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Synthesis and Properties of the First Stable Germabenzene

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Abstract: The first stable germabenzene (**1a**) bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, was successfully synthesized by the reaction of the corresponding chlorogermane (**4**) with lithium diisopropylamide in THF. 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 ^{1}H and ^{13}C NMR chemical shifts of the germabenzene ring of **1a** were in good agreement with those calculated. UV−vis and Raman spectra of **1a** showed patterns similar to those of benzene, suggesting the structural similarity between germabenzene and benzene. X-ray crystallographic analysis of **1a** revealed that the germabenzene ring was almost planar, indicating the delocalization of π-electrons. Theoretical calculations (NICS(1) and ASE_{isom}) also indicated the ring current effects and aromatic stabilization of the germabenzene. While germabenzene **1a** reacted as a Ge−C double-bond compound (germene) with mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene, **1a** also reacted as a 1-germabuta-1,3-diene with C−C double- and triple-bond compounds. Furthermore, **1a** reacted with water and MeOH to give both 1, 2- and 1, 4-adducts.

Introduction

Recently, much attention has been focused on the chemistry of $[4n + 2]$ π-electron ring systems containing at least one heavier group 14 element,[1,2] since they are the heavier congeners of aromatic hydrocarbons which occupy a great part of organic chemistry.[3] Among them, some silicon analogues of aromatic compounds, i.e., silaaromatic compounds, have been observed spectroscopically in low-temperature matrixes and in the gas phase,[4] and their structures have been theoretically predicted.[1,5] However, no synthesis and isolation of the silaaromatic compounds as stable molecules had been reported until quite recently due to their extremely high reactivity. We recently succeeded in the synthesis and characterization of a kinetically stabilized 2-silanaphthalene, the first example of a stable neutral silaaromatic compound, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt).[6] More recently, we reported the synthesis of a stable Tbt-substituted silabenzene[7a] and its structural determination by X-ray crystallographic analysis.[7b]

Meanwhile, the experimental and theoretical studies of the germanium analogues of aromatic compounds, i.e., germaaromatic compounds,[8] are far fewer than those of silaaromatic compounds. Märkl et al. previously reported the synthesis of 1,4-di-*tert*-butylgermabenzene,[9] but the generation was supported only by the formation of its $[2 + 2]$ dimer and the trapping reaction with 2,3-dimethyl-1,3-butadiene. Furthermore, they described the spectroscopic detection of 1,4-dialkylgermabenzenes in the gas phase by variable-temperature photoelectron

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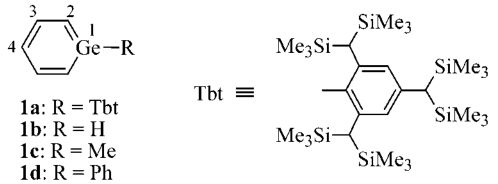
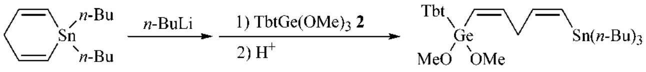
10.1021/ja0262941 CCC: $22.00

Scheme 1



1a: R = Tbt
1b: R = H
1c: R = Me
1d: R = Ph

Scheme 2



3

Table 1. Conditions and Yields of **3** in the Transmetalation Reaction

run	*n*-BuLi (molar equiv)	reaction conditions	results
1	2.1	0 °C/2.5 h/Et_2O	complex mixture
2	2.2	rt/12 h/Et_2O	**3** (trace)[a]
3	2.1	rt/12 h/THF	no reaction
4	1.1	rt/48 h/Et_2O	**3** (61%)
5	1.0	reflux/92 h/Et_2O	**3** (27%)

[a] Complex mixture containing a trace amount of **3**.

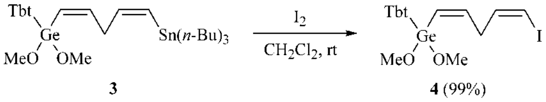
spectroscopy (VTPES) experiments.[10] In addition, Kiprof and Brown recently reported the theoretical calculation of germabenzene and its valence isomers.[11] Very recently, we reported on the synthesis and structure of 2-germanaphthalene, kinetically stabilized with a Tbt group,[12] which is the first example of a stable neutral germaaromatic compound. The successful results in the sila- and germaaromatic systems naturally prompted us to extend this method to the synthesis of a germabenzene, which is the most fundamental germaaromatic compound having a simple 6π-electron ring system. In this paper, we report the synthesis, structure, and reactivity of the first stable germabenzene **1a** bearing a Tbt group (Scheme 1).

Results and Discussion

Synthesis of Germabenzene. We planned the synthesis of germabenzene **1a** by the dehydrohalogenation of 1-halogermacyclohexa-2,5-diene as well as the case of the stable silabenzene.[7a] At first, we attempted the synthesis of the germacyclohexa-2,5-diene derivatives bearing a Tbt group on the germanium atom by the transmetalation reaction of stannacyclohexa-2,5-diene[12] with *n*-BuLi and the subsequent addition of TbtGe(OMe)$_3$ (**2**), which was synthesized by the reaction of TbtLi with $GeCl_4$ followed by the treatment with MeOH in the presence of Et_3N (Scheme 2). The reactions under various conditions were performed as shown in Table 1.

