

Synthesis of Bis(germacyclopropa)benzenes and Structures of Their Annulated Benzene Rings

Tomoyuki Tajima, Takahiro Sasamori, Nobuhiro Takeda, Norihiro Tokitoh,*
Ken Yoshida, and Masaru Nakahara

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

Received September 2, 2005

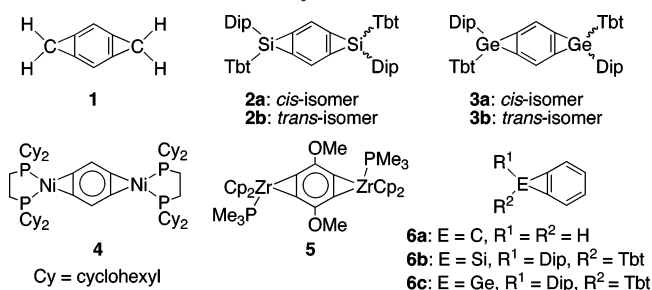
Extremely hindered bis(germacyclopropa)benzenes (**3a,b**; the IUPAC name is 4,8-digermatricyclo-[5.1.0.0^{3,5}]octa-1,3(5),6-triene) were synthesized as stable crystalline compounds by the reaction of the corresponding dilithiogermene Tbt(Dip)GeLi₂ (**8**; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl) with 1,2,4,5-tetrabromobenzene. The structures of the two stereoisomeric bis-(germacyclopropa)benzenes (**3a**, cis isomer; **3b**, trans isomer) were definitively determined by X-ray crystallographic analysis. The central benzene ring of **3a** was found to be folded, in contrast to the planar benzene ring of **3b**. The X-ray crystallographic analyses of **3a** and **3b** and the theoretical calculations for some model molecules revealed that the annulated benzene rings have no distinct bond alternation.

Introduction

Cycloproparenes,¹ i.e., strained aromatic hydrocarbon compounds fused with a three-membered ring, have attracted theoretical and experimental interest due to their unique structures and reactivities. Nevertheless, the synthesis of bis-(cyclopropa)benzene (**1**; Chart 1), in which two cyclopropene rings are fused to the central benzene ring, has not been achieved yet,² probably due to its high strain energy and the lack of suitable synthetic methods. The attention to the structure of such a strained ring system has been drawn mainly from the viewpoint of the Mills–Nixon effect.³ In contrast to this effect, it is well-known that the lengths of the juncture bonds of many types of cycloproparenes are found to be shorter than that of a benzene, as evidenced by computational works^{4a–e} and experimental results.^{4f–m} On the other hand, no experimental evidence has been obtained for the benzene nucleus annulated with multiple small hydrocarbon rings thus far, though the hypothesis itself is stated also for such multiring annulated systems that they are expected to have considerable bond alternation.⁵ In this context, elucidation of the structural features of benzene derivatives annulated with multiple small rings might be important to understand the strains of small-ring compounds systematically.

Although no stable example had been known for heteracyclopobenzene, i.e., cyclopropabenzene derivatives having a bridging heteroatom instead of a carbon atom, except for some transient, intermediary species reported so far,⁶ we have recently reported the synthesis of the first stable silacyclopobenzene (**6b**)^{7a,d} and germacyclopobenzene (**6c**),^{7b} i.e., heavier element analogues of a cyclopropabenzene derivative, by the reactions

Chart 1. Bis(cyclopropa)benzene (**1**) and Related Ring Systems



of the corresponding overcrowded dilithiometalloenes^{7–10} Tbt-(Dip)ELi₂ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl; E = Si, Ge), with *o*-dibromobenzene. The new isolated metallacyclopobenzene **6b,c** were fully characterized to show their unique molecular structures and reactivities.¹¹ More recently, we succeeded in the synthesis of the first stable bis(silacyclopobenzene) **2a,b** by the

* To whom correspondence should be addressed. Tel: +81-774-38-3200. Fax: +81-774-38-3209. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

(1) For reviews, see: (a) Halton, B. *Chem. Rev.* **2003**, *103*, 1327–1370. (b) Halton, B. *Chem. Rev.* **1989**, *89*, 1161–1185. (c) Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349–364.

(2) For the attempted synthesis of a bis(cyclopropa)benzene, see: (a) Banwell, M. G.; Halton, B. *Aust. J. Chem.* **1979**, *32*, 2689–2699. (b) Banwell, M. G.; Halton, B. *Aust. J. Chem.* **1979**, *32*, 849–858. (c) Banwell, M. G.; Halton, B. *Aust. J. Chem.* **1980**, *33*, 2277–2290. For the attempted synthesis of a bis(cyclopropa)[a,c]naphthalene, see: (d) Brinker, U. H.; Wüster, H.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 577–578.

(3) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510–2524.

(4) Many groups have cast serious doubts on the Mills–Nixon effect; see: (a) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277–8280. (b) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583–9587. (c) Bürgi, H. B.; Baldrige, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454–1456. (d) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034–12040. (e) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 1755–1759. (f) Bachrach, S. M. *J. Organomet. Chem.* **2002**, *634*, 39–46. (g) Billups, W. E.; Amry, B. E.; Lin, L. *J. Org. Chem.* **1984**, *39*, 3436–3437. (h) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150–3152. (i) Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304–305. (j) Neidlein, R.; Christie, D.; Poignee, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Perez, C.; Huebner, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 294–295. (k) Bläser, D.; Boese, R.; Brett, W. A.; Rademacher, P.; Schwager, H.; Stanger, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 206–209. (l) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313–317. (m) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399–3412. (n) Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Mohler, D. L.; Rogers, D. W.; Rüchard, C.; Sawhney, A. K.; Verevkin, S. P.; Vollhardt, C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, *122*, 7819–7820.

