Experimental evidence and bond characterization of a cyclopropenylgermylene

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Abstract

The reduction of *p*-anisyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)dichlorogermane (**1**) with potassium in the presence of an excess of *tert*-butyldimethylsilane in benzene under reflux gave *p*-anisyl(*tert*-butyldimethylsilyl)(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)germane (**4**) in 15% yield. The formation of **4** indicates that *p*-anisyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)germylene (**2**), which is the first example of a (cycloprop-2-en-1-yl)germylene derivative, was generated and trapped by the hydrosilane. The DFT calculations revealed that the *cis*-2-*p*-anisyl-1,3,4-tri-*tert*-butyl-2-germabicyclo[1.1.0]butane-2,4-diyl structure *cis*-**5** is 8.0 kJ/mol more stable than *cis*-**2**. The NBO analysis revealed that *cis*-**5** has a 2-germabicyclo[1.1.0]butane diradical character.
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1. Introduction

Cyclopropene is one of the smallest ring compounds and has a high reactivity due to its strained structure [1,2]. Some unique isomerizations of silicon compounds with a cycloprop-2-en-1-yl group have been reported [2j–7]. In particular, the reactivities of the unsaturated silicon compounds with the cycloprop-2-en-1-yl group are interesting. Fink and coworkers [3] reported that the photolysis of 2-mesityl-1,1,1,3,3,3-hexamethyl-2-(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)trisilane produces mesityl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)silylene, which isomerizes to the corresponding silacyclobutadiene. Very recently, we reported the structure and reactions of the lattice-framework disilene, 2,3,4,6,7,8,2′,3′,4′,6′,7′,8′-dodeca-*tert*-butyl-[5,5′]bi{1,5-disilatricyclo-[4.2.0.0^{1,4}]octylidene}-2,7,2′,7′-tetraene, which is prepared

by the reduction of tribromo(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)silane (Scheme 1) [7–9]. Although the reaction mechanism for the formation of the disilene is unclear, the disilene is one of the formal tetramers of (1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)silylyne.

On the other hand, a germanium compound with the cycloprop-2-en-1-yl group has not yet been reported. We have been interested in the chemistry of such compounds, especially a germylene with the cycloprop-2-en-1-yl group. During the course of this study, we succeeded in preparing *p*-anisyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)dichlorogermane (**1**). Compound **1** should be regarded as a useful precursor for the corresponding germylene, *p*-anisyl-(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)germylene (**2**). In this paper, we report the generation of **2** by the reduction of **1**, which was prepared from tri-*p*-anisyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)germane (**3a**). Germylene **2** is the first example of a cyclopropenylgermylene derivative. The intermediate **2** was trapped by *tert*-butyldimethylsilane. The structure and bonding characteristics of **2** were investigated by DFT calculations.

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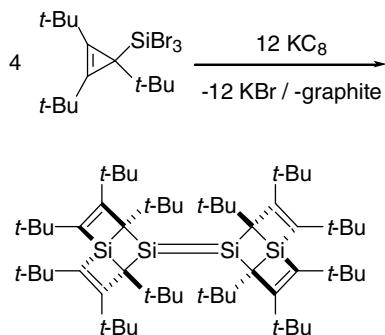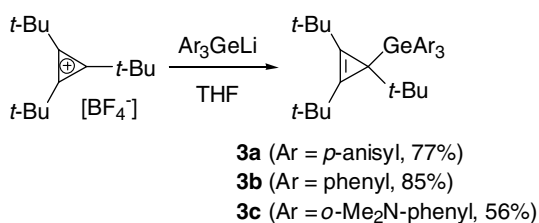
Scheme 1.