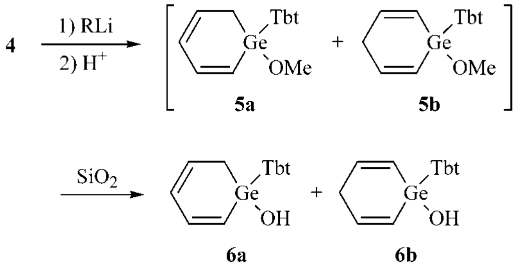
No desired germacyclohexa-2,5-diene was obtained in all cases, while a complex mixture containing a trace amount of 5-tributylstannyl-1,4-pentadienylgermane (**3**) was afforded in the reaction with 2 molar equivalents of *n*-BuLi (run 2). The reaction with 1 molar equivalent of *n*-BuLi in Et_2O gave **3** in a moderate yield (run 4), and the formation of **3** was interpreted in terms of the mono-transmetalation of stannacyclohexa-2,5-diene. The reactions of isolated **3** with various bases (MeLi, *n*-BuLi, and *t*-BuLi) did not give the desired germacyclohexa-2,5-diene, probably due to the low reactivity of **3**. Thus, another synthetic route to germacyclohexa-2,5-diene derivatives, i.e., halodestannylation of **3** and subsequent lithium−halogen exchange reaction followed by the intramolecular cyclization, was investigated. The halodemetalation reaction of **3** with iodine in CH_2Cl_2 afforded the corresponding 5-iodo-1,4-pentadienylgermane (**4**) quantitatively (Scheme 3).

Scheme 3



3 **4** (99%)

Scheme 4



5a **5b** **6a** **6b**

The lithium−halogen exchange reaction of vinyl iodide **4** with *n*-BuLi or *t*-BuLi resulted in the cyclization of intermediary vinyllithium to give the expected germacyclohexa-2,4-diene (**5a**) and/or germacyclohexa-2,5-diene (**5b**), the formation of which was confirmed by ^1H NMR spectroscopy (Scheme 4).

Since both germacyclohexadienes **5a** and **5b** were unstable under ambient conditions, probably due to their lability for hydrolysis, they were readily converted into the corresponding hydroxygermanes **6a** and **6b**, respectively, during the chromatographic separation on silica gel. In Table 2 are shown the results of the optimization of the yields of hydroxygermane **6a**.

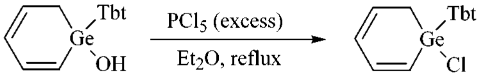
Table 2. Conditions and Yields of Each Product in the Cyclization of **4**

run	RLi (molar equiv)	reaction conditions	products[a]
1	*n*-BuLi (1.2)	0 °C/1 h/Et_2O	**4** (69%), **6b** (26%)
2	*n*-BuLi (2.2)	0 °C/1 h/Et_2O	**4** (15%), **6a** (21%), **6b** (21%)
3	*t*-BuLi (2.2)	−10 °C/2 h/Et_2O	**4** (23%), **6a** (39%), **6b** (trace)
4	*t*-BuLi (2.4)	−30 °C/2 h/Et_2O	**4** (6%), **6a** (48%)
5	*t*-BuLi (2.3)	−40 °C/2 h/Et_2O	**4** (10%), **6a** (49%)

[a] Isolated yields.

Although the reaction of **4** with 1.2 molar equivalents of *n*-BuLi at 0 °C did not give **6a** but only **6b** (26%) together with a large amount of recovered starting material **4** (run 1), the use of an excess amount of *n*-BuLi (2.2 molar equivalents) at 0 °C led to the competitive formation of **6a** and **6b** (both in 21%) along with 15% of recovered **4** (run 2). The yield of **6a** was further increased to 49% by lowering the reaction temperature and using *t*-BuLi instead of *n*-BuLi (runs 3−5). Chlorination of **6a** with excess of PCl_5 in Et_2O resulted in the quantitative formation of the corresponding chlorogermane **7**, which can be a suitable precursor for germabenzene **1a** (Scheme 5).

Scheme 5



6a **7** (96%)

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Scheme 6

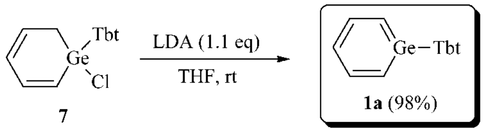

Table 3. Observed and Calculated ^{1}H and ^{13}C NMR Chemical Shifts (ppm) of Germabenzenes **1**

	observed[a]	calculated[b]		
	1a (R = Tbt)	**1b** (R = H)	**1c** (R = Me)	**1d** (R = Ph)[c]
H2	7.85	7.55	7.25	7.20
H3	8.06	7.93	7.83	7.89
H4	6.72	6.69	6.50	6.58
C2	132.23	135.81	130.70	130.06
C3	140.96	141.00	140.95	140.48
C4	114.56	115.79	114.25	114.36

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

Dehydrochlorination of **7** with lithium diisopropylamide (LDA) in THF at room temperature proceeded efficiently, and almost pure germabenzene **1a** was successfully isolated as colorless crystals by very simple procedures, i.e., the decantation for the removal of inorganic salts and the subsequent evaporation of volatile materials (Scheme 6).

Although germabenzene **1a** is highly moisture sensitive, it is thermally very stable under an inert atmosphere either in the solid state (mp 118−122 °C) or in solution (benzene, at 100 °C for 3 h in a sealed tube) and no dimerization or decomposition was observed. **1a** is the first synthetic example of a stable germabenzene. The stability of **1a** is in a sharp contrast to that of 1,4-di-*tert*-butyl-1-germabenzene, which reportedly undergoes the facile dimerization even at 0 °C.[10]

NMR Spectra. ^{1}H and ^{13}C NMR chemical shifts of germabenzene **1a** are listed in Table 3 along with the calculated values for some model compounds, i.e., germabenzene **1b**, 1-methyl-1-germabenzene **1c**, and 1-phenyl-1-germabenzene **1d**.

The ^{1}H and ^{13}C NMR spectra of **1a** showed that the germabenzene ring had a C_2 axis passing through the Ge and C4 atoms in solution. All the ^{1}H NMR chemical shifts assigned to the germabenzene ring protons (6.72, 7.85, and 8.06 ppm) of **1a** were observed in the aromatic region, and the ^{13}C NMR chemical shifts of the germabenzene ring carbons (114.56, 132.23, and 140.96 ppm) of **1a** were also located in the aromatic region. The observed values are in excellent agreement with calculated ones. These results clearly indicate the delocalized π-electronic system and the aromatic character of the germabenzene ring of **1a**.

