Organometallics **2002,** *21,* 4309−4311

Synthesis and Isolation of the First Germacyclopropabenzene: A Study to Elucidate the Intrinsic Factor for the Ring Deformation of Cyclopropabenzene Skeletons

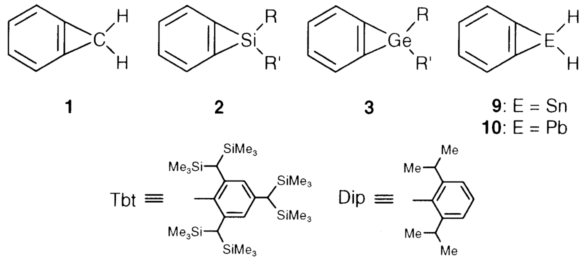
Norihiro Tokitoh,*,† Ken Hatano,‡ Takayo Sasaki,† Takahiro Sasamori,†
Nobuhiro Takeda,† Nozomi Takagi,§ and Shigeru Nagase§

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan,
Institute for Fundamental Research of Organic Chemistry, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan, and Institute for Molecular Science,
Myodaiji, Okazaki 444-8585, Japan

Received July 9, 2002

Summary: The treatment of an overcrowded diaryldilithiogermane, Tbt(Dip)GeLi$_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl), generated by exhaustive reduction of the corresponding dibromogermane Tbt(Dip)GeBr$_2$, with 1,2-dibromobenzene resulted in the isolation of the first stable germacyclopropabenzene, which was fully characterized by ^{1}H and ^{13}C NMR spectra, FAB-MS, and X-ray structural analysis. As for the ring deformation of cyclopropabenzene and its heavier group 14 element analogues, the experimental results are in good agreement with those obtained by theoretical calculations.

Chart 1



Since the finding of significant deformation for the fused aromatic rings in the series of benzocycloalkanes,[1] one of the most important subjects assigned to organic chemists has been to solve the riddle of such deformation.[2] Cyclopropabenzene (**1**) has attracted special attention because it has the most severely enforced deformation in this series. Although the systematic comparison of the structural features of cyclopropabenzene with those of its heteroatom analogues would be very useful and informative in elucidating the intrinsic factor for the deformation of the aromatic ring in this fused-ring system, there has been no example of a stable heteracyclopropabenzene so far.[3]

Meanwhile, we have already succeeded in the generation of the overcrowded diaryldilithiosilane Tbt(Dip)SiLi$_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl) and found that this new organosilicon building block is useful for the synthesis of a variety of cyclic organosilicon compounds by the reaction with bifunctional electrophiles.[4] Recently, we have synthesized and isolated silacyclopropabenzene **2a** (R = Tbt, R′ = Dip) as the first example of a stable heteracyclopropabenzene by taking advantage of the characteristic reactivity of the sterically hindered dilithiosilane toward 1,2-dibromobenzene.[5] An X-ray crystallographic analysis revealed that the central benzene ring of **2a** is much less perturbed by annelation than that of cyclopropabenzene (**1**) (Chart 1). The successful isolation of silacyclopropabenzene **2a** naturally prompted us to examine the systematic structural comparison of metallacyclopropabenzenes of heavier group 14 elements. In this paper, we present the synthesis and crystallographic structural analysis of the first germacyclopropabenzene **3a** together with theoretical calculations on the molecular geometries of all heteracyclopropabenzenes containing a heavier group 14 element.

Similarly to the generation of dilithiosilane Tbt(Dip)SiLi$_2$, the overcrowded dibromogermane Tbt(Dip)GeBr$_2$ (**4**) was subjected to exhaustive reduction using an excess amount of lithium naphthalenide (5 molar equiv) at −78 °C in tetrahydrofuran in the hope of obtaining the dilithiogermane Tbt(Dip)GeLi$_2$ (**5**).[6] The almost

---

* To whom correspondence should be addressed. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp. Tel: +81-774-38-3200. Fax: +81-774-38-3209.
† Kyoto University.
‡ Kyushu University.
§ Institute for Molecular Science.