(5) For recent theoretical calculations on **1**, see: (a) Soncini, A.; Havenith, R. W. A.; Fowler, P. W.; Jenneskens, L. W.; Steiner, E. *J. Org. Chem.* **2002**, *67*, 4753–4758. (b) Bachrach, S. M. *J. Organomet. Chem.* **2002**, *643*, 39–46.

reaction of an overcrowded dilithiosilane, $\text{Tbt}(\text{Dip})\text{SiLi}_2$, with 1,2,4,5-tetrabromobenzene.^{7c,d} Meanwhile, the bis(metallacyclopropa)benzenes bis(nickelacyclopropa)benzene (**4**) and bis(zirconacyclopropa)benzene (**5**) have been prepared and their crystal structures were reported by Buchwald and Bennett, respectively.¹² Interestingly, **4** and **5** feature not bis(metallacyclopropa)benzene character but transition-metal–benzyne complex character, as judged by the results of their X-ray crystallographic analysis.

Here, we describe the synthesis of the first stable bis(germacyclopropa)benzenes (**3a**, cis isomer; **3b**, trans isomer), the heavier congeners of **1** and **2**, by the reaction of the corresponding overcrowded dilithiogermane $\text{Tbt}(\text{Dip})\text{GeLi}_2$ (**8**) with 1,2,4,5-tetrabromobenzene. The structural features of **3a,b** were revealed by X-ray crystallographic analyses along with theoretical studies on the structures of some model molecules. The aromaticity of the central benzene rings of **3a,b** is also evaluated on the basis of their structures, NMR studies, and NICS calculations together with those of related compounds.

Results and Discussion

Synthesis of Bis(germacyclopropa)benzenes 3a,b. Treatment of the diaryldilithiogermane $\text{Tbt}(\text{Dip})\text{GeLi}_2$ (**8**), which was

(6) (a) Thétaz, C.; Wentrup, C. *J. Am. Chem. Soc.* **1976**, *98*, 1258–1259. (b) Yranzo, G. I.; Elguero, J.; Flammang, R.; Wentrup, C. *Eur. J. Org. Chem.* **2001**, 2209–2220. (c) Torres, M.; Clement, A.; Bertie, J. E.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978**, *43*, 2490–2493. (d) Cadogan, J. I. G.; Sharp, J. T.; Trattles, M. J. *J. Chem. Soc., Chem. Commun.* **1974**, 900–901. (e) Schultz, R.; Schweig, A. *Tetrahedron Lett.* **1984**, *25*, 2337–2340. (f) Kaiser, R. I.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2350–2352. (g) Steinfeld, J. I. *Spectrochim. Acta* **1990**, *46A*, 589–596.

(7) (a) Hatano, K.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 4829–4830. (b) Tokitoh, N.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Takagi, N.; Nagase, S. *Organometallics* **2002**, *21*, 4309–4311. (c) Tajima, T.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2003**, *32*, 220–221. (d) Tajima, T.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Organomet. Chem.* **2003**, *686*, 118–126.

(8) (a) Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, 931–932. (b) Tokitoh, N.; Sadahiro, T.; Hatano, K.; Sasaki, T.; Takeda, N.; Okazaki, R. *Chem. Lett.* **2002**, 34–35.

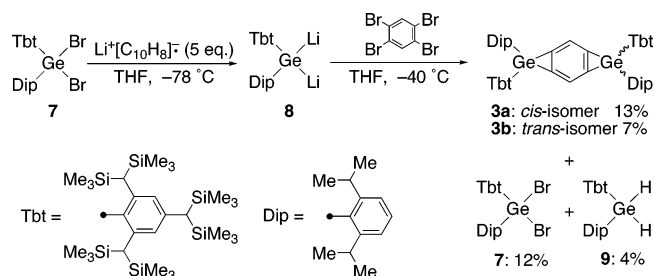
(9) (a) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231–10232. (b) Ichinohe, M.; Arai, Y.; Sekiguchi, A.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 4141–4143. (c) Sekiguchi, A.; Izumi, R.; Ihara, S.; Ichinohe, M.; Lee, V. Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 1598–1600. (d) Sekiguchi, A.; Izumi, R.; Lee, V. Y.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 14822–14823. (e) Sekiguchi, A.; Izumi, R.; Lee, V. Y.; Ichinohe, M. *Organometallics* **2003**, *22*, 1483–1486. (f) Nakata, N.; Izumi, R.; Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 5058–5059. (g) Sekiguchi, A.; Inoue, S.; Ichinohe, M.; Arai, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9626–9629. (h) Nakata, N.; Izumi, R.; Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2005**, *34*, 582–583.