UV−Vis Spectra. Germabenzene **1a** showed four absorption maxima at 225 (sh), 298 (ϵ 1 × 10^3), 322 (ϵ 8 × 10^2), and 326 nm (ϵ 7 × 10^2) in hexane. These absorption maxima of **1a** can be assigned to the *E*1 (225 nm), *E*2 (298 nm), and *B* (322 and 326 nm) bands, although these are shifted to longer wavelengths compared to those of benzene [184 (*E*1 band), 204 (*E*2 band), and 256 (*B* band) nm].[14] These values resembled considerably those of the Tbt-substituted silabenzene[7b] and also those of transient silabenzenes observed in low-temperature matrixes.[1a,15] These results suggest that this conjugated ring system containing a germanium atom has aromatic character similarly to the cases of benzene and silabenzene.

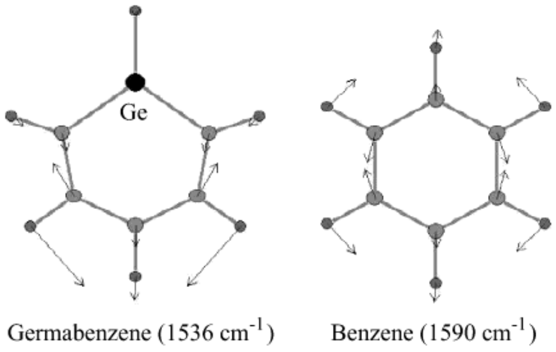

Figure 1. Calculated vibration modes of germabenzene (1536 cm^{-1}) and benzene (1590 cm^{-1}).

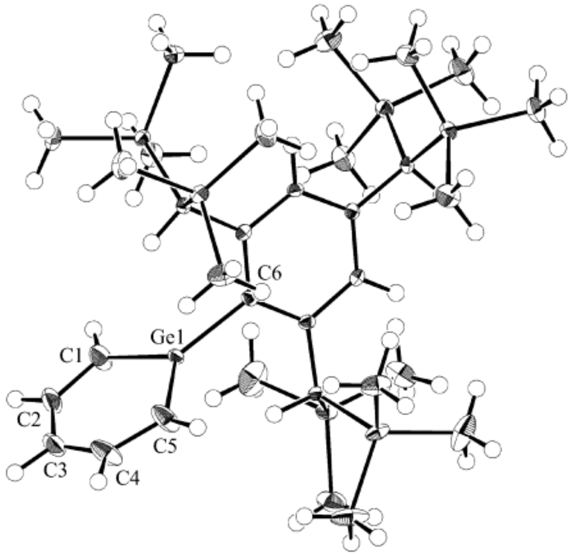

Figure 2. ORTEP drawing of germabenzene **1a** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ge1−C1 1.829(2), Ge1−C5 1.827(2), C1−C2 1.389(3), C2−C3 1.389(3), C3−C4 1.385(3), C4−C5 1.396(3), C1−Ge1−C5 105.81(9), C1−Ge1−C6 125.61(8), C5−Ge1−C6 128.56(8), Ge1−C1−C2 117.88(15), C1−C2−C3 126.55(19), C2−C3−C4 125.48(18), C3−C4−C5 126.55(19), Ge1−C5−C4 117.82(16).

Raman Spectra. The Raman spectrum of **1a** showed the most intense Raman line at 1533 cm^{-1}, which corresponds to the most intense line of 1530 cm^{-1} observed for Tbt-substituted silabenzene. This strongest vibrational frequency observed for **1a** is in good agreement with the theoretically calculated one (1536 cm^{-1} for the parent germabenzene **1b**, computed at the B3LYP/6-31G(d) level and scaled by 0.96).[16] Furthermore, the calculated vibration mode for the most intense line of **1b** is similar to those of parent benzene (1590 cm^{-1}) and silabenzene (1528 cm^{-1}) as a whole (Figure 1).[17] These results also support the structural similarity among germabenzene, silabenzene, and benzene.

Structure. The molecular geometry of **1a** was definitely determined by X-ray crystallographic analysis at −170 °C, and the ORTEP drawing is shown in Figure 2.

The structural analysis revealed the completely trigonal planar geometry around the germanium atom and the planarity of the

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Table 4. Observed and Calculated Bond Lengths (Å) of Germabenzenes **1**

	observed		calculated[a]	
	1a (R = Tbt)	**1b** (R = H)	**1c** (R = Me)	**1d** (R = Ph)[b]
Ge−C1	1.829(2), 1.827(2)	1.845	1.848	1.848
C1−C2	1.389(3), 1.396(3)	1.394	1.395	1.395
C2−C3	1.389(3), 1.385(3)	1.402	1.402	1.402

[a] Calculated at the B3LYP/6-311+G(d,p) level. [b] The phenyl group is fixed in such a way that it is perpendicular to the germabenzene ring.

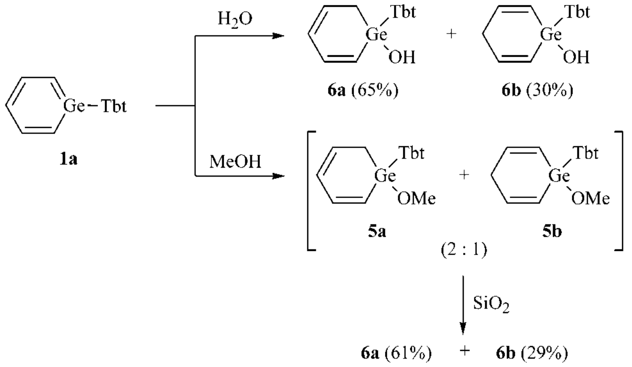
germabenzene ring (sum of the bond angles around the central germanium atom and that of the interior bond angles of the germabenzene ring are 360° and 720°, respectively). The lengths of the two Ge−C bonds in the germabenzene ring (1.827(2) and 1.829(2) Å) are almost the same, and they are in the middle between those of calculated Ge−C double (1.767 Å) and single bonds (1.908−2.001 Å).[18] The lengths of the four C−C bonds of the germabenzene ring (1.385(3)−1.396(3) Å) are almost equal to each other within the error of temperature factors, and they are also similar to the C−C bond lengths of parent benzene (1.39−1.40 Å).[3] Thus, these results strongly support that germabenzene **1a** has a delocalized 6π-electron ring system similar to that of benzene.

