

Chlorine-Substituted Germabenzene: Generation and Application as a Precursor for Aryl-Substituted Germabenzenes

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ABSTRACT: Germabenzene bearing a reactive chlorine group on the germanium atom was generated and characterized by NMR spectroscopy. Reactions of the *in-situ* generated chlorogermabenzene with aryllithium reagents gave isolable germabenzenes bearing aryl groups, such as mesityl or acridinyl groups, on the germanium atom. This reaction constitutes the first example for a nucleophilic aromatic substitution of heavy heterobenzenes at the main group center.

Benzenes containing 3rd or higher main group element have been investigated to reveal their aromatic character of 6π conjugated ring including heavy element.¹ In this context, several synthetic researches have been conducted. In the case of heavy group 14 elements, neutral sila- and germa-benzenes (**I**, **II**) stabilized by bulky aryl substituents attached on the group 14 elements have been synthesized and characterized by spectroscopic methods as well as X-ray crystallography (Figure 1a).^{2a-c} In addition, benzene rings including two silicon or germanium, disila- and digerma-benzenes (**III**, **IV**), have been reported.^{2f-2j} In case of further heavier group 14 element, tin-incorporated benzene, stannabenzene, has only been spectroscopically characterized as an equilibrium mixture with its dimeric form.³ Very recently, germa- and stanna-benzenyl anions (**V**, **VI**), which constitutes the germanium- or tin-incorporated phenyl anion, have been isolated and characterized.^{2e,4} Although additions of alcohol and C-C or C-X unsaturated molecules toward C-E (E = Si, Ge, Sn) unsaturated bonds, complexation with transition metal, and photoisomerization have been reported,²⁻⁵ functionalization of the group 14 element center with retaining heavy aromatic ring after the formation of these heterobenzenes has never been reported.

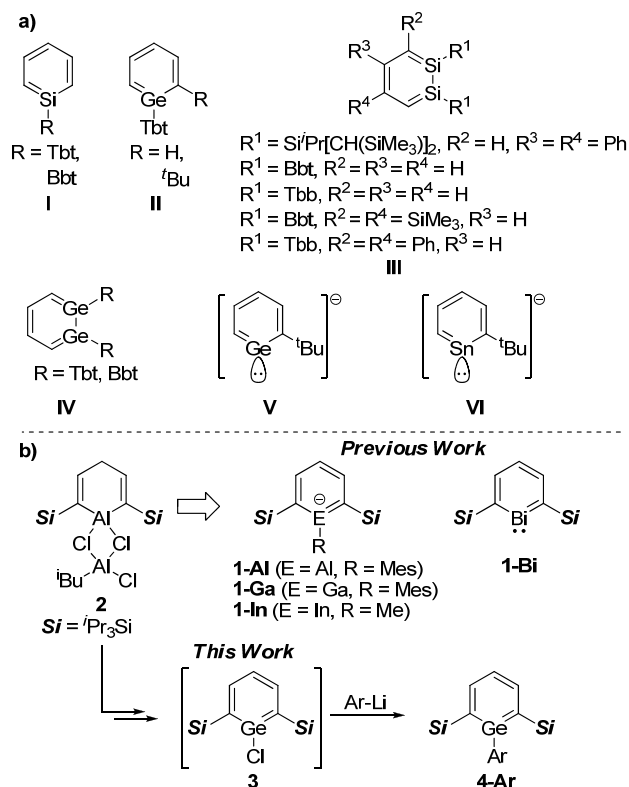


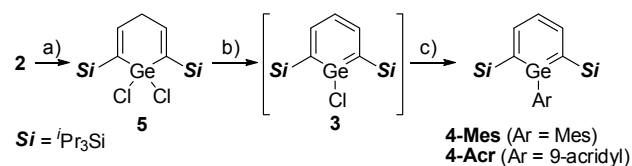
Figure 1. (a) Previously reported isolable heavy benzenes. Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl, Tbb = 4-*tert*-butyl-2,6-bis[bis(trimethylsilyl)methyl]phenyl. (b) Previous and this works.