(10) (a) Mehrotra, S. K.; Kawa, H.; Baran, J. R., Jr.; Ludvig, M. M.; Lagow, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 9003–9004. (b) Baran, J. R., Jr.; Isom, H. S.; Lagow, R. J. *Inorg. Chem. Commun.* **1998**, *1*, 222–224. (c) Kira, M.; Iwamoto, T.; Yin, D.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **2001**, 910–911. (d) Bravo-Zhivotovskii, D.; Ruderfer, I.; Melamed, S.; Botoshansky, M.; Tumanskii, B.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 739–1600. For other dimetalated germanes, see: (e) Mochida, K.; Tatsushige, N.; Hamashima, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1443–1447. (f) Bravo-Zhivotovskii, D. A.; Pigarev, S. D.; Vyazanskina, O. A.; Vyazanskin, N. S. *Zh. Obshch. Khim.* **1987**, *57*, 2644–2645. (g) Castel, A.; Rivière, P.; Satgé, J.; Ko, Y.-H. *J. Organomet. Chem.* **1988**, *342*, C1–C4. (h) Castel, A.; Rivière, P.; Satgé, J.; Ko, H. Y. *J. Organometallics* **1990**, *9*, 205–210. (i) Castel, A.; Rivière, P.; Satgé, J.; Desor, D. *J. Organomet. Chem.* **1992**, *433*, 49–61.

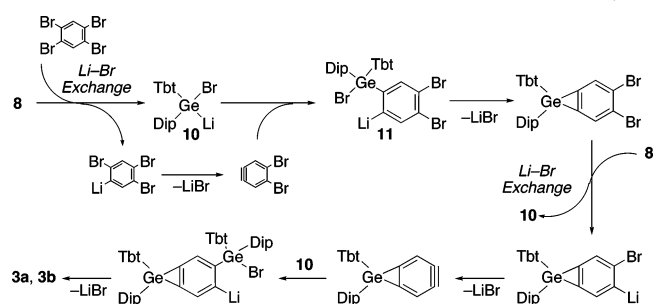
(11) (a) Tajima, T.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Commun.* **2004**, 402–403. (b) Tajima, T.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Appl. Organomet. Chem.* **2005**, *19*, 570–577. (c) Sasamori, T.; Sasaki, T.; Takeda, N.; Tokitoh, N. *Organometallics* **2005**, *24*, 612–618.

(12) (a) Bennett, M. A.; Grage, J. S.; Griffiths, K. D.; Roberts, N. K.; Robertson, G. B.; Wickramasinghe, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 941–942. (b) Buchwald, S. L.; Lucas, E. A.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4396–4397.

Scheme 1. Synthesis of 3a,b



Scheme 2. Possible Mechanism for the Formation of 3a,b



generated by the exhaustive reduction of $\text{Tbt}(\text{Dip})\text{GeBr}_2$ (**7**) with an excess amount of lithium naphthalenide (THF solution, 5 mol equiv) at -78°C in THF, with 0.6 equiv of 1,2,4,5-tetrabromobenzene at -40°C gave the bis(germacyclopropa)benzenes **3a** (cis isomer) and **3b** (trans isomer) as colorless crystals in 13 and 7% yields, respectively (Scheme 1). Although bis(germacyclopropa)benzenes **3a,b** were stable enough to be handled in the open air and/or in hydrocarbon solvents such as hexane and benzene, they underwent decomposition in halogenated solvents such as CHCl_3 or on treatment with silica gel.¹³

The formation of bis(germacyclopropa)benzenes **3a,b** can be explained by a reaction mechanism similar to that for the previously reported metallacyclopropabenzenes **6b,c**.⁷ At first, dilithiogermane **8** reacts with 1,2,4,5-tetrabromobenzene to give $\text{Tbt}(\text{Dip})\text{GeBrLi}$ (**10**)^{7b} and 1,2,4-tribromo-5-lithiobenzene via a Li–Br exchange reaction. Then, the intermediary 4,5-dibromobenzene, which should be generated by the elimination of LiBr from 1,2,4-tribromo-5-lithiobenzene, may react with germylenoid **10**^{7b} to afford the *o*-germylated phenyllithium **11**. The intramolecular cyclization of **11** followed by a subsequent similar condensation at the 3,4-positions of the resulting 3,4-dibromo-1-germacyclopropabenzene gives **3a,b** (Scheme 2). In addition, $\text{Tbt}(\text{Dip})\text{GeBr}_2$ (**7**; 12%) and $\text{Tbt}(\text{Dip})\text{GeH}_2$ (**9**; 4%) were obtained as other reaction products in this reaction. Dibromogermane **7** was most likely obtained by the competing Li–Br exchange reaction of $\text{Tbt}(\text{Dip})\text{GeBrLi}$ (**10**) with 1,2,4,5-tetrabromobenzene.^{7b} $\text{Tbt}(\text{Dip})\text{GeH}_2$ (**9**) was probably generated by the protonation of **8**. The formation of bis(germacyclopropa)benzenes **3a,b** should be interpreted in terms of the concurrent generation of different reactive species such as the germylenoid **10** and benzyne species in the reaction under the mild conditions.