2. Results and discussion

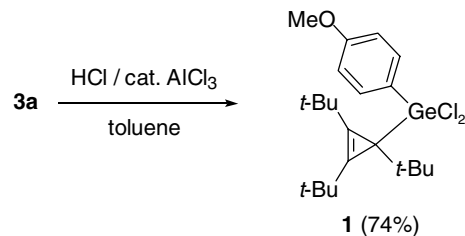### 2.1. Preparation of triaryl(1,2,3-tri-tert-butylcycloprop-2-en-1-yl)germanes

The triaryl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)germanes **3a–c** were prepared by the reaction of tri-*tert*-butyl-cyclopropenium tetrafluoroborate with the corresponding triarylgermyllithiums (Scheme 2). Compounds **3a–c** are stable in air with the corresponding melting points (**3a**: 178–180 °C, **3b**: 262–263 °C, **3c**: 216–219 °C). The structures of **3a–c** were established by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopies.

2.2. Halodearylation of triaryl(1,2,3-tri-tert-butylcycloprop-2-en-1-yl)germanes

As previously reported, the reaction of triphenyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)silane with HBr gas in the presence of a catalytic amount of AlBr$_3$ (HBr/cat. AlBr$_3$) produces tribromo(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)silane in 94% yield [7]. In contrast, the halodephenylation of **3b** with HX/cat.AlX$_3$ (X = Br, Cl) produced a reaction mixture due to the cleavage of the Ge-cyclopropenyl bond. This result indicates that the elimination of the cyclopropenyl group and phenyl group simultaneously occurred during the course of the reaction. The bromodearylation of **3a**, which has a greater electron-donating group on the phenyl ring, with HBr/cat.AlBr$_3$ also produced a reaction mixture due to the cleavage of the Ge-cyclopropenyl bond. Interestingly, the chlorodearylation of **3a** with HCl/cat.AlCl$_3$ selectively gave *p*-anisyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)dichlorogermane (**1**) in

3a (Ar = *p*-anisyl, 77%)
**3b** (Ar = phenyl, 85%)
3c (Ar = *o*-Me$_2$N-phenyl, 56%)

Scheme 2.

Scheme 3.

74% yield (Scheme 3). The structure of **1** was established by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopies. The reaction of **3c** with HCl/cat.AlCl$_3$ did not give the corresponding aryl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)dichlorogermane.

2.3. Generation and trapping of p-anisyl(1,2,3-tri-tert-butylcycloprop-2-en-1-yl)germylene (2)

The reduction of **1** with potassium in the presence of an excess of *tert*-butyldimethylsilane in benzene under reflux gave *p*-anisyl(*tert*-butyldimethylsilyl)(1,2,3-tri-*tert*-butylcy-cloprop-2-en-1-yl)germane (**4**) in the isolated yield of 15% (Scheme 4). Compound **4** was isolated by GPC (toluene as the eluent) and the structure of **4** was established by mass spectrometry and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies. The other compounds in the reaction mixture were not identified. The ^{1}H NMR spectrum of **4** in C$_6$D$_6$ shows three kinds of peaks for the *tert*-butyl groups and two kinds of peaks for the methyl groups on the silicon atom. The magnetic non-equivalence of the peaks is caused by the chiral germanium atom. The formation of **4** indicates that germylene **2** was generated and trapped by the hydros-ilane. Germylene **2** is the first example of a cyclopropenyl-germylene derivative. The reduction of **1** with potassium graphite in the presence of an excess triethylsilane in THF at −80 °C gave a complex mixture including the unreacted **1**. Also, the reduction of **1** with potassium in benzene
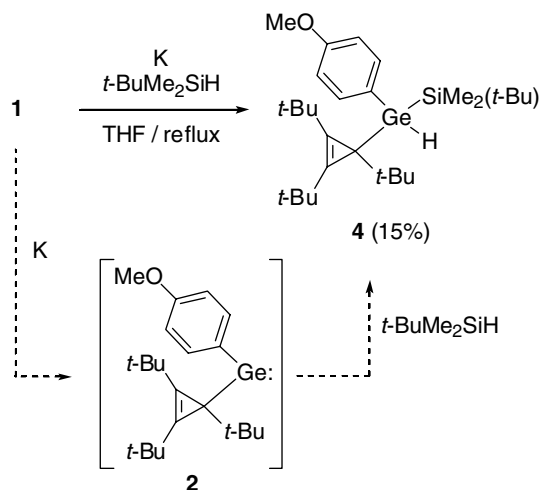
Scheme 4.

under reflux in the absence of a trapping reagent produced a complex mixture.