Previously, we reported synthesis and characterization of anionic aluminabenzene **1-Al** via aluminacyclohexadiene **2** as a synthetic intermediate (Figure 1b).⁶ By means of the reactivity of **2**, not only heavier group 13 elements, such as galli-

um and indium, but also the sixth row group 15 element, bismuth, can be introduced into benzene framework to give, galla- (**1-Ga**), inda- (**1-In**) and bisma- (**1-Bi**) benzenes.⁷ According to these results, **2** would be a suitable precursor for heavy group 14 element-incorporated benzenes. Herein, we report a systematic synthesis of germabenzene derivatives by using **2** as a precursor. A chlorine-substituted germabenzene **3** was generated by a reaction of **2** with GeCl₂·(dioxane). The generated **3** was not isolated, but could be characterized in the reaction mixture. We also demonstrate *in-situ* transformation of **3** by reactions with aryllithium into aryl-substituted germabenzenes **4-Ar**. The transformation of Ge-Cl group in germabenzene reported here is the first example of the nucleophilic aromatic substitution of heavy element-incorporated benzenes.

Dichlorogermacyclohexadiene **5** was prepared as a precursor for germabenzenes by a reaction of **2**⁶ with an excess amount of GeCl₂·(dioxane) complex (Scheme 1). The resulting **5** was isolated as colorless crystals in 42% yield. Although the mechanism for the formation of **5** is not clear at the present stage, we assume that the transmetalation of **2** with GeCl₂·(dioxane) to form a cyclic germylene intermediate, then oxidized to the Ge(IV) species **5** by aluminum chloride or GeCl₂·(dioxane) in the reaction mixture. Deprotonation of **5** by bulky bases, such as KHMDS (potassium hexamethyldisilazide) or Mes*Li (Mes* = 2,4,6-tri-*tert*-butylphenyl),⁸ generated **3** in solution. Although isolation of **3** was failed due to the low crystallinity, the formation of **3** was confirmed by NMR spectroscopy and high resolution mass spectrometry in a reaction mixture. The yield of **3** was estimated to be 83% using Mes*Li and 75% using KHMDS by ¹H NMR spectroscopy (Figure S2). The ¹H NMR spectrum of the reaction mixture showed the characteristic signals assignable to protons on the germabenzene ring of **3** at 6.60 ppm for 4-H and 8.14 ppm for 3,5-H with the coupling constant of 8 Hz. These values are comparable to those of the reported germabenzenes stabilized by bulky aryl group on the Ge atom (**II**, Figure 1, R = H).^{2d}

Scheme 1. Generation of chloro-germabenzene 3 followed by a substitution reaction with ArLi reagent at the Ge atom



a) GeCl₂·(dioxane), toluene, 46%; b) KHMDS or Mes*Li, 83% based on ¹H NMR spectroscopy for Mes*Li; c) ArLi [Ar = Mes, 9-acridinyl (Acr)], 26% for **4-Mes** from **5**, 29% for **4-Acr** from **5**

Next, transformation of **3** by a reaction with organometallic reagent was investigated. Reaction of an *in-situ* generated **3** in solution with mesityllithium (MesLi)⁹ gave mesityl-substituted germabenzene **4-Mes**, which was isolated in 26% yield by recrystallization.^{10,11} Instead of MesLi, 9-acridinyl lithium was used for the substitution of **3** to form isolable acridinyl-substituted germabenzene **4-Acr**.¹⁰ Considering the organolithium reagents can add toward Ge=C double bond,^{12,13} in which organic substituent was introduced to Ge atom, we assume that the substitution of Ge-Cl in **3** would proceed *via* 1,2-addition of ArLi toward the germabenzene ring followed by an elimi-

nation of LiCl. The structures of **4-Mes** and **4-Acr** were determined by NMR spectroscopy and X-ray crystallography. NMR signals of protons attached on the germabenzene ring and ring carbon atoms in **4-Mes** were observed at low field region (6.95 and 8.33 ppm for ¹H, 115.8, 142.1, and 148.4 ppm for ¹³C), being comparable to those of reported germabenzene (**II**, Figure 1, R = H) (6.72, 8.06, 7.85 for ¹H, 114.56, 132.23, 140.96 for ¹³C).^{2d} In the case of **4-Acr**, ¹H NMR signals of protons attached on the germabenzene ring were overlapping with signals of acridinyl moiety.

