

The photochemical reaction of 1,2-digermacyclobutane with C₆₀: possible example of a closed [6,5]-bridged fullerene derivative of germacyclopropane

Yoshio Kabe^{a,*}, Harunobu Ohgaki^a, Toru Yamagaki^b, Hiroshi Nakanishi^b,
Wataru Ando^a

^a Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

^b National Institute of Bioscience and Human-Technology, Tsukuba, Ibaraki 305, Japan

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Dedicated to Professor Nefedov on his 70th birthday and in honor of his contribution to organo-silicon and -germanium chemistry

Abstract

The photolysis of 1,2-digermacyclobutane derivatives (**1**) with bulky bistrimethylsilylmethyl (disyl) groups in a toluene solution of C₆₀ provided the germylene (**2**) and germacyclopropane (**3**) adducts of C₆₀, respectively. The structures of the two products were characterized using ¹H- and ¹³C-NMR spectra. The signals showed a dramatic change in line shape with temperature. The non-equivalence of the two disyl groups at high temperature, as well as the presence of quaternary aliphatic carbon, suggested that the germylene adduct (**2**) may be a closed [6,5] adduct: a possible first example of a closed [6,5]-bridged fullerene adduct. PM3 and ab initio calculations also support an energetically preferred closed [6,5] germacyclopropane adduct over an open [6,5] germa-annulene. The non-equivalence of the two disyl groups at low temperatures, as well as the presence of two methylene groups, indicated a germacyclopropane adduct (**3**), having a germacyclopentane structure that includes a closed [6,6] bond on the C₆₀ surface. To take into account the regio-selective formation of the [6,5] adducts, a fragmentation mechanism of the digermacyclobutane on the C₆₀ surface is proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germanium; Fullerene; Digermacyclobutane

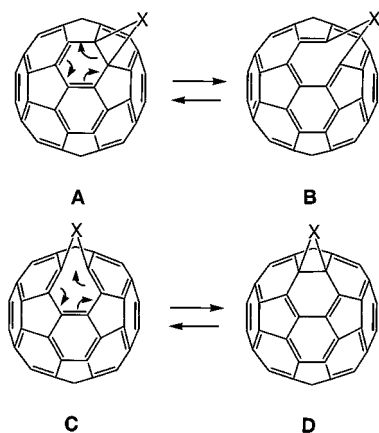
1. Introduction

In spite of the relatively brief history of fullerene science, the methano-, oxo-, aza- and sila-bridged [60] fullerenes [1–4] have already been the subject of intensive studies. Of the four possible isomers (**A–D**) resulting from the addition of one carbon or one heteroatom across a carbon–carbon bond, only two isomers, the closed [6,6] derivatives (**A**; X = CH₂, CR₂, O, NCO₂R and SiR₂), and the open [6,5] derivatives (**C**; X = CH₂, CR₂ and NR) have been isolated and unambiguously characterized. Semi-empirical (MNDO) and ab initio

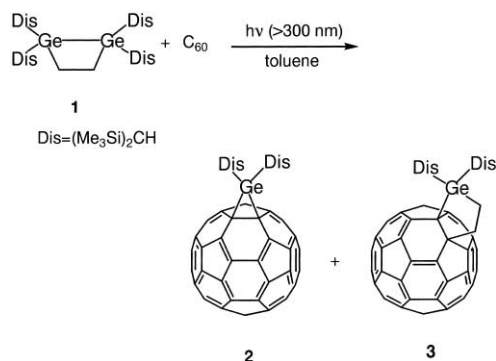
calculations [6] provide a simple, and currently accepted, rationale for the selective formation of **A** and **C** isomers: these structures do not contain a destabilizing cyclopentene double bond, whereas the **B** and **D** isomers contain either three or two double bonds in five-membered rings, respectively. Recently, the first isolation of closed [6,5]-bridged fullerene derivatives (**D**; X = NCO₂R) of aziridine has been reported [3e]. However, two following studies [3m,q] revealed that these products were open [6,5]-bridged aza-annulene structures rather than aziridines. Following this line of thought, the hypothetical isomers **B** and **D** can be derived from **A** and **C**, respectively, via valence isomerization. The introduction of a heavier element as the bridging heteroatom, such as germanium, is thought to make a transannular bond longer, and to destabilize a transannular homo-conjugation of open [6,5]-bridged annulenes (**C**) [6c]. As a result, valence isomerization is

* Corresponding authors. Tel.: +81-298-534207; fax: +81-298-536503.

E-mail address: kabe@staff.chem.tsukuba.ac.jp (Y. Kabe).



Scheme 1.