Molecular Structures of 3a,b in the Solid State. The molecular structures of **3a,b** were definitively determined by X-ray crystallographic analysis at -170°C (Figures 1 and 2). The selected bond lengths and angles of **3a,b** are listed in Table 1, together with the optimized structural parameters of model molecules **3c–e** (**3c**, $\text{R}^{1-4} = \text{H}$; **3d**, $\text{R}^{1-4} = \text{Me}$; **3e**, $\text{R}^{1-4} =$

(13) The bis(silacyclopropa)benzenes **2a,b** were surprisingly stable as compared with **3a,b**. Compounds **2a,b** can be purified by preparative thin-layer chromatography on silica gel without any decomposition.^{7c,d}

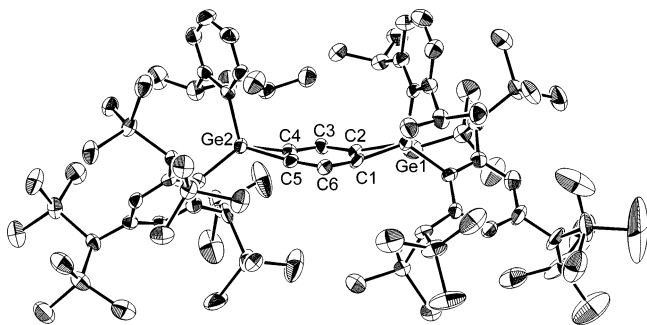


Figure 1. ORTEP drawing of **3a** with thermal ellipsoid plots (50% probability). Hydrogen atoms are omitted for clarity.

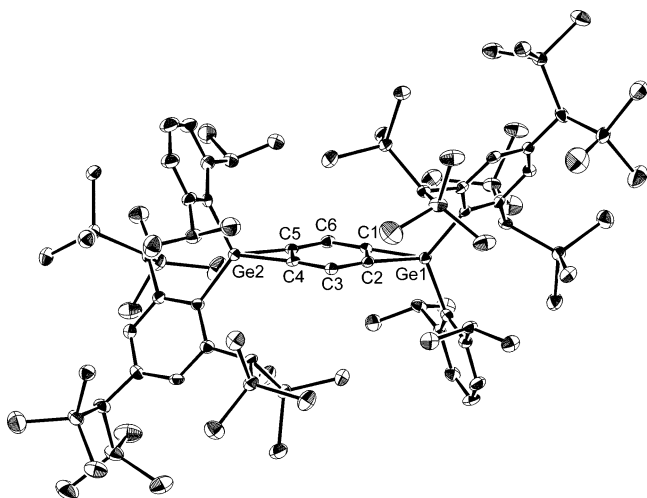


Figure 2. ORTEP drawing of **3b** with thermal ellipsoid plots (50% probability). Hydrogen atoms and a solvated hexane molecule are omitted for clarity.

Ph). The structural analysis for **3b** revealed the planarity of the bis(germacyclopropa)benzene ring. The sums of the bond angles around the juncture carbon atoms (C1, C2, C4, and C5) and the sum of the interior bond angles of the central benzene ring are almost 360 and 720°, respectively. On the other hand, the central benzene ring of **3a** was found to be slightly folded.

The folded benzene ring of **3a** is depicted in Figure 3 together with that of **2a**. The dihedral angle between the Ge1–C1–C2 and C6–C1–C2–C3 planes (δ) and that between the C3–C4–C5–C6 and C4–Ge2–C5 planes (ζ) are 13.69 and 11.73°, respectively. Moreover, the benzene ring is bent and the dihedral angle between the C6–C1–C2–C3 and C3–C4–C5–C6 planes (ϵ) is 1.88°. Previous works showed that the central benzene ring of bis(silacyclopropa)benzene **2a** had a similar bent structure, probably due to the steric repulsion between the two bulky Tbt groups (the corresponding dihedral angles are $\delta = 11.95^\circ$, $\zeta = 10.31^\circ$ and $\epsilon = 4.73^\circ$, respectively).^{7c,d} The bent structure of **3a** might also be due to the large steric repulsion provided by the extremely bulky steric protection groups as in the case of **2a**, in consideration of the planar geometries of the central benzene ring in the theoretically optimized structures of **3c–e**.

The computational works on bis(cyclopropa)benzene **1** (R = H) by Jenneskens et al. indicated the relatively short length (1.336 Å) for the juncture C–C bonds in its benzene ring.⁵ In the case of **3a**, the C–C bond lengths in the central benzene ring vary to a small extent (between 1.416(9) and 1.364(9) Å), while those of **3b** showed almost no variation (1.389(6)–1.403(6) Å).¹⁴ The existence of bond alternation in **3a** cannot be argued, due to relatively large standard deviations and the subtle

differences of the bond lengths. Although there may be some possibility for the existence of bond alternation in **3a**, it can be concluded that the bis(germacyclopropa)benzenes **3a,b** showed no distinct bond alternation and no obvious Mills–Nixon effect was observed in **3a,b** at this stage.

Interestingly, the central benzene ring skeletons of **3a,b** have bond angles undoubtedly deviating from those of the usual benzene rings (120°); that is, the interior angles at C3 and C6 are 111.9–112.5° and those of the C1, C2, C4, and C5 juncture carbons are 123.1–124.2°. The deviations in the interior angles of **3a** and **3b** are slightly larger than those of the previously reported germacyclopropabenzene **6c**.^{8c}

The observed structural parameters of the central benzene rings of bis(germacyclopropa)benzenes **3a,b** are supported by the calculated values for some model molecules (**3c–e**). Experimental and theoretical studies on the structural features of the bis(germacyclopropa)benzenes suggest that the structural features of the central benzene rings of **3a,b** are different from those of hydrocarbon systems: i.e., the bis(cyclopropa)benzene derivatives **1**.

