm i.d. NMR tube. After 2,3-dimethyl-1,3-butadiene (distilled from CaH_2 under Ar prior to use, 0.15 mL, 1.326 mmol) was added to the solution, the NMR tube was evacuated and sealed. Heating of the mixture at 80 °C for 2 h resulted in the disappearance of the NMR signals for **1a**. Then, the tube was opened and the solvent was removed in vacuo. Purification of the residue by GPLC ($CHCl_3$) and PTLC (hexane) afforded 4b,5,8,8a-tetrahydro-6,7-dimethyl-8a-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-8a-germaphenanthrene (**8**; 25.0 mg, 58%) as a white powder. **8**: mp 142−144 °C; ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9H), −0.07 (s, 9H), −0.05 (s, 9H), 0.01 (s, 27H), 1.26 (s, 1H), 1.45 (s, 3H), 1.64 (s, 3H), 1.86−1.96 (m, 4H), 2.33−2.47 (m, 2H), 2.64−2.68 (m, 1H), 6.20 (d, J = 13.2 Hz, 1H), 6.23 (br s, 1H), 6.35 (br s, 1H), 7.00−7.22 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.48 (q), 0.67 (q), 0.77 (q), 0.90 (q), 1.22 (q), 20.84 (q), 22.08 (q), 24.13 (t), 28.47 (d), 28.85 (d), 30.08 (d), 30.73 (d), 41.97 (t), 121.88 (d), 125.92 (d), 127.06 (d), 127.46 (s), 127.65 (d), 127.85 (s), 129.58 (d), 130.96 (s), 131.18 (d), 132.60 (d), 135.70 (s), 140.95 (s), 143.00 (d), 143.43 (s), 150.11 (s), 150.41 (s). Anal. Calcd for $C_{42}H_{76}GeSi_6$: C, 61.36; H, 9.32. Found: C, 61.00; H, 9.46.

Reaction of 1a with Elemental Sulfur. To a solution of **1a** (53.1 mg, 0.072 mmol) in benzene (1.5 mL) was added elemental sulfur (32.1 mg, 1.000 mmol as S atom) at room temperature, and the solution was stirred for 48 h. After the solvent was removed in vacuo, purification of the residue by GPLC ($CHCl_3$) and PTLC (hexane) afforded 4,10b-dihydro-4-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[2]benzogermino-

Table 1. Crystallographic Data for Compounds 1a, 6, 8, and 10

	1a	**6**	**8**	**10**
formula	$C_{36}H_{66}GeSi_6$	$C_{40}H_{76}GeSi_6$	$C_{42}H_{76}GeSi_6$	$C_{36}H_{66}GeSe_3Si_6$
fw	740.02	798.14	822.16	976.90
cryst size (mm)	0.40 × 0.40 × 0.35	0.40 × 0.20 × 0.20	0.40 × 0.40 × 0.30	0.40 × 0.20 × 0.15
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.033(4)	12.276(7)	12.241(5)	9.484(4)
b (Å)	12.112(5)	31.198(17)	13.024(6)	12.021(4)
c (Å)	17.851(6)	12.720(7)	16.056(7)	22.902(9)
α (deg)	72.423(15)	90	106.988(6)	75.562(16)
β (deg)	86.91(2)	105.517(6)	94.263(4)	81.901(18)
γ (deg)	75.064(9)	90	96.959(5)	68.746(13)
V (Å^3)	2196.6(14)	4694(4)	2414.0(19)	2352.8(15)
Z	2	4	2	2
D_{calcd} (g cm^{-3})	1.119	1.129	1.131	1.379
no. of indep rflns	7709	8221	8319	6835
no. of params	479	445	462	464
R1 ($I > 2\sigma(I)$)	0.053	0.088	0.038	0.045
wR2 (all data)	0.138	0.128	0.081	0.112
goodness of fit	1.04	1.28	1.09	1.09