Theoretical calculations for the model compounds **1b**−**1d** (R = H, Me, Ph) were also performed for comparison (Table 4). The Ge−C and C−C bond lengths of the germabenzene rings are little affected by substituents on the germanium atom, and the agreement between the experimental and theoretical values is excellent.

Reactivity of Germabenzene. Since germaaromatic compounds can be regarded as both aromatic compounds and low-coordinated organogermanium compounds, elucidation of the reactivity of germaaromatics is an interesting subject. In particular, it is expected that germabenzenes have reactivity as aromatic compounds, Ge−C double-bond compounds, and 1-germabuta-1,3-dienes. However, the reactivity of germaaromatic compounds is less studied because of their instability and difficulty in their synthesis. To our knowledge, only one reaction of 1,4-di-*tert*-butylgermabenzene with 2,3-dimethyl-1,3-butadiene to give [2 + 4] cycloadduct has been reported by Märkl et al.[10] Thus, we examined reactions of stable germabenzene **1a** with some reagents. Germabenzene **1a** was allowed to react with water to give both the 1,2-adduct **6a** (65%) and the 1,4-adduct **6b** (30%). The reaction of **1a** with methanol also gave the corresponding 1,2-adduct **5a** and the 1,4-adduct **5b** in a ratio of 2:1, judging from the integral of the ^{1}H NMR signals. The formation of methoxygermanes **5a** and **5b** in this ratio was also confirmed by the chromatographic separation of the mixture on silica gel, giving the hydroxygermanes **6a** and **6b** in 61 and 29% yields, respectively (Scheme 7).

In the reaction of **1a** with mesitonitrile oxide, a 1,3-dipolar reagent, [2 + 3] cycloaddition proceeded to afford the corresponding cycloadduct **8** in 86% yield. Furthermore, 2,3-dimethyl-1,3-butadiene also reacted with **1a** to give the [2 + 4] cycloadduct **9** in 69% yield. On the other hand, **1a** reacted as a 1-germabuta-1,3-diene with C−C double and triple bonds such as those in styrene and phenylacetylene to give the corresponding [4 + 2] cycloadducts **10** (62%) and **11** (58%), respectively (Scheme 8).

Scheme 7



Scheme 8

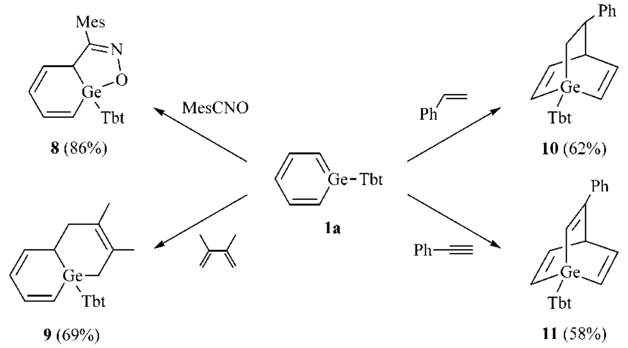


Chart 1. Calculated NICS(1) (ppm) Values for Germabenzene and Benzene at the GIAO-B3LYP/6-311G(d) Level

Aromaticity of Germabenzene. As described above, the spectral data and the structural analysis of germabenzene **1a** strongly indicate its aromaticity, while **1a** shows reactivities as not an aromatic compound but as a Ge−C double-bond compound. These properties, which appear to contradict each other, are reasonably explained by the calculations of nucleus-independent chemical shift (NICS)[19] and aromatic stabilization energy (ASE), as well as the case of stable 2-silanaphthalene.[6b] Computing the NICS(1) value at 1 Å above the ring of germabenzene **1b** showed the large negative value (−9.0 ppm) for **1b**, which is comparable to that for benzene (−11.1 ppm) (Chart 1).

This result predicted that germabenzene **1b** also has considerable aromatic character, as does benzene. In addition, we carried out the calculations of aromatic stabilization energies ($\mathrm{ASE_{isom}}$)[6b,20] for benzene and germabenzene based on the isomerization reactions of toluene and germatoluene, as shown in Chart 2.

These $\mathrm{ASE_{isom}}$ values were found to be almost the same, suggesting that the aromatic stabilization effect is very slightly reduced by the replacement of the one ring carbon in benzene by a germanium atom. Considering that germabenzene is highly reactive in contrast to benzene, one may feel that germabenzene is not aromatic. However, the high reactivity of germabenzene

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

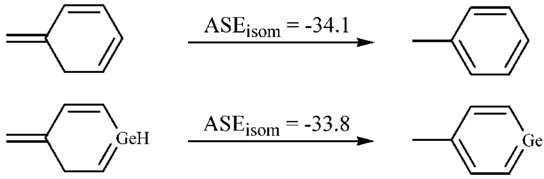
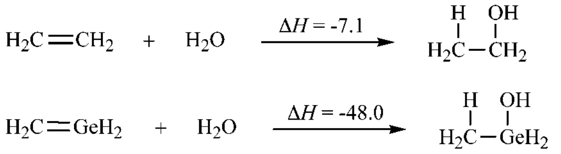


Chart 3. Heats of Reaction for the Addition of Water to Ethylene and Germene (kcal/mol, B3LYP/6-311+G(d,p))



$$H_2C{=}CH_2 + H_2O \xrightarrow{\Delta H = -7.1} H_2C(H){-}CH_2(OH)$$

$$H_2C{=}GeH_2 + H_2O \xrightarrow{\Delta H = -48.0} H_2C(H){-}GeH_2(OH)$$

is ascribed to the fact that a Ge=C double bond is inherently much more reactive than a C=C double bond. For example, addition of water to a Ge=C double bond is calculated to be more exothermic than addition of water to a C=C double bond by more than 40 kcal/mol (Chart 3). Therefore, the addition of water to the Ge=C double bond of germabenzene readily proceeds, although germabenzene has almost the same aromatic stabilization effect as benzene (ca. 34 kcal/mol). Thus, the high reactivity of germabenzene 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 bond, which cannot be suppressed even by the aromatic stabilization energy of germabenzene.