Scheme 2.

thought to be favored by closed [6,5]-bridged heterocyclopropanes (**D**). As a part of our continuing study of silicon and germanium small-ring chemistry [5], we report here that the photochemical fragmentation of digermacyclobutane (**1**) in the presence of C60 affords a germylene, as well as germacyclopentane adducts, of C60 (**2** and **3**). The former is possibly the first example of a closed [6,5]-bridged derivative (**D**) of germacyclopentane, while the latter is a closed [6,6]-bridged fullerene derivative (**A**) of germacyclopentane (Scheme 1).

2. Results and discussion

2.1. Synthesis of 1,2-digermacyclobutane (**1**)

1,2-Digermacyclobutane (**1**) was prepared using a published procedure [5c]. Ethylene gas was bubbled through a solution of bis(disyl)germylene ((Dis)₂Ge) in toluene. After removal of the solvent, purification of the residue was carried out by silica gel column chromatography to give an air- and moisture-stable compound.

2.2. Photolysis of 1,2-digermacyclobutane (**1**) in the presence of C60

The photolysis of **1** in the presence of C60 gave adducts **2** and **3** in 57 and 43% conversion yields, respectively. Adduct **2** was unusually soluble in organic solvents, and was slightly unstable on exposure to air and moisture, whereas adduct **3** was fairly stable to air and moisture. Fast atom bombardment mass spectroscopy (FABMS) of **2** showed a molecular ion peak at mass = 1112, and this value was assigned to the molecular formula of C60 and germylene ((Dis)₂Ge). FABMS of **3** also showed a molecular ion peak at mass = 1140, which was assigned to C60 and germacyclopentane ((Dis)₂GeCH₂CH₂) (Scheme 2).

The ¹H-NMR spectrum of **2** was highly dependent on the solvent and temperature. At room temperature, four broad signals from SiMe₃ of the disyl groups were observed in decalin-*d*₁₈. On increasing the temperature of the decalin-*d*₁₈ solution to 100°C, the four broad signals coalesced, and became sharper as shown in Fig. 1(a). On cooling to room temperature, the four signals once again broadened: this process was reversible. The four different SiMe₃ signals were attributed to two diastereotopically different disyl groups, i.e. the germanium being located on the unsymmetrical [6,5]-bridged isomer rather than on the symmetrical [6,6]-bridged isomer. Furthermore, free rotation of the disyl groups was inhibited, and there was steric hindrance between these and the C60 surface, which allowed only the formation of the two conformers, **2a** and **2b**, and not the two other possible conformers, **2c** and **2d**, shown in Scheme 3. If the conformational interconversion between **2a** and **2b** is a rapid process, then it can be supposed that two signals from the SiMe₃ groups would be observed. However, NMR studies in *o*-dichlorobenzene-*d*₄ at temperatures above 160°C were hampered by the relative thermal instability of **2** at high temperature leading to its decomposition. When the interconversion process became slower and was finally frozen, it led to the observation of peaks from four and eight SiMe₃ groups from the two corresponding conformers **2a** and **2b**, as shown in Scheme 3. Even though the free rotation of the disyl groups was inhibited, thermal vibrations of the disyl groups would mean that conformers **2a** and **2b** would exhibit an averaged C_s symmetry, to afford four equivalent SiMe₃ groups. This is the reason why four signals from the SiMe₃ groups were observed in decalin-*d*₁₈ at high temperature as described above. The PM3-optimized **2a** and **2b** conformers with C_s symmetry are shown in Fig. 3. At room temperature, eight signals from the SiMe₃ groups were observed in CS₂-CH₂Cl₂ and C₆D₆, which correlate with the four broad SiMe₃ group signals in decalin-*d*₁₈, as shown in Fig. 1(b). On the other hand, in the ¹H-¹³C COSY spectrum of **2**, cross-peaks correspond-