¹H and ¹³C NMR Spectroscopic Studies of 3a,b. Bis(germacyclopropa)benzenes **3a,b** exhibited very complicated ¹H and ¹³C NMR spectra at room temperature. To solve this problem, we have measured their ¹H and ¹³C NMR spectra at various temperatures. The NMR chemical shifts for the protons and carbons of the central benzene rings of **3a,b** were found in the aromatic region. In the ¹H NMR spectrum of **3a** in tetrachloroethane-*d*₂ at 30 °C, two protons of the central benzene ring appeared as a singlet signal at 7.77 ppm.¹⁵ In contrast to the case of **3a**, the aromatic protons of bis(germacyclopropa)benzene **3b** were observed nonequivalently as two signals at 7.87 and 7.98 ppm in C₆D₁₂ at 30 °C. At 50 °C, the coalesced signal assignable to the aromatic protons of the bis(germacyclopropa)benzene ring was observed as one broad signal at 7.93 ppm (Figure 4). This dynamic behavior was observed as fully reversible processes.

The ¹³C NMR spectrum of **3b** in C₆D₁₂ at 80 °C showed signals at 126.3 (C^β) and 150.0 ppm (C^α),¹⁶ which can be assigned to the ¹³C NMR chemical shifts for the carbon atoms of the central benzene ring, in good agreement with those calculated in some model molecules (Table 2). The ¹³C NMR chemical shifts of **3b** observed here are in the region similar to those of silacyclopropabenzene **6b** (150.0 (C^α) and 126.6 ppm (C^β)) and germacyclopropabenzene **6c** (153.4 (C^α) and 126.6 ppm (C^β)).

Signals in the ¹³C NMR spectra of **3a** could not be assigned, due to their being much more complicated than those of **3b** even at higher temperatures. Thus, measurements of the ¹³C NMR spectra of **3a** were performed under several conditions (for example, the measurement at 135 °C in tetrachloroethane-*d*₂), but the spectra were still complicated and **3a** slowly decomposed under such severe conditions. Such complication of the ¹³C NMR spectra of **3a** is probably due to the highly restricted rotation of the some C–C bonds in **3a**.

Calculations of Nucleus-Independent Chemical Shift (NICS)¹⁷ Values for Bis(metallacyclopropa)benzenes. It is

(14) Typical C–C bond lengths of benzene are 1.39–1.40 Å: Allen, F. H.; Kennard, O.; Watson, D. C.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

(15) In the ¹H NMR of **3a** in C₆D₁₂ at 30 °C, the singlet observed at 7.84 ppm can be assigned to the two protons of the central benzene ring. The aliphatic region of the ¹H NMR spectrum of **3a** was too complicated to be assigned.

(16) Variable-temperature ¹³C NMR spectra of **3b** were measured in the range of 30–80 °C. See the Supporting Information.

Table 1. Observed and Calculated Bond Lengths (Å) and Angles (deg) of Bis(germacyclopropa)benzenes

	obsd		calcd ^a		
	3a (cis isomer) R ¹ = R ³ = Dip R ² = R ⁴ = Tbt	3b (trans isomer) R ¹ = R ⁴ = Dip R ² = R ³ = Tbt	3c R ¹⁻⁴ = H	3d R ¹⁻⁴ = Me	3e R ¹⁻⁴ = Ph
Bond Lengths					
Ge1–C1	1.928(7)	1.937(4)	1.929	1.931	1.932
Ge1–C2	1.934(6)	1.944(4)	1.929	1.931	1.932
Ge2–C4	1.939(7)	1.935(4)	1.929	1.931	1.932
Ge2–C5	1.908(6)	1.938(4)	1.929	1.931	1.932
C1–C2	1.408(10)	1.394(6)	1.391	1.400	1.400
C2–C3	1.381(8)	1.394(6)	1.392	1.392	1.393
C3–C4	1.396(9)	1.397(6)	1.392	1.392	1.393
C4–C5	1.364(9)	1.389(6)	1.391	1.400	1.400
C5–C6	1.416(9)	1.391(6)	1.392	1.392	1.393
C6–C1	1.403(9)	1.403(6)	1.392	1.392	1.393
Bond Angles					
C1–C2–C3	123.1(6)	123.8(4)	123.8	123.2	123.4
C2–C3–C4	113.3(6)	112.5(4)	112.3	113.6	113.3
C3–C4–C5	124.2(6)	123.7(4)	123.8	123.2	123.4
C4–C5–C6	123.9(6)	124.2(4)	123.8	123.2	123.4
C5–C6–C1	111.9(6)	112.3(4)	112.3	113.6	113.3
C6–C1–C2	123.5(6)	123.6(4)	123.8	123.2	123.4
Ge1–C1–C2	68.8(4)	69.2(2)	68.9	68.7	68.8
Ge1–C2–C1	68.4(4)	68.7(3)	68.9	68.7	68.8
C1–Ge1–C2	42.8(3)	42.10(17)	42.2	42.5	42.5
Ge2–C4–C5	68.0(4)	69.1(3)	68.9	68.7	68.8
Ge2–C5–C4	70.4(4)	68.9(3)	68.9	68.7	68.8
C4–Ge2–C5	41.5(3)	42.05(18)	42.2	42.5	42.5