[1] Mills, W. H.; Nixson, I. G. *J. Chem. Soc.* **1930**, 2510−2524.

[2] For example: (a) Halton, B. *Chem. Rev.* **1989**, *89*, 1161−1185. (b) Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349−364.

[3] (a) Thétaz, C.; Wentrup, C. *J. Am. Chem. Soc.* **1976**, *98*, 1258−1259. (b) Schulz, R.; Schweig, A. *Tetrahedron Lett.* **1984**, *25*, 2337−2340. (c) White, R. C.; Scoby, J.; Roberts, T. D. *Tetrahedron Lett.* **1979**, *30*, 2785−2788.

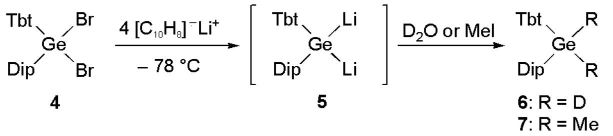
[4] Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, 931−932.

[5] Hatano, K.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 4829−4830.

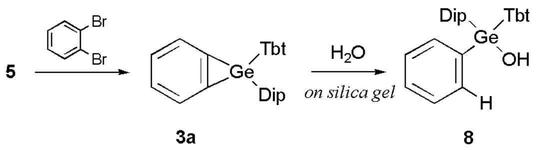
[6] (a) Generation of Ar$_2$GeM$_2$ (Ar = C$_6$H$_5$, *p*-CH$_3$C$_6$H$_4$; M = Li, Na, K) by the reduction of the corresponding Ar$_2$GeH$_2$ with alkali metals in HMPA or THF has already been reported. Although the dimetalated germanes thus generated were treated with alkyl halides to produce the corresponding substitution products in moderate yields, no coupling product was reported in the reactions with *p*-halotoluenes: Mochida, K.; Tatsushige, N.; Hamashima, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1443−1447. (b) We have preliminarily reported the reaction of the diaryldilithiogermane **5** with TeCl$_2$, giving the corresponding germanetellone, a germanium−tellurium double-bond compound: Tokitoh, N.; Sadahiro, T.; Hatano, K.; Sasaki, T.; Takeda, N.; Okazaki, R. *Chem. Lett.* **2002**, 34−35. (c) Very recently, silyl-substituted dilithiogermanes have been isolated as stable compounds: Sekiguchi, A.; Izumi, R.; Ihara, S.; Ichinohe, M.; Lee, V. Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 1598−1600.

10.1021/om020545x CCC: $22.00

Scheme 1



Scheme 2



quantitative generation of **5** was confirmed by the trapping experiments with deuterium oxide and iodomethane to give the corresponding trapping reaction products **6** and **7**, respectively (Scheme 1). Interestingly, a considerable amount of dilithiogermane **5** can be trapped with these reagents without the migration of lithium atom from the germanium center to the ortho benzyl position of the Tbt group, even at room temperature. The much higher thermal stability of **5** observed here is in sharp contrast to the ready lithium migration of its silicon analogue at −50 °C.[4]

The dilithiogermane **5** thus generated was allowed to react with 1 equiv of 1,2-dibromobenzene at −78 °C, and the following purification by HPLC and recrystallization from hexane/EtOH resulted in the isolation of the first stable germacyclopropabenzene, **3a**, in 40% yield.[7] Interestingly, **3a** was isolated as stable colorless crystals in the air but slowly decomposed on silica gel, giving the ring-opened hydrolyzed product **8**, in contrast to the high stability of its silicon analogue previously reported (Scheme 2).[8] Anyhow, it should be noted that the same synthetic approach as that for silacyclopropabenzene **2a** can be applied to its heavier congener, i.e., germacyclopropabenzene **3a**.