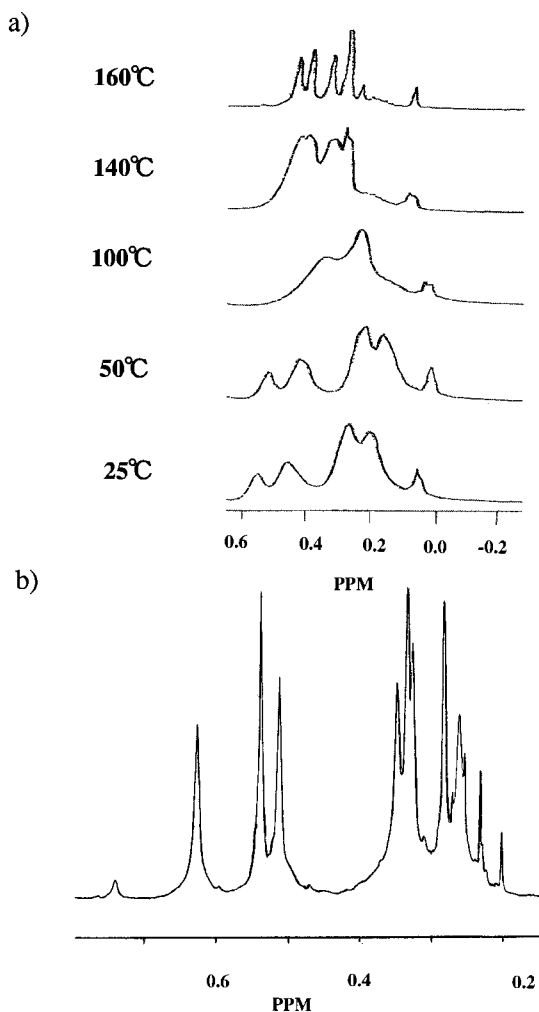
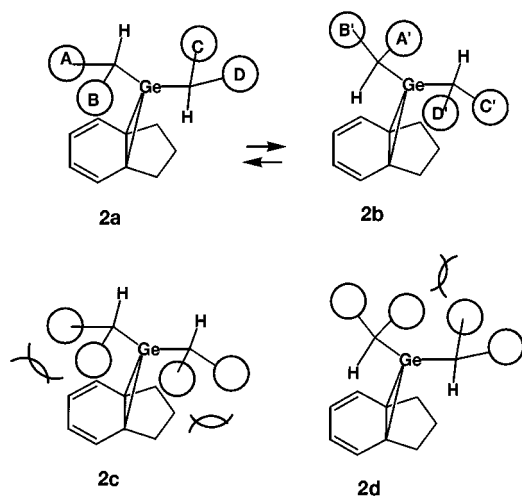


Fig. 1. (a) Temperature-dependent $^1\text{H-NMR}$ spectra of **2** in decalin- d_{18} and (b) $^1\text{H-NMR}$ spectrum of **2** in $\text{CS}_2\text{-CH}_2\text{Cl}_2$ at room temperature.



Scheme 3.

ing to the eight broad SiMe_3 protons and carbons, as well as the four CH protons and carbons were observed, as shown in Fig. 2(a). Furthermore the $^{13}\text{C-NMR}$ spectrum of **2** in $\text{CS}_2\text{-CD}_2\text{Cl}_2$ showed two saturated quaternary carbons at 69.8 and 69.5 ppm, and the remainder of the fullerene skeleton between 130 and 170 ppm, as shown in Fig. 2(b). All these results reveal that the structure of **2** can be assigned as a closed [6,5]-bridged isomer with two frozen conformers, i.e. possibly the first example of a closed [6,5]-bridged isomer of germacyclopropane.

However, in C_{60} chemistry, a closed [6,5]-bridged cyclopropane structure is unknown, in spite of numerous practical and theoretical studies [1–4]. The geometries of closed and open [5,6]-bridged dimethylmethano-, dimethylsila- and dimethylgermafullerene (**4a–c**) as model compounds were determined by complete optimization at the semi-empirical (PM3) and ab initio Hartree–Fock (HF/STO-3G) levels of theory. The calculated relative energies and transannular bond distances of these model compounds are shown in Table 1. The data in Table 1 predict that a heavier element forming the bridging atom of the open [6,5]-bridged isomer is less stable than the corresponding closed [6,5]-bridged isomer both at the PM3 and HF/STO-3G levels of theory. As a result, the order of stability was the reverse for the methano- and germafullerenes. Experimentally, this has just been proven for germafullerene (**2**) with which it is possible to form the closed [6,5]-bridged isomer. Meanwhile, the transannular bond distance, unexpectedly, does not differ much among these model compounds (**4a–c**). In order to consider the effect of valence isomerization from the closed to the open [6,5]-bridged isomer, we performed a series of additional calculations. For a set of a fixed values of the corresponding [6,5]-bridged transannular distance (reaction coordinate) ranging from 1.4 to 2.5 Å, all the other geometrical parameters for **4a–c** were optimized completely at the PM3 level. The resulting potential energy curves for the [6,5]-opening processes for **4a–c** are plotted in Fig. 4. The reaction coordinate for the [6,5]-opening process of **4c** was found to be an energetically unfavorable process with a reasonable activation barrier to the formation of open [6,5] isomers. This is also in agreement with the experimental results.