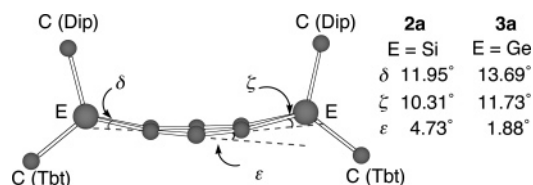
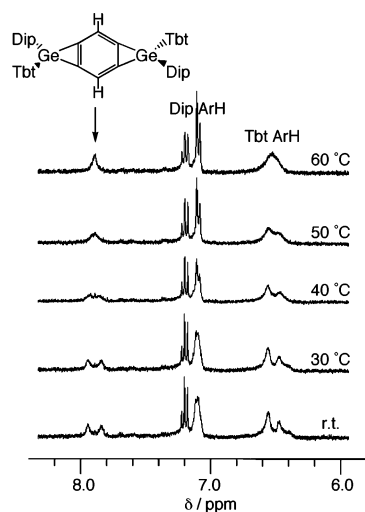
^a B3LYP/6-311+G(2d,p) for C and H and LANL2DZ for Ge.

Figure 3. Dihedral angles of 2a (E = Si) and 3a (E = Ge).

Figure 4. Variable-temperature ¹H NMR spectra for the aromatic region of 3b in cyclohexane-*d*₁₂.

important to compare the aromaticity of the central benzene ring of the bis(metallacyclopropa)benzenes with that of the related hydrocarbon systems and monometallacyclopropabenzene. Recently, Schleyer has advocated the use of the NICS as a probe for aromaticity.¹⁷ Negative larger absolute values

Table 2. Observed and Calculated ¹H and ¹³C NMR Chemical Shifts (ppm) of Bis(germacyclopropa)benzenes and Related Compounds

	δ(H ^β)	δ(C ^α)	δ(C ^β)	δ(C ^γ)
3a (R ¹ , R ³ = Dip, R ² , R ⁴ = Tbt) ^a	7.83	<i>b</i>	<i>b</i>	
3b (R ¹ , R ⁴ = Dip, R ² , R ³ = Tbt) ^c	7.93	150.0	126.3	
3c (R ¹⁻⁴ = H) ^d	8.17	145.8	131.5	
3d (R ¹⁻⁴ = Me) ^d	8.08	155.6	130.2	
6a (E = C, R ^{1,2} = H) ^e		125.4	114.7	128.8
6b (E = Si, R ¹ = Dip, R ² = Tbt) ^f		150.0	126.6	130.1
6c (E = Ge, R ¹ = Dip, R ² = Tbt) ^f		153.4	126.6	129.7

^a Measured in tetrachloroethane-*d*₂ at 90 °C. ^b Not assigned. ^c Measured in cyclohexane-*d*₁₂ at 80 °C. ^d Calculated at GIAO-B3LYP/6-311++G(2d,p)/B3LYP/6-311G(2d,p) for C and H and LANL2DZ for Ge. ^e Measured in CCl₄/CDCl₃ (3:1). ^f Measured in CDCl₃ at room temperature.

for the NICS indicate a greater aromaticity for the ring. The NICS(1) values of the related compounds are listed in Figure 5. The computation of the NICS(1) value of bis(germacyclopropa)benzene 3c showed a large negative value (−13.2 ppm), as did that of benzene (−12.8 ppm). It is suggested that bis(germacyclopropa)benzene 3c has a ring current effect similar to that of the monogermacyclopropabenzene on the basis of NICS values of cyclopropabenzene and metallacyclopropabenzene. It should be noted that the aromaticity of the benzene ring is not dramatically changed, even in the case of an arene ring fused with two three-membered rings.

(17) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

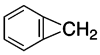
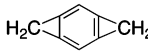
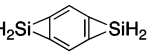
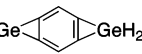
			
	6a		
NICS(0)	-11.4	-11.2	-9.4
NICS(1)	-12.8	-13.0	-12.6
			
	1		3c
NICS(0)	-10.7	-8.0	-8.7
NICS(1)	-13.2	-13.0	-13.2

Figure 5. NICS(0) and NICS(1) values (ppm) for the annelated ring systems calculated at the GIAO-HF/6-31G*/B3LYP/6-31G* level.

Conclusion

In summary, we have succeeded in the syntheses of bis-(germacyclopropa)benzenes **3a,b** as stable crystalline compounds for the first time by taking advantage of dilithiogermane **8** bearing two bulky substituents. Since the synthesis of a stable bis(cyclopropa)benzene has not been achieved yet,² the stable examples of bis(metallacyclopropa)benzenes are important from the viewpoints of structural chemistry and organoelement chemistry. In addition, dilithiometalanes were proved to be useful reagents for the synthesis of the metallacyclopropabenzene derivatives. The crystallographic analyses of the bis-(metallacyclopropa)benzenes revealed that the annelated benzene rings showed almost no distinct bond alternation. It can be concluded that annelation of metallacyclopropene rings¹⁸ to a benzene ring does not cause significant bond alternation but has very little influence on the aromaticity of the central benzene ring. We believe that these results provide very important information on the chemistry of cycloproparenes and heavier group 14 elements.

Experimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. Cyclohexane-*d*₁₂ and tetrachloroethane-*d*₂ were purchased from Cambridge Isotopes. All NMR spectra were collected on JEOL JNM AL-300 and ECA-600 spectrometers. ¹H and ¹³C NMR chemical shifts are recorded in ppm relative to SiMe₄ (δ 0) and were referenced internally with respect to the residual proton impurity (cyclohexane-*d*₁₂, δ 1.38; tetrachloroethane-*d*₂, δ 5.98) and the ¹³C resonance of the solvent (cyclohexane, δ 26.4), respectively. Wet column chromatography was performed with Wakogel C-200. Preparative gel permeation liquid chromatography (GPLC) was performed on a LC-908 or LC-918 instrument (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent toluene) and JAIGEL-OA2000 (eluent hexane). Fast atom bombardment (FAB) mass spectral data were obtained on a JEOL JMS-700

spectrometer. Elemental analyses were carried out at the Micro-analytical Laboratory of Institute for Chemical Research, Kyoto University. Melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Tbt(Dip)GeBr₂ (**7**) was prepared according to the reported procedures.^{7b}

Synthesis of Bis(germacyclopropa)benzenes 3a,b. A THF solution of lithium naphthalenide (2.36 M, 0.53 mL, 1.25 mmol, 5 mol equiv) was added to a THF solution (3 mL) of **7** (227 mg, 0.25 mmol) at -78 °C. After the mixture was stirred for 1 h at the same temperature, 1,2,4,5-tetrabromobenzene powder (58 mg, 0.15 mmol) was added to the reaction mixture at -40 °C. After the removal of the solvent, the mixture was extracted with hexane several times. The extracts were combined, filtered with Celite, and evaporated. The residue was subjected to GPLC (toluene) followed by gel permeation optical resolution chromatography¹⁹ using hexane as an eluent to give **3a** (34.9 mg, 21.3 μmol, 13%) and **3b** (14.4 mg, 8.8 μmol, 7%), respectively. The other fraction of GPLC was purified by wet column chromatography (SiO₂/hexane) to give Tbt(Dip)GeH₂ (7.9 mg, 1.0 μmol, 4%) and Tbt-(Dip)GeBr₂ (**7**; 27.2 mg, 30 μmol, 12%), respectively. Spectral data for Tbt(Dip)GeH₂ (**9**) and Tbt(Dip)GeBr₂ (**7**) have already been reported.^{7b}

3a: colorless crystals; mp 156 °C dec; ¹H NMR (C₂D₂Cl₄, 90 °C) δ -0.94 (s, 54H), 0.19 (s, 54H), 0.62 (br s, 4H), 1.08–1.34 (m, 24H), 1.38 (s, 2H), 2.81 (s, 2H), 3.67 (br s, 2H), 6.43 (br s, 4H), 6.93 (d, ³J_{HH} = 7.8 Hz, 4H), 7.08 (t, ³J_{HH} = 7.8 Hz, 2H), 7.83 (s, 2H); HRMS (FAB) *m/z* calcd for C₈₄H₁₅₄⁷⁴Ge₂Si₁₂ 1646.7705 [M⁺], found 1646.7753 [M⁺]. Anal. Calcd for C₈₄H₁₅₄Ge₂Si₁₂: C, 61.28; H, 9.43; Found: C, 61.27; H, 9.54.

3b: colorless crystals; mp 150 °C dec; ¹H NMR (C₆D₁₂, 100 °C) δ -0.11 (s, 36H), 0.05 (s, 72H), 0.87 (br s, 2H), 1.09 (br s, 4H), 1.35 (br s, 24H), 2.83 (s, 2H), 2.81 (br s, 2H), 6.40 (br s, 4H), 7.03 (d, ³J_{HH} = 7.8 Hz, 4H), 7.15 (t, ³J_{HH} = 7.8 Hz, 2H), 7.92 (s, 2H); ¹³C NMR (C₆D₁₂, 80 °C) δ 1.3 (q), 1.9 (q), 23.4 (q), 28.1 (q), 30.1 (d), 31.7 (d), 35.4 (d), 37.5 (d), 124.1 (d), 126.3 (d), 129.7 (d), 130.3 (d), 131.5 (s), 131.4 (s), 141.6 (s), 144.6 (s), 152.0 (s), 152.7 (s), 154.5 (s); HRMS (FAB) *m/z* calcd for C₈₄H₁₅₄⁷⁴Ge₂Si₁₂ 1646.7705 [M⁺], found 1646.7761 [M⁺]. Anal. Calcd for C₈₄H₁₅₄Ge₂Si₁₂: C, 61.28; H, 9.43; Found: C, 61.25; H, 9.45.

Theoretical Calculations. Theoretical calculations for model molecules **3c–e** were carried out using the Gaussian 98W program²⁰ with density functional theory at the B3LYP level.²¹ It was confirmed by frequency calculations that the optimized structures have minimum energies. The 6-311G++(2d,p) basis sets were used for C and H. The Lanl2DZ basis sets were used with effective core potential for Ge. The GIAO calculations were carried out at the 6-311G++(2d,p) levels for the optimized geometries, and the results of calculations for tetramethylsilane at the same level were used for the standard of chemical shifts.

X-ray Structural Determinations. Crystallographic data of **3a,b** are summarized in Table 3. Single crystals of **3a** were grown by

(19) Although **3a,b** featured no chirality character, the separation could only be achieved using optical resolution chromatography with (R)-phenylglycine as packing.

(20) All calculations were carried out using Gaussian 98W: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) (a) Becke, A. D. *Phys. Rev.* **1988**, A38, 3098–3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652. (c) Lee, W. Y.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785–789.