2.4. Theoretical calculations

2.4.1. Structures and relative energies

To discuss the structure and relative energy of **2** compared with the isomeric structures, we performed density functional theory (DFT) calculations using the GAUSSIAN 98 program package [10,11]. The bonding character of the calculated structures were investigated by means of the natural bond orbital (NBO) analysis.[12] The initial structures for optimization were chosen based on the optimized structures of SiC_3H_4 reported by Veszprémi et al. [13] and Maier et al. [14] As shown in Fig. 1, five stable structures *cis*-**2**, *trans*-**2**, *cis*-**5**, *trans*-**5**, and **6** were found at the B3LYP/6-31G(d) level. The selected geometric parameters of *cis*-**2**, *trans*-**2**, *cis*-**5**, *trans*-**5**, and **6** are shown in Fig. 2. Fig. 3 shows the electronic structures of *cis*-**2**, *trans*-**2**, *cis*-**5**, *trans*-**5**, and **6** based on the results of the NBO analysis, together with the electron occupancy assigned to each bond or lone-pair orbital in the structures. The *cis*-2-*p*-anisyl-1,3,4-tri-*tert*-butyl-2-germabicyclo[1.1.0] butane-2,4-diyl structure *cis*-**5**, in which C^D and C^E locate on the same side of the GeC_3 skeleton, is the most stable among all the structures optimized in this study. Another germabicyclo[1.1.0]butanediyl structure *trans*-**5**, in which C^D and C^E are on opposite sides of the GeC_3 skeleton is 18.3 kJ/mol higher in energy than *cis*-**5**. *cis*- and *trans*-*p*-Anisyl(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl)germylenes (*cis*- and *trans*-**2**) are 8.0 and 17.9 kJ/mol less stable than *cis*-**5**, respectively. 1-*p*-Anisyl-2,3,4-tri-*tert*-
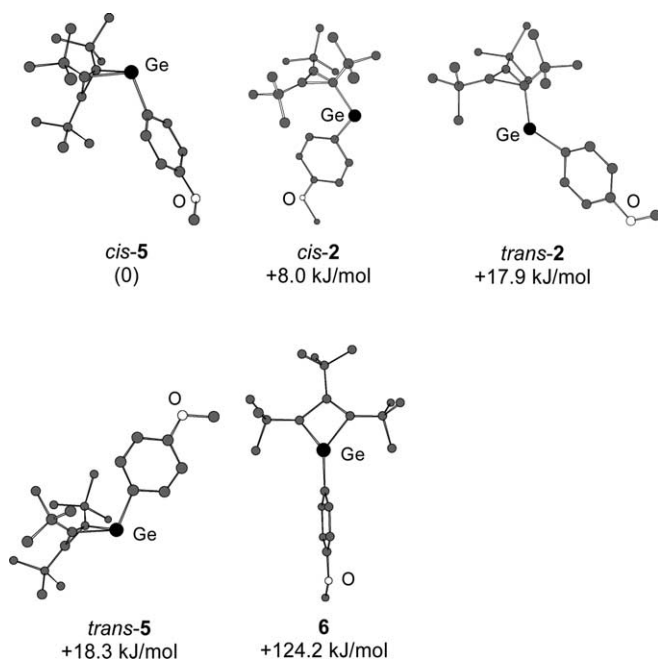

Fig. 2. Selected geometric parameters of *cis*-**2**, *trans*-**2**, *cis*-**5**, *trans*-**5**, and **6**. All the methyl groups and the *p*-anisyl group are omitted for clarity.

butyl-1-germacyclobutadiene **6**, which has a planar GeC_3 ring, is 124.2 kJ/mol less stable than *cis*-**5**.