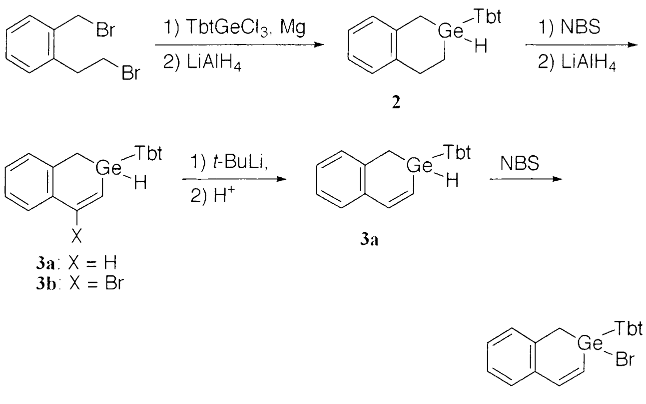
[2,1-*d*]-1,2,3,4-trithiagermole (**9**; 32.9 mg, 55%) as a pale yellow powder. **9**: mp 220−223 °C; ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9H), −0.06 (s, 9H), 0.02 (s, 18H), 0.05 (s, 9H), 0.09 (s, 9H), 1.32 (s, 1H), 2.12 (br s, 2H), 4.44 (s, 1H), 6.32 (br s, 1H), 6.36 (d, J = 12.9 Hz, 1H), 6.44 (br s, 1H), 7.14 (d, J = 12.9 Hz, 1H), 7.14−7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 0.40 (q), 0.67 (q), 0.69 (q), 0.76 (q), 0.80 (q), 1.14 (q), 29.59 (d), 29.90 (d), 30.64 (d), 46.96 (d), 122.45 (d), 125.45 (s), 127.45 (s), 127.94 (d), 128.12 (d), 128.95 (d), 131.85 (d), 134.13 (d), 134.37 (d), 135.50 (s), 141.49 (d), 146.36 (s), 151.33 (s), 151.66 (s). Anal. Calcd for $C_{36}H_{66}GeS_3Si_6$: C, 51.71; H, 7.96. Found: C, 51.63; H, 7.99.

Reaction of 1a with Elemental Selenium. To a solution of **1a** (48.9 mg, 0.066 mmol) in THF (2 mL) was added elemental selenium (49.0 mg, 0.621 mmol as Se atom) at room temperature, and the solution was stirred for 48 h. After the solvent was removed in vacuo, purification of the residue by GPLC ($CHCl_3$) and PTLC (hexane) afforded 4,10b-dihydro-4-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[2]benzogermino[2,1-*d*]-1,2,3,4-triselenagermole (**10**; 36.5 mg, 57%) as orange crystals. **10**: mp 203−205 °C dec; ^{1}H NMR ($CDCl_3$) δ −0.11 (s, 9H), −0.07 (s, 9H), 0.01 (s, 18H), 0.09 (s, 9H), 0.12 (s, 9H), 1.30 (s, 1H), 2.22 (s, 2H), 5.06 (s, 1H), 6.30 (br s, 1H), 6.37 (d, J = 12.9 Hz, 1H), 6.42 (br s, 1H), 7.06 (d, J = 12.9 Hz, 1H), 7.07−7.33 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 0.54 (q), 0.72 (q), 0.95 (q), 1.31 (q), 29.49 (d), 29.75 (d), 30.64 (d), 44.12 (d), 122.58 (d), 124.38 (s), 127.61 (d), 127.65 (d), 127.84 (d), 131.56 (d), 131.71 (d), 133.65 (s), 133.70 (d), 137.16 (s), 139.97 (d), 146.04 (s), 151.34 (s), 151.61 (s); ^{77}Se NMR ($CDCl_3$) δ 296.0, 531.4, 716.9. Anal. Calcd for $C_{36}H_{66}GeSe_3Si_6$: C, 44.26; H, 6.81. Found: C, 44.04; H, 6.82.

Reaction of 1a with *cis*-2,3-Diphenylthiirane. To a solution of **1a** (44.8 mg, 0.061 mmol) in THF (1 mL) was added *cis*-2,3-diphenylthiirane (24.0 mg, 0.113 mmol) at room temperature, and the solution was stirred for 5 h. After the solvent was removed in vacuo, purification of the residue by GPLC ($CHCl_3$) and PTLC (hexane) afforded **9** (18.1 mg, 35%).

X-ray Structural Determination. Crystallographic data for **1a**, **6**, **8**, and **10** are collected in Table 1. Single crystals of **1a** and **10** were grown by the slow evaporation of its saturated solution in hexane at room temperature in a glovebox filled with argon, while single crystals of **6** and **8** were grown by the slow evaporation of their saturated solution in dichloromethane and acetonitrile, respectively, at room temperature. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 71 Å) to $2\theta_{\max}$ = 50° at 93 K. The structures were solved by direct methods (SIR97)[17] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[18] All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. The structures of the overlapped and disordered 2-germanaphthalene rings for **1a** and trimethylsilyl groups in para position of the Tbt group for **10** were restrained to be identical with each other using the SAME and DELU instructions. The occupancies of each fragment for **1a** and **10** were refined with constraints that their sum is 1 (0.659(5):0.341(5) for **1a** and 0.775(7):0.225(7) for **10**, respectively).