Conclusion

We have succeeded in the synthesis of the first stable germabenzene **1a** by taking advantage of a bulky Tbt group. The detailed analysis of the spectral data (^{1}H and ^{13}C NMR, UV−vis, and Raman spectra) and X-ray crystallographic analysis revealed that germabenzene **1a** has a delocalized 6π-electron ring system as does benzene. On the other hand, **1a** reacted with some reagents as a germene and/or a 1-germabuta-1,3-diene despite its aromaticity. Theoretical calculations (NICS-(1) and ASE_{isom}) revealed that this reactivity was ascribed to the extremely high reactivity of the Ge−C double bond, which cannot be suppressed by the aromatic stabilization of the germabenzene ring. Taking into account all of these results, we came to the conclusion that germabenzene is highly aromatic, but it still has enough reactivity toward the addition reaction across the Ge−C double bond. We believe that these results provide us with important information about the chemistry of aromatic compounds containing heavier group 14 elements.

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) and ^{13}C NMR (100 or 75 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. Wet column chromatography (WCC) was performed on Wakogel C-200. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908, LC-918, or LC-908-C60 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (for LC-908 and LC-918) or JAIGEL 1H-40 and 2H-40 columns (for LC-908-C60) (eluent: chloroform or toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. 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. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr)[21] and 1,1-dibutyl-1-stannacyclohexa-2,4-diene[13] were prepared according to the reported procedures.

Theoretical Calculations. The geometries of germabenzenes and related reference molecules were optimized by using the Gaussian 98 program at B3LYP/6-311+G(d,p) levels of density functional theory.[22] The GIAO-B3LYP and NICS calculations were carried out with 6-311G(3d) for Ge and 6-311G(d) for C and H. In geometry optimization of phenylgermabenzene **1d**, the phenyl group was fixed perpendicularly to the germabenzene ring.

Preparation of Trimethoxy{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}germane (2). To a solution of TbtBr (9.3 g, 14.7 mmol) in THF (100 mL) was added *t*-BuLi (2.38 M in pentane, 13.5 mL, 32.1 mmol) at −78 °C. After the mixture was stirred for 30 min, $GeCl_4$ (2.0 mL, 17.1 mmol) was added at −78 °C. The reaction mixture was warmed to room temperature within 2 h. To the resulting solution containing $TbtGeCl_3$ were added MeOH (50 mL) and Et_3N (10 mL) at room temperature, and the solution was heated under reflux for 2 h. After removal of the solvents, hexane and water were added to the residue, and the mixture was extracted with hexane several times. The combined organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to give almost pure **2** (8.64 g, 82%) as a white powder. **2**: mp 172−175 °C; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 54H), 1.33 (s, 1H), 2.43 (s, 2H), 3.70 (s, 9H), 6.29 (br s, 1H), 6.41 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.43 (q), 0.67 (q), 28.12 (d), 28.50 (d), 30.59 (d), 52.13 (q), 122.14 (d), 123.53 (s), 126.95 (d), 146.39 (s), 151.30 (s), 151.57 (s). Anal. Calcd for $C_{30}H_{68}GeO_3Si_6$: C, 50.19; H, 9.55. Found: C, 50.28; H, 9.58.

Preparation of Dimethoxy(5-tributylstannylpenta-1,4-dienyl)-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}germane (3). To a solution of 1,1-dibutyl-1-stannacyclohexa-2,4-diene (690 mg, 2.31 mmol) in Et_2O (4 mL) was added *n*-BuLi (1.70 M in hexane, 1.50 mL, 2.55 mmol) at 0 °C. After the solution was stirred for 30 min, a suspension of **2** (1.48 g, 2.06 mmol) in Et_2O (4 mL) was added at room temperature, and the mixture was stirred for 48 h. After the reaction was quenched 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 removal of the solvents followed by purification with GPLC ($CHCl_3$) afforded **3** (1.32 g, 61%) as colorless crystals. **3**: mp 46−49 °C; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 18H), 0.04 (s, 36H), 0.86−0.95 (m, 15H), 1.27−1.37 (m, 7H), 1.45−1.58 (m, 6H), 2.58 (br s, 1H), 2.60 (br s, 1H), 3.17 (dd, *J* = 7.4, 7.4 Hz, 2H), 3.57 (s, 6H), 5.65 (d, *J* = 12.3 Hz, 1H), 5.93 (d, *J* = 12.3 Hz, 1H), 6.27 (br s, 1H), 6.36−6.53 (m, 3H);

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^{13}C NMR ($CDCl_3$) δ 0.73 (q), 1.00 (q), 10.25 (t), 13.71 (q), 27.33 (t), 27.47 (d), 27.67 (d), 29.22 (t), 30.43 (d), 41.32 (t), 51.76 (q), 122.32 (d), 126.25 (d), 126.83 (s), 127.13 (d), 130.68 (d), 145.41 (s), 145.88 (d), 148.58 (d), 151.20 (s), 151.47 (s). Anal. Calcd for $C_{46}H_{98}GeO_2Si_6Sn$: C, 52.97; H, 9.47. Found: C, 52.85; H, 9.57.