The molecular structures of **4-Mes** and **4-Acr** were shown in Figure 2. In the solid state, the germabenzene rings are planar indicated by the sum of the internal bond angles (**4-Mes**: 719.9°, **4-Acr**: 720.0°). In addition, the sum of the surrounding bond angles around germanium atoms are 360°, indicating planar geometry of the Ge atom. The substituted aryl groups and germabenzene ring were twisted (torsion angles of 77.7(4)° for **4-Mes** and 77.2(3)-84.8(4)° for **4-Acr**) due to the steric repulsion between these aryl groups and two bulky silyl groups attached on 2,6-positions. The Ge-C bond distances in the germabenzene rings [**4-Mes**: 1.867(4), 1.861(4) Å, **4-Acr**: 1.861(4), 1.854(4) Å, 1.857(4), 1.866(4) Å] are shorter than that of *exo*-Ge-C(Ar) single bonds [**4-Mes**: 1.941(4) Å, **4-Acr**: 1.954(3), 1.963(4) Å]. The C-C bond distances in the ring [**4-Mes**: 1.393(6)-1.405(6) Å, **4-Acr**: 1.384(6)-1.407(5) Å] are comparable to those of benzene (1.397 Å).¹⁴ These Ge-C and C-C bond distances indicated the unsaturated character of the ring. In addition, tangible bond alternation was not observed in these germabenzene rings. These structural features are in agreement with those of aromatic compound and comparable to those of the previously reported neutral germabenzenes (**II**, Figure 1, R = H).^{2d}

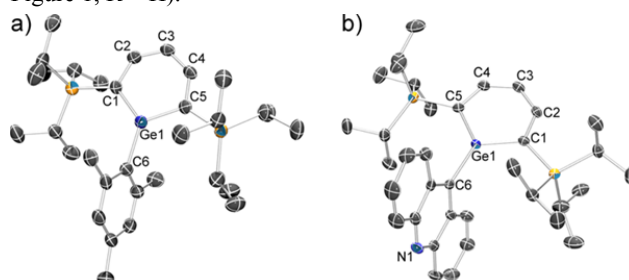


Figure 2. Molecular structures of germabenzenes **4-Mes** (top) and **4-Acr** (bottom, one of two crystallographically independent molecules is shown) (thermal ellipsoids set at 50% probability, hydrogen atoms omitted for clarity). Selected bond distances (Å) for **4-Mes**: Ge1–C1 = 1.867(4), Ge1–C5 = 1.861(4), Ge1–C6 = 1.951(4), C1–C2 = 1.414(5), C2–C3 = 1.395(5), C3–C4 = 1.387(5), C4–C5 = 1.423(5); for **4-Acr**: Ge1–C1 = 1.861(4), Ge1–C5 = 1.854(4), Ge1–C6 = 1.954(3), C1–C2 = 1.406(5), C2–C3 = 1.394(5), C3–C4 = 1.381(6), C4–C5 = 1.405(5), Ge2–C37 = 1.857(4), Ge2–C41 = 1.866(4), Ge2–C42 = 1.963(3), C37–C38 = 1.399(5), C38–C39 = 1.397(5), C39–C40 = 1.386(6), C40–C41 = 1.407(5).