Scheme 1



Results and Discussion

Synthesis of 2-Germanaphthalene. Similarly to the synthetic method of Tbt-substituted 2-silanaphthalene, 2-bromo-1-hydro-2-germanaphthalene **4** was selected as a precursor of 2-germanaphthalene **1a**. At first, 1,2,3,4-tetrahydro-2-germanaphthalene **2** was synthesized by the coupling reaction of *o*-(2-bromoethyl)benzyl bromide with $TbtGeCl_3$ using an excess amount of Mg (Scheme 1). Bromination of **2** with an excess amount of NBS followed by reduction with $LiAlH_4$ gave an inseparable mixture of the expected vinylgermane **3a** and overbrominated vinylgermane **3b**. Treatment of the mixture of vinylgermanes **3a** and **3b** with *t*-BuLi and subsequent addition of saturated aqueous NH_4Cl afforded the vinylgermane **3a** as a pure compound.

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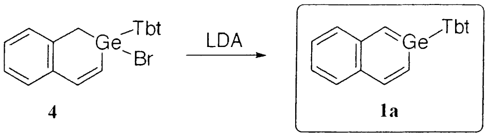
(18) Sheldrick, G. M. SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

Scheme 2



4

1a

Table 2. Observed and Calculated ^1H and ^{13}C NMR Chemical Shifts (ppm) for 2-Germanaphthalenes[a]

	1a (R = Tbt, obsd[b])	**1b** (R = H, calcd[c])	**1c** (R = Ph, calcd[c,d])
H1	8.24	8.13	7.62
H2	7.85	7.48	7.18
H3	8.55	8.50	8.40
H4	7.60	7.49	7.44
H5	7.03	7.02	6.92
H6	7.20	7.22	7.10
H7	7.65	7.45	7.36
C1	127.69	135.55	127.46
C2	130.45	128.34	125.74
C3	145.89	145.51	145.09
C4	133.71	133.17	132.48
C5	120.75	120.94	119.43
C6	126.26	125.53	124.80
C7	128.40	127.15	127.08
C8	145.15	145.61	145.20
C9	128.12	127.69	126.43

[a] See Chart 1. [b] Measured in benzene-d_6. [c] Calculated at the GIAO-B3LYP/6-311G(d) (6-311G(3d) on Ge)//B3LYP/6-31G(d) level. [d] The phenyl group is fixed in such a way that it is perpendicular to the 2-germanaphthalene.

Finally, careful bromination of **3a** with NBS (1 equiv) resulted in the quantitative formation of the corresponding bromogermane **4**, which is a suitable precursor of 2-germanaphthalene **1a** (Scheme 1).

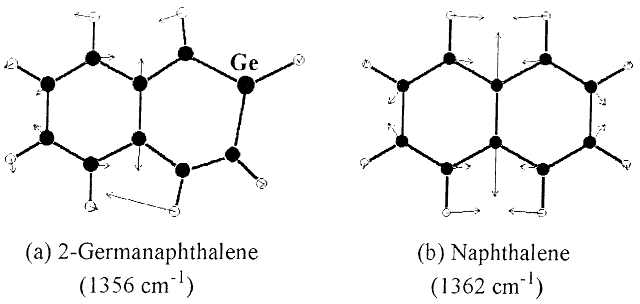
2-Germanaphthalene **1a** was synthesized by the dehydrobromination of bromogermane **4** with LDA in THF at room temperature (Scheme 2).

Although **1a** is highly moisture sensitive, it is thermally very stable under an inert atmosphere either in the solid state (at 100 °C for 30 min) or in solution (benzene, at 100 °C for 1 h in a sealed tube), and neither dimerization nor decomposition was observed.

NMR Spectra. The ^1H and ^{13}C NMR signals of **1a** were assigned using 2D NMR techniques together with the NOE and decoupling experiments. The assignments of ^1H and ^{13}C NMR signals are listed in Table 2 along with the calculated values for some model compounds: i.e., 2-germanaphthalene (**1b**) and 2-phenyl-2-germanaphthalene (**1c**), where the observed values for **1a** are in good agreement with the calculated ones for **1b** and **1c**.

All the ^1H NMR signals of the 2-germanaphthalene ring protons (7.03–8.55 ppm) of **1a** were observed in the aromatic region, and the ^{13}C NMR signals of the 2-germanaphthalene ring carbons (120.75–145.89 ppm) were also located in the sp^2 region. Thus, these results clearly indicate the delocalized π-electronic system for **1a**.

The aromatic character of Tbt-substituted 2-silanaphthalene **1a** was discussed on the basis of the lower-field shifts of its H2 and H3 protons as compared to those of the 1,2-dihydro derivative **3a**, as well as the case of 2-silanaphthalene.[8] Approximately 1 ppm lower field shifts were observed in **1a** (H2, 7.85 ppm; H3, 8.55 ppm) compared with **3a** (H2, 6.53 ppm; H3, 7.23 ppm). These shifts are similar to those between naphthalene (H2, 7.46 ppm; H3, 7.81 ppm) and 1,2-dihydronaphthalene (H2, 5.82 ppm; H3, 6.33 ppm) and those between 2-silanaphthalene (H2, 7.24 ppm; H3, 8.48 ppm) and 1,2-dihydro-2-silanaphthalene (H2, 6.27 ppm; H3, 7.30 ppm)[8] and support the aromatic character of the 2-germanaphthalene ring.