Preparation of 5-Iodopenta-1,4-dienyl(dimethoxy){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}germane (4). To a solution of **3** (731 mg, 0.70 mmol) in CH_2Cl_2 (10 mL) was added I_2 (213 mg, 0.84 mmol) at room temperature, and the mixture was stirred for 1 h. After the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 several times. The combined organic layer was dried over $MgSO_4$, and removal of the solvents followed by purification with GPLC ($CHCl_3$) afforded **4** (601 mg, 99%) as colorless crystals. **4**: mp 100−103 °C; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 18H), 0.05 (s, 36H), 1.33 (s, 1H), 2.55 (br s, 1H), 2.57 (br s, 1H), 3.33 (dd, J = 7.2, 7.2 Hz, 2H), 3.58 (s, 6H), 5.72 (d, J = 12.9 Hz, 1H), 6.21−6.34 (m, 3H), 6.39 (br s, 1H), 6.50 (dt, J = 7.2, 12.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.75 (q), 1.01 (q), 27.49 (d), 27.74 (d), 30.45 (d), 38.88 (t), 51.79 (q), 77.21 (d), 83.60 (d), 122.29 (d), 126.60 (s), 127.15 (d), 138.52 (d), 145.51 (s), 145.69 (d), 151.14 (s), 151.40 (s). Anal. Calcd for $C_{34}H_{71}GeIO_2Si_6$: C, 46.41; H, 8.13. Found: C, 46.61; H, 8.28.

Cyclization of 4. To a solution of **4** (788 mg, 0.90 mmol) in Et_2O (15 mL) was added *t*-BuLi (2.36 M in pentane, 0.85 mL, 2.01 mmol) at −40 °C, and the solution was stirred for 2 h. After the solution was warmed to room temperature and stirred for 12 h, the reaction was stopped by the addition of 1 M HCl (10 mL). 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 solvent was removed to give the crude product as white solids, containing 1-methoxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclohexa-2,4-diene (**5a**) and the unreacted **4** in a molar ratio of 5:1 (observed by ^{1}H NMR). Purification using WCC (hexane/$CHCl_3$ = 3:1) afforded 1-hydroxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclohexa-2,4-diene (**6a**) (311 mg, 49%) as a white powder, which was formed by hydrolysis of methoxygermane **5a** on the SiO_2, together with **4** (79 mg, 10%). **6a**: mp 161−163 °C; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 18H), 0.04 (s, 36H), 0.67 (s, 1H), 1.31 (s, 1H), 2.04−2.07 (m, 2H), 2.28 (br s, 2H), 5.90−5.97 (m, 1H), 6.08−6.15 (m, 1H), 6.26 (br s, 1H), 6.38 (br s, 1H), 6.47 (d, J = 12.9 Hz, 1H), 6.70 (dd, J = 6.3, 12.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.50 (q), 0.69 (q), 0.85 (q), 1.03 (q), 21.20 (t), 28.17 (d), 28.47 (d), 30.31 (d), 121.99 (d), 125.33 (d), 126.91 (d), 129.27 (s), 129.83 (d), 131.27 (d), 138.52 (d), 144.85 (s), 150.15 (s), 150.49 (s). Anal. Calcd for $C_{32}H_{66}GeOSi_6$: C, 54.29; H, 9.40. Found: C, 53.91; H, 9.46.

Chlorination of 6a. A mixture of **6a** (209 mg, 0.30 mmol) and excess PCl_5 (601 mg, 2.88 mmol) in Et_2O (20 mL) was refluxed for 3.5 h. After removal of the solvent, hexane was added to the residue, and the mixture was filtered with Celite. Evaporation of the filtrate under reduced pressure afforded almost pure 1-chloro-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclohexa-2,4-diene (**7**) (208 mg, 97%) as a white powder. **7**: mp 174−176 °C; ^{1}H NMR (C_6D_6) δ 0.14 (s, 18H), 0.20 (s, 18H), 0.23 (s, 18H), 1.45 (s, 1H), 2.37−2.59 (m, 2H), 2.44 (br s, 2H), 5.68−5.74 (m, 1H), 5.86−5.92 (m, 1H), 6.39 (dd, J = 6.6, 12.9 Hz, 1H), 6.51 (br s, 1H), 6.63 (br s, 1H), 6.71 (d, J = 12.9 Hz, 1H); ^{13}C NMR (C_6D_6) δ 0.88 (q), 0.90 (q), 1.29 (q), 1.35 (q), 24.32 (t), 29.18 (d), 29.50 (d), 30.92 (d), 122.71 (d), 125.53 (d), 127.59 (d), 129.07 (d), 129.25 (s), 131.78 (d), 137.66 (d), 146.18 (s), 151.05 (s), 151.52 (s). Anal. Calcd for $C_{32}H_{65}ClGeSi_6$: C, 52.91; H, 9.02. Found: C, 52.94; H, 9.07.

Synthesis of Germabenzene 1a. In a glovebox filled with argon, **7** (43.8 mg, 0.060 mmol) was dissolved in THF (1 mL, dried over K mirror and distilled by trap-to-trap method), and LDA (2.0 M in heptane/THF/ethylbenzene, 33 μL, 0.066 mmol) was added to the solution. After the solution was stirred for 1 h, the solvents were removed under reduced pressure, and hexane was added to the residue. The mixture was left for 10 h, and the generated precipitate was removed by decantation. Removal of the solvent afforded almost pure 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germabenzene (**1a**) (40.7 mg, 98%). **1a**: mp 118−122 °C (dec); ^{1}H NMR (C_6D_6) δ 0.13 (s, 36H), 0.16 (s, 18H), 1.50 (s, 1H), 2.32 (br s, 1H), 2.40 (br s, 1H), 6.62 (br s, 1H), 6.72 (br s, 1H), 6.72 (tt, J = 1.0, 8.4 Hz, 1H), 7.85 (dd, J = 1.0, 12.0 Hz, 2H), 8.06 (ddd, J = 1.0, 8.4, 12.0 Hz, 2H); ^{13}C NMR (C_6D_6) δ 0.66 (q), 0.82 (q), 31.06 (d), 36.02 (d), 36.33 (d), 114.56 (d), 121.72 (d), 126.30 (s), 128.28 (d), 132.32 (d), 140.96 (d), 146.49 (s), 149.98 (s×2); UV−vis (hexane) λ_{max} 225 nm (ϵ 5 × 10^3), 298 nm (ϵ 1 × 10^3), 322 nm (ϵ 8 × 10^2), 326 nm (ϵ 7 × 10^2). HRMS (FAB): found m/z 691.2950 ($[M + H]^+$), calcd for $C_{32}H_{65}GeSi_6$ 691.2884.