The $^1\text{H-NMR}$ spectrum of **3** shows two types of proton signals assigned as CH_2 , which were observed at 2.34 and 3.80 ppm and shown in Fig. 5(a). In the $^{13}\text{C-NMR}$ spectrum of **3**, the corresponding two CH_2 carbons were recorded at 19.3 and 42.5 ppm, and the two aliphatic quaternary carbons of the C_{60} skeleton at 72.5 and 73.0 ppm, as shown in Fig. 6(a). The 30 aromatic carbons appearing around 130–170 ppm are due to the C_{60} skeleton with C_s symmetry, as shown in Fig. 6(b), in which the germacyclopentane structure is also included as a closed [6,6]-bridged transannular bond on the C_{60} . When a solution of **3** in $\text{CS}_2\text{-CDCl}_2$

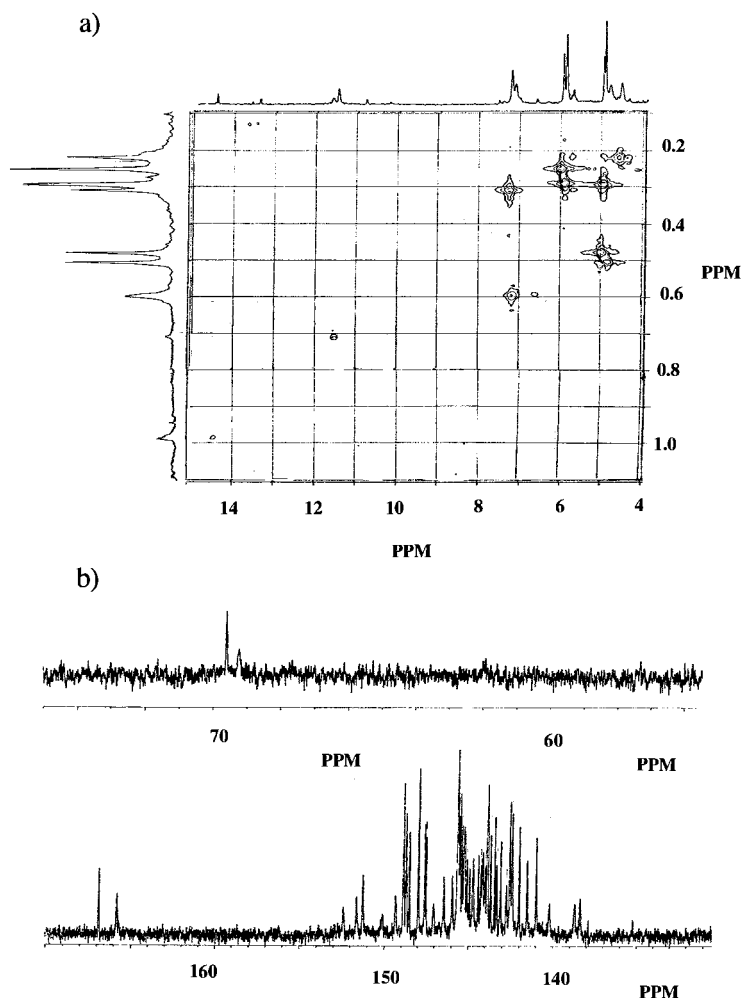


Fig. 2. (a) ^1H - ^{13}C COSY spectrum of **2** and (b) selected range of ^{13}C -NMR spectra of **2**.

(3:1) was cooled to -60 and -90°C , one of the SiMe_3 proton signals split into four signals, and one of the CH_2 proton signals split into two signals, as shown in Fig. 5(b). Furthermore, the number of fullerene carbons almost doubled, as shown in Fig. 6(b). These results reveal that the ring inversion of the germacyclopentane envelope structure was frozen at low temperatures to that shown in Scheme 4. In this frozen cyclopentane structure, the germanium atom is chiral, so the two SiMe_3 groups of the two disyl groups seem to be diastereotopically non-equivalent, and afford a total of four signals from the SiMe_3 groups.

With the formation of the closed [6,5]-bridged derivative of germacyclopentane (**2**) and the closed [6,6]-bridged derivative of germacyclopentane (**3**) having been established, one plausible mechanism thought to be operative is shown in Scheme 5. Photochemical double germylation would first take place to give the digermacyclohexadiene derivative (**5**) as a possible intermediate. This photochemical double-silylation and germylation are precedent reactions [4d–g]. Then, **5**

undergoes a fragmentation reaction in a concerted or stepwise manner to afford the observed product (**2**) and germacyclopentane (**6**) [5b]. Germacyclopentane (**6**) finally adds to the [6,6] bond of another C_{60} molecule to give the other observed product (**3**). A similar fragmentation mechanism excluding nitrogen as a fragment, was proposed in the formation of the open [6,5]-bridged adduct with diazoalkane [1k,6e,f]. As the stable disyl germylene directly reacts with C_{60} to afford only an insoluble C_{60} polymer, the selective extrusion of germacyclopentane (**6**) on intermediate (**5**) must be occurring in this mechanism.