(a) 2-Germanaphthalene (1356 cm^{-1})

(b) Naphthalene (1362 cm^{-1})

Figure 1. Calculated vibration modes with maximum intensity: (a) 2-germanaphthalene; (b) naphthalene.

UV–Vis Spectra. The UV–vis spectrum of 2-germanaphthalene **1a** in hexane showed three absorption maxima (269 ($\epsilon = 2 \times 10^4$), 335 ($\epsilon = 1 \times 10^4$), and 386 nm ($\epsilon = 2 \times 10^3$ M^{-1} cm^{-1})) most likely assignable to the E1, E2, and B bands, respectively. These values shift to wavelength longer than those for naphthalene (221 ($\epsilon = 1.33 \times 10^5$), 286 ($\epsilon = 9.3 \times 10^3$), and 312 nm ($\epsilon = 2.9 \times 10^2$ M^{-1} cm^{-1})),[19] respectively. This propensity is similar to that observed for 2-silanaphthalene (267 ($\epsilon = 2 \times 10^4$), 327 ($\epsilon = 7 \times 10^3$), and 387 nm ($\epsilon = 2 \times 10^3$ M^{-1} cm^{-1})).[8] These results suggest that the 2-germanaphthalene ring system has aromatic character as well as in the cases of naphthalene and 2-silanaphthalene.

Raman Spectra. The Raman spectrum of **1a** showed the most intense Raman signal at 1363 cm^{-1}, which corresponds to the most intense signals of 1382 and 1368 cm^{-1} for naphthalene and 2-silanaphthalene,[8] respectively. This strongest vibrational frequency observed for **1a** is in good agreement with the theoretically calculated value of the most intense line in **1b** (1356 cm^{-1}, computed at the B3LYP/6-31G(d) level and scaled by 0.96).[20] Furthermore, the calculated vibration modes of **1b** considerably resemble those of naphthalene and 2-silanaphthalene, suggesting the structural similarity among naphthalene, 2-silanaphthalene, and 2-germanaphthalene **1a** (Figure 1).

Structure. The molecular geometry of **1a** was finally determined by an X-ray crystallographic analysis (Figure 2). Crystal data for **1a** are summarized in Table 1. The structural analysis revealed the planarity of the 2-germanaphthalene ring and the trigonal-planar geometry around the germanium atom. In addition, the benzene ring of the Tbt group is almost perpendicular to the 2-germanaphthalene ring, and hence it is considered that there is very little conjugative interaction between the two aromatic rings. The bond lengths of the two Ge–C bonds in the 2-germanaphthalene ring (1.803(5) and 1.859(5) Å) are between those of the calculated Ge–C double (1.767 Å) and single bonds (1.908–2.001 Å).[21] In particular, the former Ge–C bond length is close to the Ge–C double bond length of the previously reported germene $Mes_2Ge{=}CR_2$ (1.803(4) Å;

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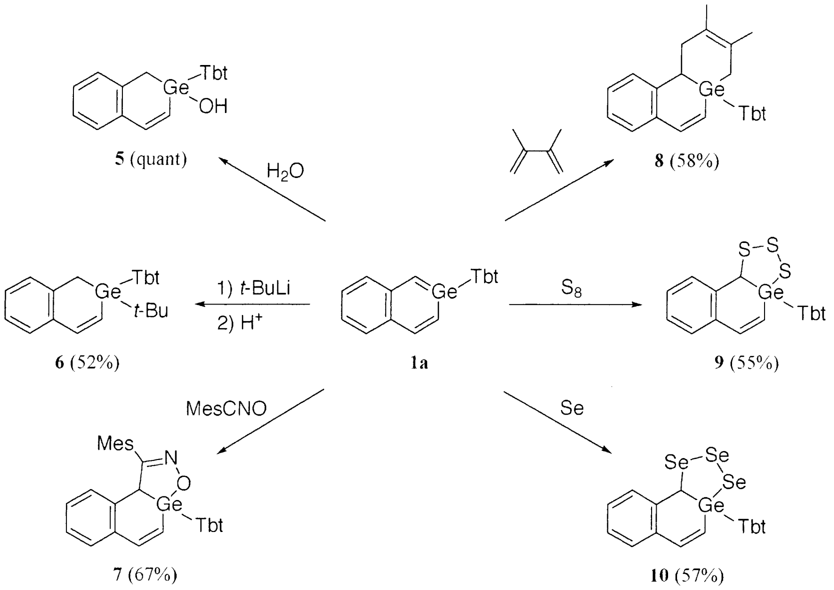
(19) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. In *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991.