Crystal Data of 1a. Formula $C_{32}H_{64}GeSi_6$, MW = 689.96, orthorhombic, space group $Pna2_1$, a = 18.4873(10), b = 10.9402(7), and c = 20.2958(10) Å, V = 4104.9(4) Å^3, Z = 4, D_{calcd} = 1.116 g cm^{-3}, μ = 0.940 mm^{-1}; R_1 ($I > 2\sigma(I)$) = 0.022, wR_2 (all data) = 0.056, GOF = 1.09 for 7962 reflections and 390 parameters. Colorless and prismatic single crystals of **1a** were grown by the slow evaporation of its hexane solution in a glovebox filled with argon. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71071 Å) to 2θ_{max} = 55° at 103 K. The structure was solved by direct methods (SIR97)[23] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[24] Hydrogen atoms of the Tbt group were placed using AFIX instructions, while all the other atoms were refined anisotropically.

Reaction of 1a with Water. To a solution of **1a** (24.5 mg, 0.036 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, purification of the residue by PTLC (hexane/$CHCl_3$ = 3:1) afforded **6a** (16.6 mg, 65%) and 1-hydroxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclohexa-2,5-diene (**6b**) (7.7 mg, 30%) as a white powder. **6b**: mp 166−170 °C; ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 18H), 0.03 (s, 36H), 0.62 (s, 1H), 1.31 (s, 1H), 2.39 (br s, 2H), 2.89−3.17 (m, 2H), 6.26 (br s, 1H), 6.36 (ddd, J = 2.0, 2.0, 14.1 Hz, 2H), 6.37 (br s, 1H), 6.70 (ddd, J = 3.3, 3.3, 14.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.54 (q), 0.70 (q), 0.86 (q), 27.97 (d), 28.27 (d), 30.29 (d), 32.63 (t), 121.99 (d), 126.91 (d), 128.35 (s), 129.85 (d), 143.15 (d), 144.75 (s), 150.44 (s), 150.75 (s). Anal. Calcd for $C_{32}H_{66}GeOSi_6$: C, 54.29; H, 9.40. Found: C, 54.22; H, 9.49.

Reaction of 1a with Methanol. To a solution of **1a** (40.1 mg, 0.058 mmol) in THF (0.5 mL) was added MeOH (0.5 mL) at room temperature, and the solution was stirred for 30 min. Removal of the solvents afforded a 2:1 mixture of methoxygermanes **5a** and **5b** (as judged by ^{1}H NMR). Separation and purification of the mixture by PTLC (hexane/$CHCl_3$ = 3:1) gave hydroxygermanes **6a** (24.9 mg, 61%) and **6b** (12.0 mg, 29%). **5a**: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 18H), 0.03 (s, 36H), 1.30 (s, 1H), 1.88−2.13 (m, 2H), 2.37 (br s, 2H), 3.40 (s, 3H), 5.91−5.97 (m, 1H), 6.11−6.18 (m, 1H), 6.25 (br s, 1H), 6.38 (br s, 1H), 6.40 (d, J = 13.5 Hz, 1H), 6.82 (dd, J = 6.0, 13.5 Hz, 1H). **5b**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18H), 0.03 (s, 36H), 1.29 (s, 1H), 2.47 (br s, 2H), 2.99−3.16 (m, 2H), 3.33 (s, 3H), 6.22 (ddd, J = 1.8, 1.8, 13.8 Hz, 2H), 6.25 (br s, 1H), 6.36 (br s, 1H), 6.78 (ddd, J = 4.0, 4.0, 13.8 Hz, 2H).

Reaction of 1a with Mesitonitrile Oxide. To a solution of **1a** (32.1 mg, 0.049 mmol) in THF (1 mL) was added mesitonitrile oxide (29.1 mg, 0.181 mmol) at room temperature, and the solution was stirred for 12 h. After the solvent was removed, purification of the residue by GPLC ($CHCl_3$) afforded 3-mesityl-7a-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3a,7a-dihydro-1-oxa-2-aza-7a-germaindene (**8**) (35.9 mg, 86%) as a white powder. **8**: mp 200−203 °C; ^{1}H NMR ($CDCl_3$)

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[24] Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

δ 0.01 (s, 18H), 0.04 (s, 9H), 0.05 (s, 9H), 0.08 (s, 18H), 1.37 (s, 1H), 1.67 (br s, 1H), 1.82 (br s, 1H), 2.11 (s, 3H), 2.13 (s, 3H), 2.27 (s, 3H), 3.45 (d, $J = 7.5$ Hz, 1H), 5.92 (dd, $J = 7.5$, 10.5 Hz, 1H), 6.08 (dd, $J = 6.6$, 10.5 Hz, 1H), 6.37 (br s, 1H), 6.47 (br s, 1H), 6.55 (d, $J = 13.2$ Hz, 1H), 6.85 (br s, 2H), 6.87 (dd, $J = 6.6$, 13.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.37 (q), 0.62 (q), 0.70 (q), 0.88 (q), 1.23 (q), 19.79 (q), 20.20 (q), 21.04 (q), 30.07 (d$\times$2), 30.60 (d), 38.29 (d), 121.69 (d), 125.13 (d), 126.72 (d), 127.45 (d), 128.13 (s), 128.35 (d), 128.60 (d), 129.15 (d), 130.29 (s), 135.63 (s), 137.55 (s), 137.87 (s), 139.95 (d), 146.04 (s), 150.58 (s), 158.50 (s$\times$2). Anal. Calcd for $C_{42}H_{75}GeNOSi_6$: C, 59.27; H, 8.88; N, 1.65. Found: C, 59.19; H, 9.10; N, 1.81.