To investigate the electronic structure of isolated germabenzenes, UV-vis absorption spectra of **4-Mes** and **4-Acr** were measured (Figure 3a). **4-Mes** shows absorption maxima at 346 nm, being slightly shifted to longer wavelength region than that of previously reported Tbt-substituted germabenzene (**II**, Figure 1, R = H) (λ_{max} = 326 nm).^{2d} On the other hand, the absorption spectrum of **4-Acr** showed the characteristic absorption band derived from acridinyl group

(346–386 nm). These absorption bands were red-shifted relative to those of acridine (Figure S9) probably due to a higher π -orbital level (HOMO–1) of acridinyl moiety in **4-Acr** than π -orbital level (HOMO) of acridine because of the π - σ interaction between a filled π -orbital of acridinyl moiety and Ge–C σ -bonds in the germabenzene ring. In addition to the absorption derived from acridine moiety, the weak absorption around 400–450 nm was observed.¹⁵

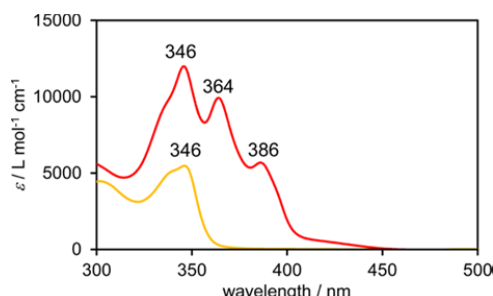


Figure 3. UV-vis spectra of **4-Mes** (yellow line) and **4-Acr** (red line) in hexane at ambient temperature.

To reveal the absorption character of germabenzene **4-Acr**, we performed the DFT calculations.¹⁶ The structural optimizations of **4-Mes** and **4-Acr** at the B3LYP/6-31G(d) level of theory reproduced the experimentally observed structures.¹⁷ The calculated HOMO and LUMO of **4-Mes** are localized on the germabenzene ring (Figure S13). The HOMO of **4-Acr** is similarly localized on the germabenzene moiety, while the LUMO is spread around acridine moiety (Figure S14). This well-separated HOMO and LUMO in **4-Acr** would be responsible to a charge-transfer absorption from the germabenzene ring to acridine moiety. By the TD-DFT calculations of **4-Acr** at the B3LYP/6-311+G(2d,p) level, the HOMO–LUMO transition was calculated at 495 nm with small oscillator strength, being in agreement with the experimentally observed weak absorption around 400–450 nm. To get insight into the electronic character of **4-Mes** and **4-Acr**, we performed the nucleus-independent chemical shift (NICS) analysis at the B3LYP/6-311+G(2d,p) level.¹⁸ The resulting negative NICS values (**4-Mes**: NICS(0) = –5.4, NICS(1) = –7.9; **4-Acr**: NICS(0) = –4.9, NICS(1) = –6.9] suggest the presence of diatropic ring current derived from germabenzene ring in **4-Mes** and **4-Acr**.

In summary, the chlorine-substituted germabenzenes was spectroscopically characterized. By means of the reactivity of chlorogermabenzene **3**, isolable germabenzene derivatives bearing Mes or acridinyl groups were synthesized and characterized. The CT-type absorption between germabenzene and acridinyl moiety was revealed by TD-DFT calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Details of experimental procedure, crystallographic analysis, theoretical calculations (PDF) Crystallographic data (CIF) Calculated Cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interests.