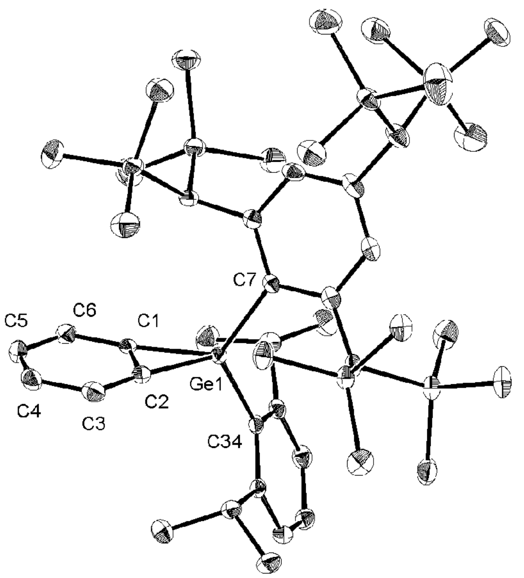


Figure 1. ORTEP drawing of germacyclopropabenzene **3a** with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and angles (deg): Ge(1)−C(1), 1.9403(18); Ge(1)−C(2), 1.9318(18); Ge(1)−C(7), 1.9666(17); Ge(1)−C(34), 1.9761(18); C(1)−C(2), 1.391(3); C(1)−C(6), 1.385(3); C(2)−C(3), 1.388(3); C(3)−C(4), 1.392(3); C(4)−C(5), 1.397(3); C(5)−C(6), 1.391(3); C(1)−Ge(1)−C(2), 42.11(8); C(1)−Ge(1)−C(7), 121.54(7); C(1)−Ge(1)−C(34), 113.13(7); C(2)−Ge(1)−C(7), 119.36(7); C(2)−Ge(1)−C(34), 117.07(7); C(7)−Ge(1)−C(34), 120.05(7); Ge(1)−C(1)−C(2), 68.62(11); Ge(1)−C(1)−C(6), 169.47(16); C(2)−C(1)−C(6), 121.88(17); Ge(1)−C(2)−C(1), 69.27(10); Ge(1)−C(2)−C(3), 168.68(16); C(1)−C(2)−C(3), 122.00(17); C(2)−C(3)−C(4), 116.28(18); C(3)−C(4)−C(5), 121.72(18); C(4)−C(5)−C(6), 121.61(18); C(1)−C(6)−C(5), 116.51(18).

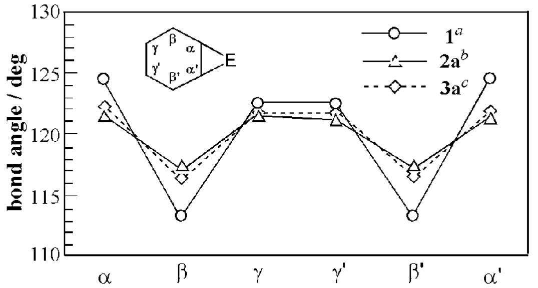


Figure 2. Comparison of bond angles in cyclopropabenzenes **1**, **2a**, and **3a**. Legend for footnotes: [a]data were collected at −153 °C;[13] [b]data were collected at −180 °C;[5] [c]this work.

The molecular structure of **3a** determined by X-ray crystallographic analysis is shown in Figure 1 together with some selected bond lengths and angles.[9] The germacyclopropabenzene skeleton was found to have a completely planar geometry. The sums of bond angles at C1 and C2 are both almost 360°, and the sum of interior bond angles in the benzene ring is 720.0°. All six C−C lengths in the central benzene ring of **3a** are in the range of usual C−C distances reported for a nonperturbed benzene ring (1.39−1.40 Å).[12] To clarify the structural differences in the benzene moiety of the series of cyclopropabenzenes (**1**, **2a**, and **3a**) characterized by X-ray analyses, the bond angles and lengths for **1**, **2a**, and **3a** are shown in Figures 2 and 3, respectively.