Reaction of 1a with 2,3-Dimethyl-1,3-butadiene. In a glovebox filled with argon, **1a** (38.3 mg, 0.056 mmol) was dissolved in C_6D_6 (0.5 mL), and the solution was put into a 5ϕ NMR tube. After 2,3-dimethyl-1,3-butadiene (distilled from CaH_2 under Ar prior to use, 0.30 mL, 2.652 mmol) was added to the solution, the NMR tube was evacuated and sealed. Heating of the mixture at 80 °C for 3 h resulted in the disappearance of the NMR signals for **1a**. The tube was then opened, and the solvent was removed. Purification of the residue by GPLC ($CHCl_3$) afforded 2,3-dimethyl-4a-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}-1,4,4a,8a-tetrahydro-4a-germanaphthalene (**9**) (29.8 mg, 69%) as a white powder. **9**: mp 194−196 °C; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 36H), 0.04 (s, 18H), 1.28 (s, 1H), 1.62 (s, 3H), 1.66 (s, 3H), 1.80 (d, $J = 12.9$ Hz, 1H), 1.91 (br s, 1H), 1.95 (br s, 1H), 2.06 (d, $J = 12.9$ Hz, 1H), 2.14 (m, 1H), 2.26 (dd, $J = 3.3$, 13.8 Hz, 1H), 2.41 (dd, $J = 4.2$, 13.8 Hz, 1H), 5.80 (dd, $J = 6.3$, 10.8 Hz, 1H), 5.91 (dd, $J = 6.0$, 10.8 Hz, 1H), 6.02 (d, $J = 12.9$ Hz, 1H), 6.28 (br s, 1H), 6.39 (br s, 1H), 6.45 (dd, $J = 6.3$, 12.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.74 (q), 0.81 (q), 1.18 (q), 21.70 (q), 21.88 (q), 25.61 (d), 26.56 (t), 28.09 (d), 28.36 (d), 30.04 (d), 37.90 (t), 121.87 (d), 126.63 (d), 126.97 (d), 127.17 (s), 127.95 (s), 128.88 (d), 131.37 (s), 134.09 (d), 137.36 (d), 143.40 (s), 150.40 (s), 150.73 (s). Anal. Calcd for $C_{38}H_{74}GeSi_6$: C, 59.11; H, 9.66. Found: C, 58.82; H, 9.67.

Reaction of 1a with Styrene. In a glovebox filled with argon, **1a** (36.5 mg, 0.053 mmol) was dissolved in C_6D_6 (1.0 mL), and the solution was put into a 5ϕ NMR tube. After styrene (distilled from CaH_2 under Ar prior to use, 0.04 mL, 0.349 mmol) was added to the solution, the NMR tube was evacuated and sealed. The NMR signals of **1a** disappeared after the mixture was left to for 16 h. The tube was then opened, and the solvent was removed. Purification of the residue by HPLC ($CHCl_3$) and GPLC (hexane/$CHCl_3$ = 3:1) afforded 8-phenyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germabicyclo[2.2.2]-octa-2,5-diene (**10**) (26.0 mg, 62%) as a white powder. **10**: mp 90−92 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 36H), 0.06 (s, 18H), 1.00 (dd, $J = 6.0$, 12.3 Hz, 1H), 1.35 (s, 1H), 1.51 (dd, $J = 10.2$, 12.3 Hz, 1H), 2.12 (br s, 1H), 2.17 (br s, 1H), 2.96 (m, 1H), 3.77 (m, 1H), 6.35 (br s 1H), 6.47 (br s, 1H), 6.58 (d, $J = 11.1$ Hz, 1H), 6.68−6.80 (m, 2H), 7.06 (dd, $J = 7.5$, 11.1 Hz, 1H), 7.03−7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.57 (q), 0.72 (q), 0.90 (q), 21.46 (t), 29.20 (d), 29.46 (d), 30.27 (d), 43.23 (d), 46.39 (d), 121.78 (d), 125.77 (d), 126.63 (d), 126.83 (s), 127.84 (d), 128.07 (d), 135.46 (d), 138.58 (d), 141.78 (d), 144.39 (s), 146.25 (d), 148.33 (s), 150.66 (s), 150.94 (s). Anal. Calcd for $C_{40}H_{72}GeSi_6$: C, 60.50; H, 9.14. Found: C, 60.14; H, 9.31.

Reaction of 1a with Phenylacetylene. In a glovebox filled with argon, **1a** (36.5 mg, 0.053 mmol) was dissolved in C_6D_6 (1.0 mL), and the solution was put into a 5ϕ NMR tube. After phenylacetylene (distilled from CaH_2 under Ar prior to use, 0.04 mL, 0.546 mmol) was added to the solution, the NMR tube was evacuated and sealed. The mixture was heated at 80 °C, and the NMR signals of **1a** disappeared after 108 h. The tube was then opened, and the solvent was removed. Purification of the residue by GPLC ($CHCl_3$) and PTLC (hexane/$CHCl_3$ = 3:1) afforded 3-phenyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germabicyclo[2.2.2]octa-2,5,7-triene (**11**) (23.8 mg, 58%) as a white powder. **11**: mp 185−186 °C; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 36H), 0.08 (s, 18H), 1.38 (s, 1H), 2.24 (br s, 1H), 2.27 (br s, 1H), 5.44 (m, 1H), 6.40 (br s, 1H), 6.52 (br s, 1H), 6.91 (d, $J = 2.4$ Hz, 1H), 7.01 (dd, $J = 1.2$, 9.6 Hz, 2H), 7.23−7.44 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 0.58 (q), 0.73 (q), 0.87 (q), 29.50 (d), 29.70 (d), 30.39 (d), 50.97 (d), 121.86 (d), 125.25 (d), 125.81 (s), 126.68 (d), 127.13 (d), 128.39 (d), 135.20 (d), 140.52 (d), 142.33 (s), 144.20 (d), 144.74 (s), 150.78 (s), 150.98 (s), 155.82 (s). Anal. Calcd for $C_{40}H_{70}GeSi_6$: C, 60.65; H, 8.91. Found: C, 60.59; H, 8.95.

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Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1a**; a table for the observed Raman shifts for **1a**; and total electronic energies and atomic coordinations for all molecules used in Charts 2 and 3 (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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