3. Experimental

3.1. General data

All reactions were carried out under an Ar atmosphere. The NMR spectra were recorded on a Bruker AM-500 spectrometer. The mass spectra were obtained

on a Shimadzu GCMS-QP2000A, and a JEOL SX102A mass spectrometer. An LC-08 gel permeation chromatograph (Japan Analytical Ind. Co. Ltd) with a Jaigel-1H column (20 ft × 60 mm × 2 mm) was used for preparative HPLC.

3.2. Materials

The 1,2-digermacyclobutane (**1**) was prepared using a published procedure [5c]. All solvents and reagents were purified by standard procedures. The shoots containing C60 and C70 were prepared by plasma discharge of graphite electrodes [7a,b], which were purified by removal of C70 fractions using a silica gel absorption method [7c].

3.3. Photolysis of **2** in the presence of C60

An equimolar quantity of C60 (72 mg, 0.10 mol) was added to a solution of **2** (40 mg, 0.050 mol) in 20 ml of toluene, and the mixture was irradiated using a high pressure mercury lamp (> 300 nm) for 4 h. The purple color of the reaction mixture turned red. Purification by HPLC, using hexane as the eluent, gave four fractions. The first fraction (retention time, 65 min) was 1,2-digermacyclobutane (**1**, 28.4 mg), the second fraction (retention time, 70 min) was **2** (19.0 mg) in 57% conversion yield, the third fraction (retention time, 83 min) was **3** (15.0 mg) in 47% conversion yield, and the fourth fraction was C60 (50.4 mg). The structure of **2** was determined to have a germacyclopropane skeleton by