Germacyclopropabenzene **3a** has a slightly squashed benzene moiety, in which all bond angles deviate from the ideal sp^2 bond angle (120°). As can be seen in Figure

---

(7) **3a**: colorless crystals; mp 235−237 dec; ^{1}H NMR (CDCl$_3$, 400 MHz) δ −0.10 (s, 36H), 0.02 (s, 18H), 0.92 (d, 6H, $^3J_{HH} = 6.5$ Hz), 1.28 (s, 1H), 1.33 (d, 6H, $^3J_{HH} = 6.5$ Hz), 2.49 (brs, 1H), 2.72 (brs, 1H), 3.70 (sept, 2H, $^3J_{HH} = 6.5$ Hz), 6.23 (br s, 1H), 6.38 (brs, 1H), 7.10 (d, 2H, $^3J_{HH} = 7.7$ Hz), 7.24 (AA′BB′, 2H, $^4J_{HH} = 2.8$, $^3J_{HH} = 5.0$ Hz), 7.25 (t, 1H, $^3J_{HH} = 7.7$ Hz), 7.61 (AA′BB′, 2H, $^4J_{HH} = 2.8$, $^3J_{HH} = 5.0$ Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 1.04 (q), 1.08 (q), 1.25 (q), 22.7 (q), 27.9 (q), 27.9 (d), 28.3 (d), 30.6 (d), 35.0 (d), 122.8 (d), 123.1 (d), 126.2 (d), 128.0 (d), 129.1 (d), 129.6 (s), 129.7 (d), 139.0 (s), 143.9 (s), 149.8 (s), 150.3 (s), 150.5 (s), 153.4 (s); high-resolution FAB-MS *m/z* calcd for $C_{45}H_{81}Si_6{}^{72}Ge$ 861.4174 ([M + H]$^+$), found 861.4178 ([M + H]$^+$). Anal. Calcd for $C_{45}H_{80}Si_6Ge$: C, 62.68; H, 9.35. Found: C, 62.38; H, 9.51.

(8) The surprising stability of the ring-opening reaction of silicon analogue **2a** was already reported in ref 5. Compound **2a** can be purified by preparative thin-layer chromatography on silica gel without any decomposition. The reactivity of germacyclopropabenzene **3a** will be described elsewhere.

(9) Crystallographic data for **3a**: the structure was solved by direct methods (SIR-97)[10] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97);[11] $C_{45}H_{80}Si_6Ge$, mol wt 862.22, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.8813(3)$ Å, $b = 12.0099(11)$ Å, $c = 23.125(4)$ Å, $\alpha = 76.709(3)°$, $\beta = 84.638(3)°$, $\gamma = 72.6833(13)°$, $V = 2548.8(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.123$ Mg/m^3, $\mu = 0.770$ mm^{-1}, R1($I > 2\sigma(I)$) = 0.0309, wR2(all data) = 0.0789, T =103(2) K, GOF = 1.045.

(10) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

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

(12) Allen, F. K.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

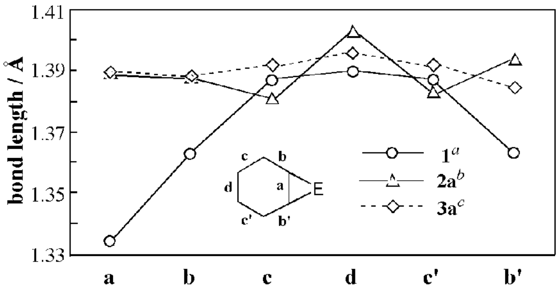


Figure 3. Comparison of bond lengths in cyclopropabenzenes **1**, **2a**, and **3a**. Legend for footnotes: ^{a}data were collected at −153 °C;[13] ^{b}data were collected at −180 °C;[5] ^{c}this work.