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REFERENCES

- (1) For reviews, see: (a) Lee, V. Y. and Sekiguchi, A. In *Organometallic Compounds of Low-Coordinate Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds*; John Wiley & Sons, Ltd.: Chichester, 2010. (b) Tokitoh, N. New Progress in the Chemistry of Stable Metallaaromatic Compounds of Heavier Group 14 Elements. *Acc. Chem. Res.* **2004**, *37*, 86–94. (c) Tokitoh, N. Synthesis of Aromatic Species Containing a Heavier Group 14 Element by Taking Advantage of Kinetic Stabilization. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 429–441. (d) Ashe, A. J., III *Acc. Chem. Res.* The Group 5 heterobenzenes. **1978**, *11*, 153–157. (e) Ashe, A. J., III The Group 5 Heterobenzenes, Arsabenzene, Stibabenzene, and Bismabenzene. *Top. Curr. Chem.* **1982**, *105*, 125–155.
- (2) (a) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. Synthesis and Properties of an Overcrowded Silabenzene Stable at Ambient Temperature. *Angew. Chem., Int. Ed.* **2000**, *39*, 634–636. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. Crystal Structure of a Stable Silabenzene and Its Photochemical Valence Isomerization into the Corresponding Silabenzvalene. *J. Am. Chem. Soc.* **2000**, *122*, 5648–5649. (c) Tokitoh, N.; Wakita, K.; Matsumoto, T.; Sasamori, T.; Okazaki, R.; Takagi, N.; Kimura, M.; Nagase, S., The Chemistry of Stable Silabenzenes. *J. Chin. Chem. Soc.* **2008**, *55*, 487–507. (d) Nakata, N.; Takeda, N.; Tokitoh, N. Synthesis and Properties of the First Stable Germabenzene. *J. Am. Chem. Soc.* **2002**, *124*, 6914–6920. (e) Mizuhata, Y.; Fujimori, S.; Sasamori, T.; Tokitoh, N. Germabenzenylium: A Germanium Analogue of a Phenyl Anion. *Angew. Chem., Int. Ed.* **2017**, *56*, 4588–4592. (f) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S., Reactivity of a Disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiPr}[\text{CH}(\text{SiMe}_3)_2]_2$) toward π -Bonds: Stereospecific Addition and a New Route to an Isolable 1,2-Disilabenzene. *J. Am. Chem. Soc.* **2007**, *129*, 7766–7767. (g) Han, J. S.; Sasamori, T.; Mizuhata, Y.; Tokitoh, N., Reactivity of an aryl-substituted silicon–silicon triple bond: 1,2-disilabenzenes from the reactions of a 1,2-diaryldisilyne with alkynes. *Dalton Trans.* **2010**, *39*, 9238–9240. (h) Sugahara, T.; Guo, J.-D.; Hashizume, D.; Sasamori, T.; Nagase, S.; Tokitoh, N., The selective formation of a 1,2-disilabenzene from the reaction of a disilyne with phenylacetylene. *Dalton Trans.* **2018**, *47*, 13318–13322. (i) Sasamori, T.; Sugahara, T.; Agou, T.; Guo, J.-D.; Nagase, S.; Streubel, R.; Tokitoh, N., Synthesis and Characterization of a 1,2-Digermabenzene. *Organometallics* **2015**, *34*, 2106–2109. (j) Sugahara, T.; Guo, J.-D.; Sasamori, T.; Karatsu, Y.; Furukawa, Y.; Ferao, A. E.; Nagase, S.; Tokitoh, N., Reaction of a Stable Digermyne with Acetylenes: Synthesis of a 1,2-Digermabenzene and a 1,4-Digermabarrelene. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1375–1384.
- (3) Mizuhata, Y.; Fujimori, S.; Noda, N.; Kanetsato, S.; Tokitoh, N. Generation of Stannabenzenes and Their Monomer-Dimer Equilibration. *Dalton Trans.* **2018**, *47*, 14436–14444.
- (4) Fujimori, S.; Mizuhata, Y.; Tokitoh, N., Stannabenzenylium: The First Isolable Tin-Containing Benzene Derivative. *Chem.–Eur. J.* **2018**, *24*, 17039–17045.