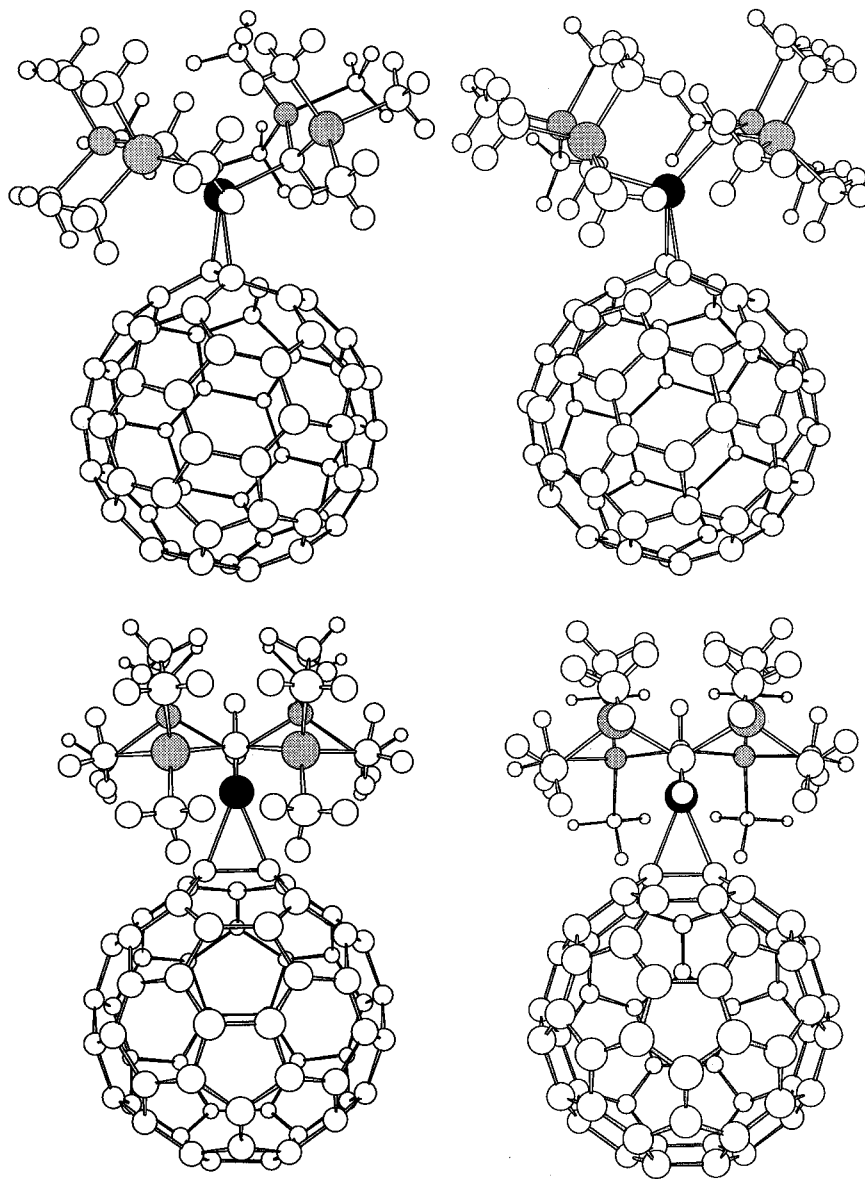


Fig. 3. Two views of the PM3-optimized structures of **2a** (right) and **2b** (left) with C_s symmetry. Ge, solid circle; Si, shaded circle; C and H, open circle.

Table 1
PM3 and HF/STO-3G optimized energies and transannular bond distances of **4a–c**

Structure	Relative energy (kcal mol ⁻¹) ^a		Transannular distance (Å)	
	PM3	HF/STO-3G	PM3	HF/STO-3G
Closed-[6,5] 4a	+15.9	+3.0	1.63	1.60
Open-[6,5] 4a	0.0	0.0	2.19	2.19
Closed-[6,5] 4b	+1.2	-8.1	1.60	1.63
Open-[6,5] 4b	0.0	0.0	2.33	2.38
Closed-[6,5] 4c	-8.2	-15.3	1.54	1.62
Open-[6,5] 4c	0.0	0.0	2.33	2.36

^a Values are relative to each open-[6,5] isomer as 0.0 kcal mol⁻¹.

temperature-dependent ¹H- and ¹³C-NMR, distortionless enhancement by polarization transfer (DEPT), ¹H-¹³C COSY and FABMS, as described in the text. The structure of **3** was also determined to have a germacyclopropane framework by ¹H- and ¹³C-NMR, DEPT, ¹H-¹³C COSY and FABMS, described above. Compound **2**: black powder; ¹H-NMR (C₆D₆): δ 0.34 (SiCH₃), 0.40 (SiCH₃), 0.42 (SiCH₃), 0.46 (SiCH₃), 0.54 (SiCH₃), 0.57 (SiCH₃), 0.68 (SiCH₃); ¹³C-NMR (C₆D₆): δ 4.8 (SiCH₃), 4.9 (SiCH₃), 5.1 (SiCH₃), 6.16 (SiCH₃), 6.17 (SiCH₃), 6.22 (SiCH₃), 7.2 (SiCH₃), 7.5 (SiCH₃), 12.1 (GeCHSi), 14.3 (GeCHSi), 69.86 (GeC₆₀), 69.92 (GeC₆₀), 141.28, 141.69, 142.03, 142.58, 142.65, 142.77, 142.89, 142.90, 142.95, 143.25, 143.27, 143.49, 143.52,