(20) For the scaling factor of 0.96, see: Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

(21) Grev, R. S.; Schaefer, H. F., III. *Organometallics* **1992**, *11*, 3489.

Scheme 3



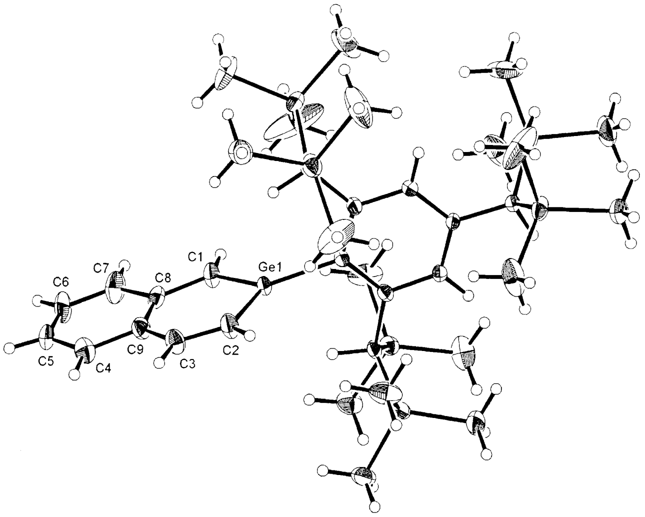


Figure 2. ORTEP drawing of 2-germanaphthalene **1a** (major fragment, 30% probability).

CR_2 = fluorenylidene),[22] which is stabilized by the conjugation of the Ge−C double bond with the fluorenylidene moiety. The C−C bond lengths (1.337(12)−1.450(8) Å) of the 2-germanaphthalene ring were found to vary within almost the same range as reported for naphthalene (1.378−1.426 Å).[23] Furthermore, theoretical calculations for the model compounds **1b** and **1c** were also performed for comparison (Table 3). The experimentally obtained bond lengths for **1a** are fairly in good agreement with those theoretically calculated for **1b** and **1c**.

Reactivity of 2-Germanaphthalene. Despite the high thermal stability of 2-germanaphthalene **1a**, its Ge−C double bond is quite reactive toward various reagents, as shown in Scheme 3.

Thus, 2-germanaphthalene **1a** reacted with water and t-BuLi/H^+ to give the corresponding adducts **5** (quantitative) and **6** (52%), respectively. In the reaction of **1a** with mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene (DMB), [2 + 3] and [2 + 4] cycloaddition reactions proceeded to afford the corresponding cycloadducts **7** and **8** in 67 and 58% yields, respectively. All of these reactions are similar to those of the previously reported germenes whose reactivity has already been explored.[1a,24] Moreover, reactions of **1a** with excess sulfur and selenium afforded the novel Ge-containing cyclic trisulfide **9** (55%) and triselenide **10** (57%), respectively, as stable crystalline compounds.[11]

Table 3. Observed and Calculated Bond Lengths (Å) of 2-Germanaphthalenes

	1a (R = Tbt, obsd[a])	**1b** (R = H, calcd[b])	**1c** (R = Ph, calcd[b])
C1−Ge1	1.803(5)	1.810	1.812
Ge1−C2	1.859(5)	1.851	1.853
C2−C3	1.368(7)	1.374	1.374
C3−C9	1.429(8)	1.433	1.433
C9−C4	1.416(8)	1.423	1.422
C4−C5	1.337(12)	1.376	1.376
C5−C6	1.391(15)	1.414	1.414
C6−C7	1.368(9)	1.374	1.375
C7−C8	1.413(8)	1.429	1.429
C8−C1	1.450(8)	1.421	1.421
C8−C9	1.430(7)	1.446	1.446

[a] The major fragment; two overlapped fragments were restrained to have the same structure. [b] Calculated at the B3LYP/6-31G(d) level.

It has been reported that E=S and E=Se double bonds (E = Ge, Sn) react with an epoxide and an episulfide to afford the corresponding five-membered-ring products.[25] Therefore, the reaction of styrene oxide and *cis*-2,3-diphenylthiirane with **1a** was examined in the hope of obtaining the corresponding five-membered heterocycles by the reactions of the Ge=C double-bond

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(22) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Draeger, M.; Dammel, R. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828.