- (5) (a) Nakata, N.; Takeda, N.; Tokitoh, N. η^6 -Germabenzene Complexes of Chromium and Molybdenum. *Angew. Chem., Int. Ed.* **2003**, *42*, 115-117. (b) Shinohara, A.; Takeda, N.; Sasamori, T.; Matsumoto, T.; Tokitoh, N. Synthesis and Properties of η^6 -Silabenzene-M(CO)₃ Complexes (M = Cr, Mo). *Organometallics* **2005**, *24*, 6141-6146. (c) Fujimori, S.; Mizuhata, Y.; Tokitoh, N., Ru-Complexes of an anionic germabenzene ligand. *Chem. Commun.* **2018**, *54*, 8044-8047.
- (6) Nakamura, T.; Suzuki, K.; Yamashita, M. An Anionic Alumina-benzene Bearing Aromatic and Ambiphilic Contributions. *J. Am. Chem. Soc.* **2014**, *136*, 9276-9279.
- (7) (a) Nakamura, T.; Suzuki, K.; Yamashita, M. An Isolable Anionic Gallabenzene: Synthesis and Characterization. *Organometallics* **2015**, *34*, 1806-1808. (b) Nakamura, T.; Suzuki, K.; Yamashita, M. Anionic indabenzene: synthesis and characterization. *Chem. Commun.* **2017**, *53*, 13260-13263. (c) Ishii, T.; Suzuki, K.; Nakamura, T.; Yamashita, M. An Isolable Bismabenzene: Synthesis, Structure, and Reactivity. *J. Am. Chem. Soc.* **2016**, *138*, 12787-12790.
- (8) Mes*Li was prepared according to the literature procedure. See: Borger, J. E.; Ehlers, A. W.; Lutz, M.; Slootweg, J. C.; Lammertsma, K., Functionalization of P₄ Using a Lewis Acid Stabilized Bicyclo[1.1.0]tetraphosphabutane Anion. *Angew. Chem., Int. Ed.* **2014**, *53*, 12836-12839.
- (9) MesLi was prepared according to the literature procedure. See: Hubner, A.; Bernert, T.; Sanger, I.; Alig, E.; Bolte, M.; Fink, L.; Wagner, M.; Lerner, H.-W. Solvent-free mesityllithium: solid-state structure and its reactivity towards white phosphorus. *Dalton Trans.* **2010**, *39*, 7528-7533.
- (10) The reaction yield was 72% for **4-Mes** and 73% for **4-Acr** based on ¹H NMR spectroscopic analysis. The low isolated yields would be attributed to their high solubility.
- (11) The reaction of **5** with 2 equivalents of MesLi gave **4-Mes** in 81% NMR yield. See Supporting Information for details.
- (12) (a) Wiberg, N.; Passler, T.; Wagner, S., Addukte der Ethene Me₂E=C(SiMe₃)₂ (E=Si, Ge, Sn) mit LiR und RN₃: Wie rasch bilden sie sich? *J. Organomet. Chem.* **2000**, *598*, 304-312. (b) Farhadpour, B.; Guo, J.; Pavelka, L. C.; Baines, K. M. Addition of Organometallic Reagents to a Stable Silene and Germene. *Organometallics* **2015**, *34*, 3748-3755. (c) Couret, C.; Escudie, J.; Delpon-Lacaze, G.; Satge, J. Dimesitylneopentylgermene, a new stable germene. *Organometallics* **1992**, *11*, 3176-3177. (d) Pavelka, L. C.; Holder, S. J.; Baines, K. M. Addition polymerization of 1,1-dimesitylneopentylgermene: synthesis of a polygermene. *Chem. Commun.* **2008**, 2346-2348.
- (13) The isolable germabenzene can react with unsaturated compounds similar to Ge=C double bond. See ref 2d.
- (14) Minkin, V. J.; Glukhovtsev, M. N.; Simkin, Y. B. In *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994.
- (15) Although the UV-vis absorption spectrum in THF was slightly shifted to longer wavelength region, the solvent effect of the broad absorption band around 400-450 nm could not be discussed in detail due to unclear absorption peak.
- (16) Details of the calculations are described in Supporting Information.
- (17) The slightly larger torsion angles between germabenzene ring and substituted aryl groups in the optimized structures would be attributed to the crystal packing force.
- (18) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion. *Chem. Rev.* **2005**, *105*, 3842-3888.

Novel Synthetic Method for Germabenzenes