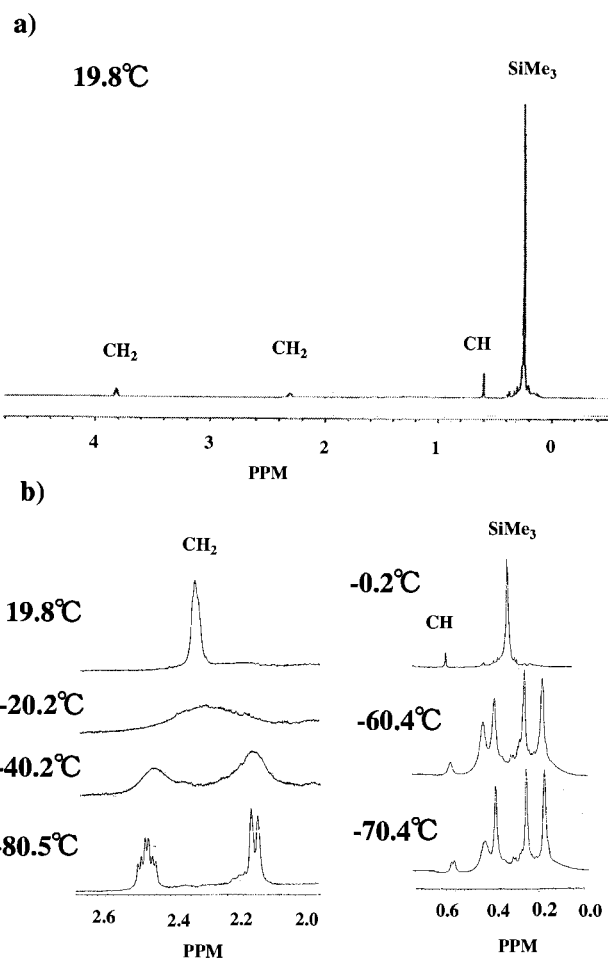


Fig. 5. (a) ¹H-NMR spectrum of **3** in CS₂-CH₂Cl₂ and (b) temperature-dependent ¹H-NMR spectra of **3** in CS₂-CH₂Cl₂.

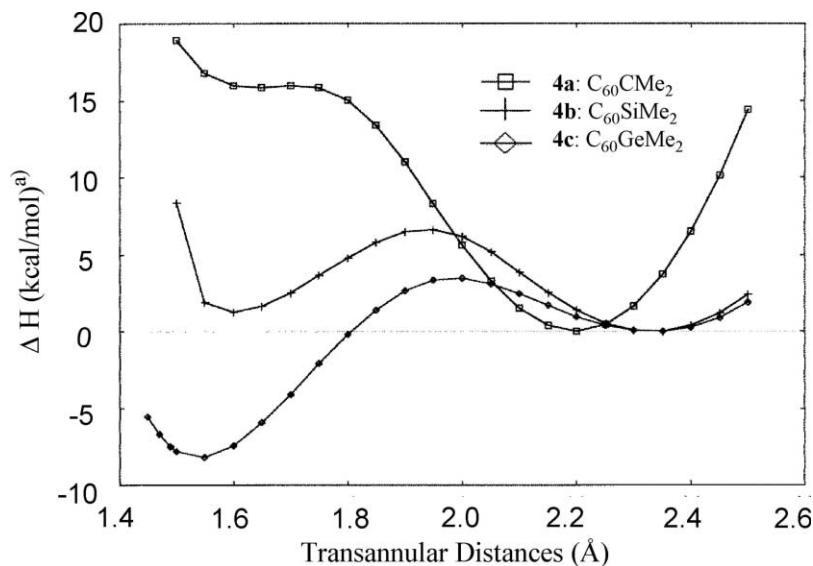


Fig. 4. PM3-minimum energy reaction pathways for the closing [6,5] open transannular bond of **4a–c**. The curves are plotted relative to the heat of formation of the [6,5] open isomer (0.0 kcal mol⁻¹).