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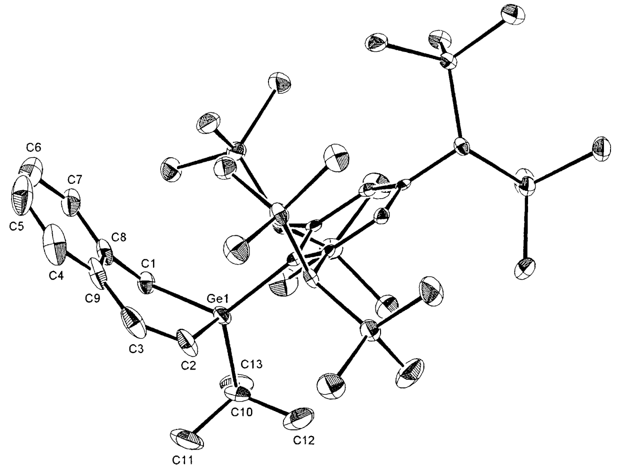


Figure 3. ORTEP drawing of *t*-Bu adduct **6** (50% probability).

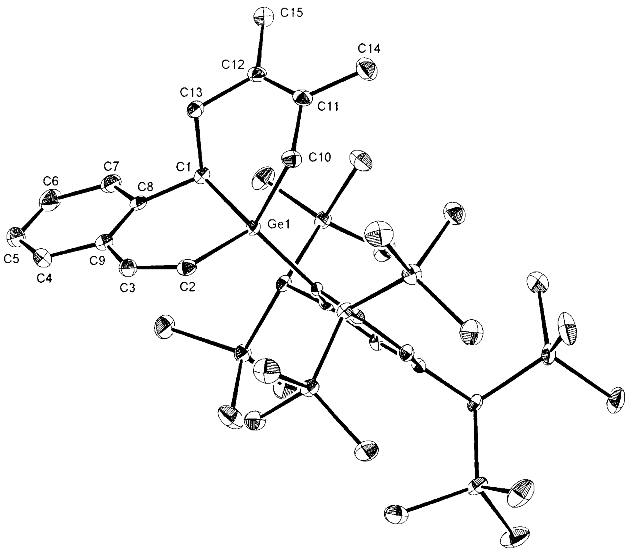
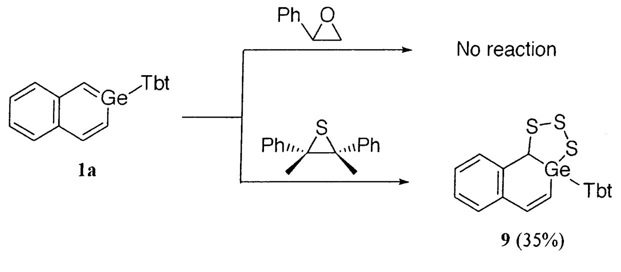


Figure 4. ORTEP drawing of DMB adduct **8** (50% probability).

Scheme 4



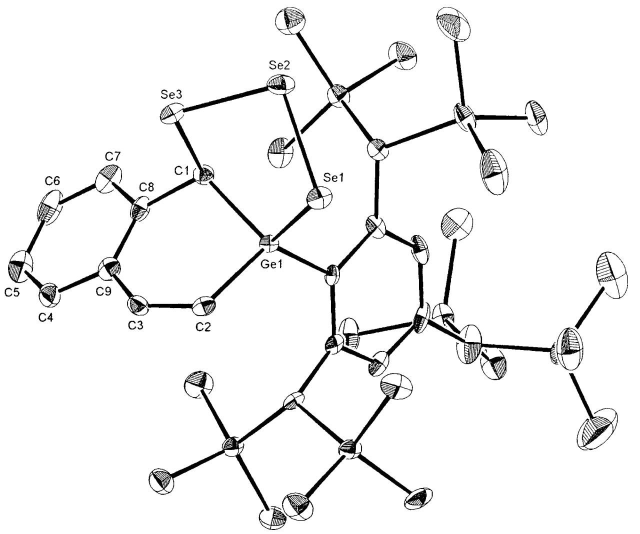


Figure 5. ORTEP drawing of selenium adduct **10** (major fragment, 30% probability).

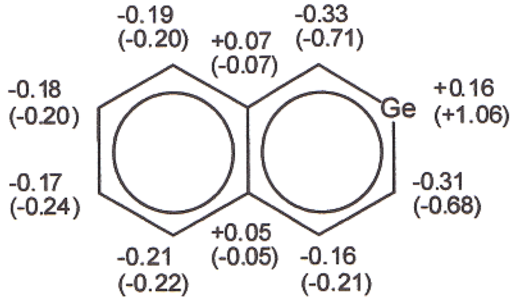
Table 4. Selected Bond Lengths of 6, 8, and 10 (Å)