(18) For germacyclopropenes: (a) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, M. Y.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, 290, C27–C30. (b) Ando, W.; Ohgaki, H.; Kabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 659–661. (c) Tokitoh, N.; Kishikawa, K.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 827–828. (d) Fukaya, N.; Ichinohe, M.; Kabe, Y.; Sekiguchi, A. *Organometallics* **2001**, 20, 3364–3366. (e) Meiners, F.; Saak, W.; Weidenbruch, M. Z. *Anorg. Allg. Chem.* **2002**, 628, 2821–2822. For other heavy cyclopropanes and cyclopropenes, see: (f) Sekiguchi, A.; Lee, V. Y. *Chem. Rev.* **2003**, 103, 1429–1447. (g) Sekiguchi, A.; Lee, V. Y. In *Organosilicon Chemistry V, From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 92–100. (h) Lee, V. Y.; Sekiguchi, A. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rapoport, Z., Apeloig, Y., Eds.; Wiley: New York, 2002; Vol. 2, Chapter 14, pp 903–933. (i) Roskamp, E.; Rpskamp, C. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 1A, pp 305–331.

Table 3. Crystallographic Data for 3a and 3b·(hexane)

	3a	3b·(hexane)
formula	C ₈₄ H ₁₅₄ Ge ₂ Si ₁₂	C ₉₀ H ₁₆₈ Ge ₂ Si ₁₂
mol wt	1646.33	1732.50
cryst color	colorless	colorless
cryst dimens/mm	0.20 × 0.20 × 0.20	0.50 × 0.30 × 0.03
cryst syst	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
unit cell syst		
<i>a</i> /Å	12.833(2)	15.2827(14)
<i>b</i> /Å	16.0045(17)	43.085(2)
<i>c</i> /Å	48.473(7)	17.3703(15)
α /deg	90	90
β /deg	90	112.659(4)
γ /deg	90	90
<i>V</i> /Å ³	9956(2)	10554.8(15)
<i>Z</i>	4	4
<i>D_c</i> /g cm ⁻³	1.098	1.090
μ /mm ⁻¹	0.785	0.744
<i>F</i> (000)	3560	3760
radiation	Mo K α (λ = 0.710 70 Å)	
temperature (K)	103(2)	
θ range/deg	2.39–25.00	1.73–25.00
<i>hkl</i> range	–15 ≤ <i>h</i> ≤ 15 –19 ≤ <i>k</i> ≤ 19 –57 ≤ <i>l</i> ≤ 57	–18 ≤ <i>h</i> ≤ 18 –50 ≤ <i>k</i> ≤ 51 –20 ≤ <i>l</i> ≤ 20
no. of measd rflns	84 168	89 731
no. of unique rflns	19 532 (<i>R</i> _{int} = 0.1116)	18 478 (<i>R</i> _{int} = 0.0744)
completeness to θ /%	99.8	99.3
max and min transmn	0.8588 and 0.8588	0.9780 and 0.7075
refinement method	full-matrix least squares on <i>F</i> ²	
no. of data/restraints/params	17 490/65/965	18 478/100/1009
goodness of fit on <i>F</i> ²	1.153	1.218
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0809 <i>wR</i> 2 = 0.1729	<i>R</i> 1 = 0.0785 <i>wR</i> 2 = 0.1252
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0967 <i>wR</i> 2 = 0.1799	<i>R</i> 1 = 0.0947 <i>wR</i> 2 = 0.1312
largest diff peak and hole/e Å ⁻³	0.490 and –0.359	0.732 and –0.582

the slow evaporation of its saturated solution in hexane and EtOH in the refrigerator, while single crystals of **3b** were grown in hexane, respectively. Sample preparation consisted of coating the crystal with hydrocarbon oil, mounting it on a glass fiber, and placing it under a cold stream of N₂ on the diffractometer. The intensity data of **3a,b** were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.710 71 Å). The structures were solved by direct methods (SIR97)²²

and refined by full-matrix least-squares procedures on *F*² for all reflections (SHELXL-97).²³ All hydrogen atoms were placed using AFIX instructions, while all of the other atoms were refined anisotropically. In the case of **3a**, the disordered trimethylsilyl groups at the para position of the Tbt group were restrained to be identical with each other using the DFIX and SIMU instructions. The occupancies of disordered fragments were refined (0.59:0.41). In the case of **3b**, the solvated hexane molecule was disordered and the occupancies were restrained to be identical with each other using the DFIX and SIMU instructions. The occupancies of the disordered fragments were refined (0.62:0.38). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center: CCDC No. 277662 and No. 277663 for **3a,b**, respectively.

Acknowledgment. This work was partially supported by Grants-in-Aid for the COE Research on Elements Science (No. 12CE2005), Scientific Researches (Nos. 14078213, 14204064, and 15655011), and the 21st Century COE on Kyoto University Alliance for Chemistry (Novel Organic Materials Creation & Transformation Project) and Nanotechnology Support Project from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. This manuscript was written at TU Braunschweig during the tenure of a von Humboldt Senior Research Award of N. Tokitoh, who is grateful to the Alexander von Humboldt Stiftung for their generosity and to Professors Reinhard Schmutzler and Wolf-Walther du Mont for their warm hospitality. T.T. acknowledges Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We are grateful to Japan Analytical Industry Co., Ltd., for active support for the preparative HPLC.

Supporting Information Available: CIF files giving crystallographic data for **3a,b**, including all refinement parameters, bond lengths and angles, and positional and thermal parameters, and text and a figure giving details of variable-temperature ¹³C NMR studies of **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0507629

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

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