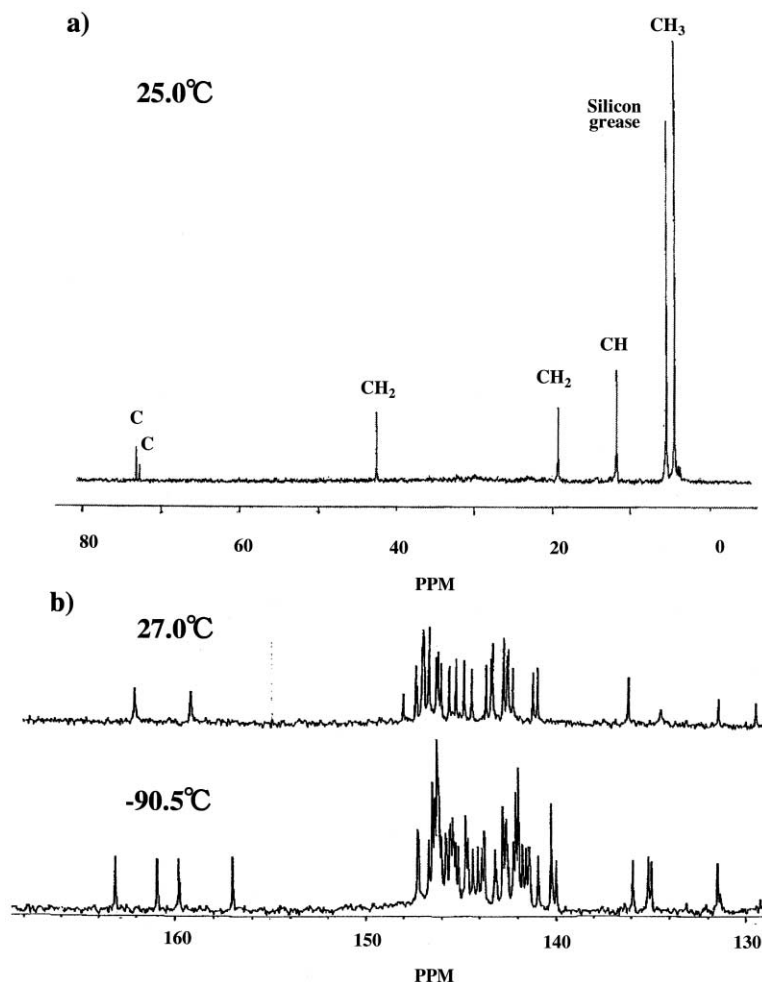


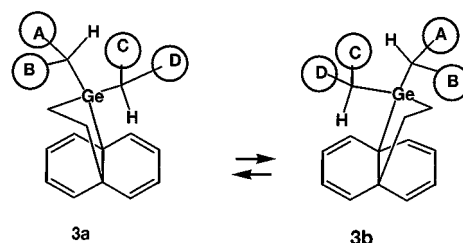
Fig. 6. (a) ^{13}C -NMR spectrum of **3** in CS_2 - CH_2Cl_2 and (b) temperature-dependent ^{13}C -NMR spectra of **3** in CS_2 - CH_2Cl_2 .

143.73, 143.97, 144.04, 144.20, 144.48, 144.52, 144.72, 144.75, 144.88, 145.01, 145.02, 145.15, 145.22, 145.35, 145.38, 145.43, 145.61, 145.64, 145.72, 145.76, 145.83, 145.90, 146.03, 146.62, 147.23, 147.57, 147.66, 148.03, 148.63, 148.83, 148.88, 148.97, 149.01, 149.43, 149.45, 151.43, 151.66, 165.81, 166.63; 52 peaks as fullerene skeleton. Compound **3**: black powder; ^1H -NMR (C_6D_6): δ 0.38 (s, 18H, SiCH_3), 0.44 (s, 18H, SiCH_3), 0.83 (s, 2H, GeCHSi), 2.34 (br, 2H, GeCH_2CH_2), 3.80 (t, 2H, GeCH_2CH_2); ^{13}C -NMR (C_6D_6): δ 4.6 (SiCH_3), 5.5 (SiCH_3), 11.9 (GeCHSi), 19.3 (GeCH_2CH_2), 42.5 (GeCH_2CH_2), 72.5 (GeC_{60}), 73.0 ($\text{GeCH}_2\text{CH}_2\text{C}_{60}$), 135.8, 140.7, 140.9, 141.9, 142.19, 142.23, 142.32, 142.36, 143.0, 143.1, 143.3, 144.1, 144.6, 144.9, 145.2, 145.7, 145.9, 146.0, 146.3, 146.4, 146.60, 16.63, 146.64, 146.8, 147.0, 147.7, 158.7 (br), 161.5 (br).

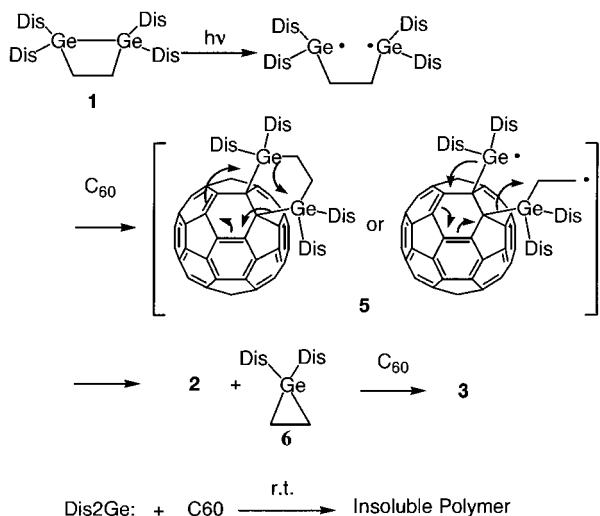
3.4. Computational studies

Calculations were carried out on an HPC-alpha 21264 workstation provided by HIT Inc. in Japan. Semi-empirical (PM3) and ab initio (HF/STO-3G) cal-

culations were performed using the GAUSSIAN 98 computer program [8]. Initial geometries for the closed-[6,5] and open-[6,5] isomers were constructed using the Chem 3D graphical interface provided by Cambridge Soft Inc. All geometry optimizations were performed in *Z*-matrix using the energy gradient minimization method. The reaction coordinates for the closing of the transannular bond were performed by the relaxed potential energy scan method. The structures of the conformers were optimized by fixing a fullerene skeleton as the PM3-optimized closed [6,5] geometries. Ab initio optimizations were carried out using the PM3-opti-



Scheme 4.



mized open and closed [6,5] geometries as the input structures.

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