Compound **6**			
Ge1−C1	1.965(5)	C6−C7	1.381(7)
Ge1−C2	1.957(5)	C7−C8	1.382(7)
C2−C3	1.331(8)	C8−C1	1.513(6)
C3−C9	1.458(8)	Ge1−C10	2.009(5)
C9−C4	1.410(8)	C10−C11	1.541(7)
C4−C5	1.370(9)	C10−C12	1.528(7)
C5−C6	1.382(8)	C10−C13	1.525(7)
Compound **8**			
Ge1−C1	1.982(2)	C8−C9	1.414(3)
Ge1−C2	1.937(2)	C8−C1	1.516(3)
C2−C3	1.335(3)	C1−C13	1.559(3)
C3−C9	1.471(4)	C13−C12	1.508(3)
C9−C4	1.407(3)	C12−C11	1.334(3)
C4−C5	1.382(4)	C12−C15	1.513(3)
C5−C6	1.381(4)	C11−C14	1.508(3)
C6−C7	1.387(3)	C11−C10	1.513(3)
C7−C8	1.391(3)	C10−Ge1	1.984(2)
Compound **10**			
Ge1−Se1	2.4022(10)	C9−C4	1.400(7)
Se1−Se2	2.3503(10)	C4−C5	1.378(8)
Se2−Se3	2.3250(11)	C5−C6	1.388(8)
Se3−C1	1.984(4)	C6−C7	1.387(7)
Ge1−C1	1.979(5)	C7−C8	1.394(7)
Ge1−C2	1.932(4)	C8−C9	1.421(6)
C2−C3	1.336(7)	C8−C1	1.506(6)
C3−C9	1.457(7)		

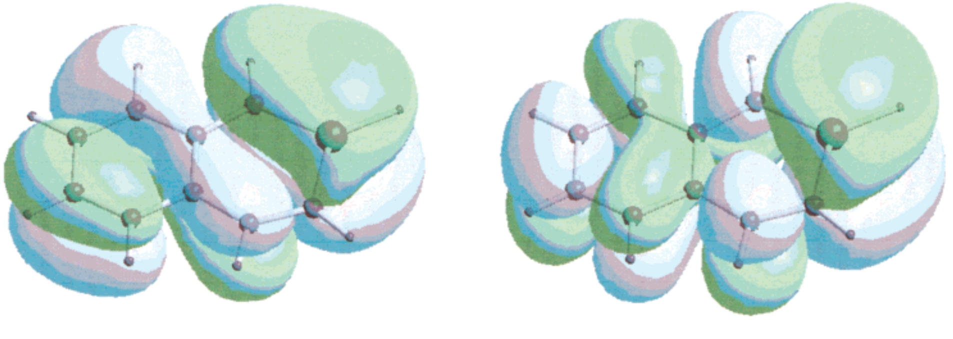
moiety of **1a**. However, the reaction of **1a** with styrene oxide did not occur even at 80 °C, and the reaction with *cis*-2,3-diphenylthiirane afforded trisulfide **9** in 35% yield. Thus, *cis*-2,3-diphenylthiirane served as a sulfur source for **1a** in this reaction (Scheme 4).

The structures of **6**, **8**, and **10** were established by X-ray crystallographic analysis (Figures 3−5). Crystal data and selected bond lengths for **6**, **8**, and **10** are summarized in Tables 1 and 4, respectively. The high reactivity of 2-germanaphthalene **1a** and the inspection of the molecular structures of **6**, **8**, and **10** indicate that the Tbt group affords enough reaction space around the central Ge atom, despite its severe steric hindrance.

2-Germanaphthalene **1a** reacted with various reagents and afforded the corresponding adducts to the double bond between the germanium atom and the carbon atom at the 1-position of the 2-germanaphthalene ring. These results agreed with the highly double bond character of the Ge−C(1) bond indicated in the X-ray crystallographic analysis of **1a**. In addition, these reactivities can be supported by the charge distribution and molecular orbital theory. Figure 6 gives a drawing of the calculated Mulliken and NPA (natural population analysis)[16] charge distributions and the LUMO and HOMO of parent 2-germanaphthalene (**1b**). The charge distributions of 2-germanaphthalene at the MP2/6-31G(d) level show greatly positive charge on the germanium atom, and the LUMO of 2-germanaphthalene has large coefficients on the germanium atom. The HOMO contains a bonding π-orbital on the 1,2-positions of the 2-germanaphthalene ring with a large coefficient, while the LUMO has an antibonding π-orbital on the same



charge distributions



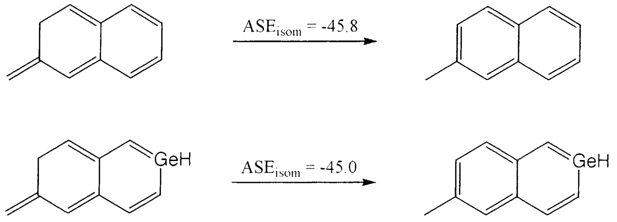
HOMO **LUMO**

Figure 6. Charge distributions (top, Mulliken charges and NPA charges in parentheses) and molecular orbitals (bottom, HOMO (left) and LUMO (right)) of the parent 2-germanaphthalene **1b**.

bond. These molecular orbitals indicate favorable interaction at the 1,2-position with the molecular orbitals of 2,3-dimethyl-1,3-butadiene in the [2 + 4] cycloaddition. The high electrophilicity on the germanium atom of 2-germanaphthalene can also be interpreted in terms of the theoretical calculations.