2, the same tendency (α, $\gamma > 120° > \beta$) was observed for the series of cyclopropabenzenes **1**−**3**, and this can be interpreted in terms of the influence of the three-membered-ring annelation. As for the bond lengths, cyclopropabenzene **1**, the most tightly annelated system, is most significantly perturbed as compared with other heavier congeners **2a** and **3a**. The obvious C−C bond shortening compared with the typical aromatic C−C length is reported for the juncture C−C bond ***a*** and its neighboring bonds ***b*** and ***b'*** of **1** (Figure 3).[13] However, such C−C shortening was not recognized for germacyclopropabenzene **3a** (***a*** = 1.391(3) Å and ***b***, ***b'*** = 1.388(3), 1.385(3) Å) (Figure 1). Thus, the structural features of benzene nuclei in germacyclopropabenzne **3a** are very similar to those of the previously reported silicon analogue **2a**.[5]

The most extreme structural difference between the hydrocarbon system **1** and its heteroatom analogues (**2a** and **3a**) is the length of the juncture bond ***a***, which is most probably due to their disparate ways of releasing of the strain energy.[5] Annelation of a three-membered ring to a benzene ring naturally enforces severe distortion upon the juncture carbons (C1 and C2), leading to deviation from the ideal sp^2 geometry. The extreme bond shortening observed in cyclopropabenzene **1** is one of the modes that compensates for this localized distortion. On the other hand, such bond shortening is not necessary for the heavier congeners, since **2a** and **3a** have longer C−M bonds (M = Si, Ge) than the C−C bonds in **1**. They can release the strain energy at juncture carbons by the expanded three-membered ring to the direction of their outer apex.[4] The X-ray analyses for **2a** and **3a** strongly suggest that the distinct molecular distortion and bond localization observed in cyclopropabenzene **1** is a characteristic property due to tight annelation and also are in good agreement with theoretical calculations for parent sila- and germacyclopropabenzenes.

For a systematic study of heteracyclopropabenzenes containing a group 14 element, theoretical calculations were carried out for the heavier congeners of cyclopropabenzene, i.e., **3b** (R = R′ = H), **9** (E = Sn), and **10** (E = Pb).[14] All of them were found to have a planar heteracyclopropabenzene skeleton as an energy minimum, as in the case of silacyclopropabenzene **2b** (R = R′ = H),[5] and no remarkable geometrical difference was observed among the benzene moieties of heavier cyclopropabenzenes (**2b**, **3b**, **9**, and **10**). Our conclusion on the structures of sila- and germacyclopropabenzenes (**2** and **3**) is that the three-membered ring containing a heavier group 14 element can enjoy annelation with much less perturbation.

Further studies on the preparations of unprecedented ring systems, i.e., other heavier cyclopropabenzene analogues and bis(heteracyclopropa)benzenes, are currently in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for COE Research on Elements Science (No. 12CE2005), a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 11166250) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and Grants-in-Aid for Scientific Research (A) (Nos. 11304045 and 14204064) from the Japan Society for the Promotion of Science.

Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, torsion angles, and thermal and positional parameters for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020545X

---

(13) Neidlein, R.; Christen, D.; Poignée, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Pérez, C.; Hübner, T. *Angew. Chem., Int. Ed. Engl.* **1975**, *27*, 294−295.

(14) Calculated at the B3LYP/6-311G(2d, p) level (TZ(2d for Ge, Sn, and Pd)): **3b** (E = Ge), **a** = 1.385 Å, **b** = 1.390 Å, **c** = 1.392 Å, **d** = 1.403 Å, α = 122.14°, β = 116.21°, γ = 121.65°; **9** (E = Sn), **a** = 1.390 Å, **b** = 1.391 Å, **c** = 1.392 Å, **d** = 1.401 Å, α = 121.71°, β = 116.87°, γ = 121.42°; **10** (E = Pb), **a** = 1.389 Å, **b** = 1.388 Å, **c** = 1.394 Å, **d** = 1.399 Å, α = 121.82°, β = 116.75°, γ = 121.43°.