Aromaticity of 2-Germanaphthalene. As described above, the spectral data and the structural analysis of 2-germanaphthalene **1a** strongly indicate its aromaticity. On the other hand, we have already revealed that 2-silanaphthalene has aromaticity as well as naphthalene by theoretical calculations (nucleus-independent chemical shifts (NICS)[26] and aromatic stabilization energy (ASE)).[8b] Similarly to the case of 2-silanaphthalene, the aromatic character of 2-germanaphthalene was evaluated by computing the NICS(1) and $\mathrm{ASE_{isom}}$ values. Moreover, the diamagnetic susceptibility exaltation (Λ)[27] of 2-germanaphthalene was also calculated by the CSGT method.[28] The NICS(1) value at 1 Å above the ring and Λ value of 2-germanaphthalene **1b** showed large negative values (NICS(1), −9.3 ppm for the C_5Ge ring and −10.9 ppm for the C_6 ring, Λ, −27.9 ppm cgs), which were comparable to that for naphthalene (NICS(1), −11.4 ppm; Λ, −30.4 ppm cgs).[29] In addition, the results of calculations for aromatic stabilization energies ($\mathrm{ASE_{isom}}$)[8b,12,30] of naphthalene and 2-germanaphthalene based on the isomerization reactions of methyl-substituted aromatic isomers are summarized in Chart 2. The $\mathrm{ASE_{isom}}$ value for 2-germanaphthalene was found to be almost the same as that for naphthalene, suggesting that the aromatic stabilization effect is very slightly reduced by the replacement of the one ring carbon in naphthalene by a germanium atom. These results indicate that the 2-germanaphthalene has ring current effects and is stabilized by aromatization in the same manner as naphthalene.

Chart 2. Calculated Aromatic Stabilization Energies ($\mathrm{ASE_{isom}}$ in kcal/mol, B3LYP/6-311+G(d,p)//Opt)



Meanwhile, 2-germanaphthalene is highly reactive, in contrast to the ordinary aromatic hydrocarbons. Judging from only this result, one can conclude 2-germanaphthalene to be nonaromatic. However, molecules with a Ge−C double bond are inherently much more reactive than those with a C−C double bond. For example, addition of water to a Ge−C double bond is more exothermic than that to a C−C double bond by about 40 kcal/mol.[12] Therefore, the addition of water to the Ge−C double bond of 2-germanaphthalene readily proceeds, although 2-germanaphthalene has almost the same aromatic stabilization effect as that of naphthalene (ca. 45 kcal/mol). Thus, the high reactivity of

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(29) The evaluation of Λ for **1b** and naphthalene are described in the Supporting Information.

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2-germanaphthalene is not contradictory to its aromaticity but is reasonably interpreted in terms of the strong tendency to undergo an addition reaction across the Ge−C double bond, which cannot be thoroughly suppressed even by the aromatic stabilization of 2-germanaphthalene.

Conclusion

We succeeded in the synthesis of 2-germanaphthalene **1a**, the first example of a stable neutral aromatic compound containing a germanium atom, by taking advantage of a bulky Tbt group. A detailed analysis of the spectral data (^{1}H and ^{13}C NMR, UV−vis, and Raman spectra) and X-ray crystallographic analysis revealed that 2-germanaphthalene **1a** has a delocalized 10-π-electron ring system, as does naphthalene. 2-Germanaphthalene **1a** reacted with some reagents as a Ge−C double-bond compound (germene) to give the corresponding adducts to the double bond between the germanium atom and the carbon atom at the 1-position of the 2-germanaphthalene ring. Large negative NICS(1) values, diamagnetic susceptibility exaltation (Λ), and theoretical energetic evaluations also indicate the existence of ring current effects and aromatic stabilization in the 2-germanaphthalene ring. Thus, all the results here obtained experimentally and theoretically indicate the aromatic character of 2-germanaphthalene **1a**.

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Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1a**, **6**, **8**, and **10**, a table of the observed Raman shifts for **1a** and total electronic energies and atomic coordinates for all molecules used in Chart 2, and a scheme and a table for evaluation of Λ for **1b** and naphthalene. This material is available free of charge via the Internet at http://pubs.acs.org.

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