The optimized structures of *cis*- and *trans*-**2** apparently contain the divalent germanium atom. As shown in Fig. 2, the geometric parameters for the cyclopropenyl ring in both structures are almost identical. The C^A–Ge–C^D bond angles in *cis*-**2** (109.0°) and *trans*-**2** (118.2°) are comparable to the corresponding values for the solid-state structure of bis(2,4,6-tri-*tert*-butylphenyl)germylene (108.0°) [15] and [bis(trimethylsilyl)methyl][tris(trimethylsilyl)methyl]germylene (111.3°) [16], while this bond angle is larger than the value in dimethylgermylene (95.9°) optimized at the B3LYP/6-311+G(d,p) level. The large C^A–Ge–C^D bond angle in **2** would be caused by steric repulsion between the bulky substituents on the germanium atom. The C^A–Ge–C^D and C^E–C^A–Ge bond angles in *trans*-**2** are larger than those in *cis*-**2**. The larger bond angles as well as the lower thermodynamic stability of *trans*-**2** indicate that the steric repulsion between the *p*-anisyl group and the *tert*-butyl group on C^A is more significant in *trans*-**2** than that in *cis*-**2**. The NBO

Fig. 1. Optimized structures and relative energies of *cis*-**2**, *trans*-**2**, *cis*-**5**, *trans*-**5**, and **6** obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. Hydrogen atoms are omitted for clarity.
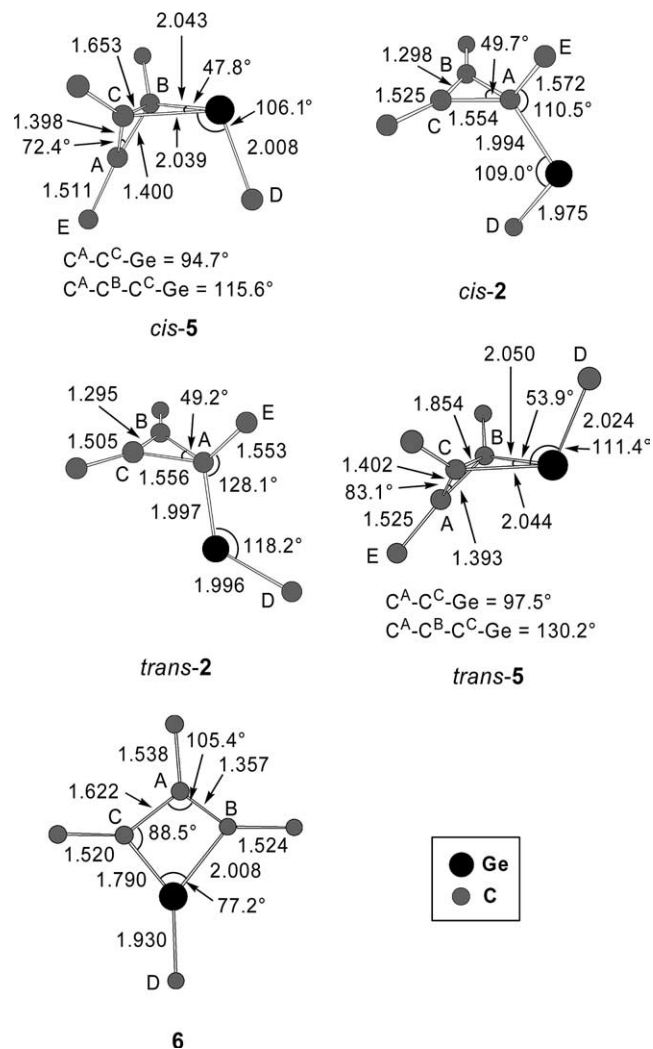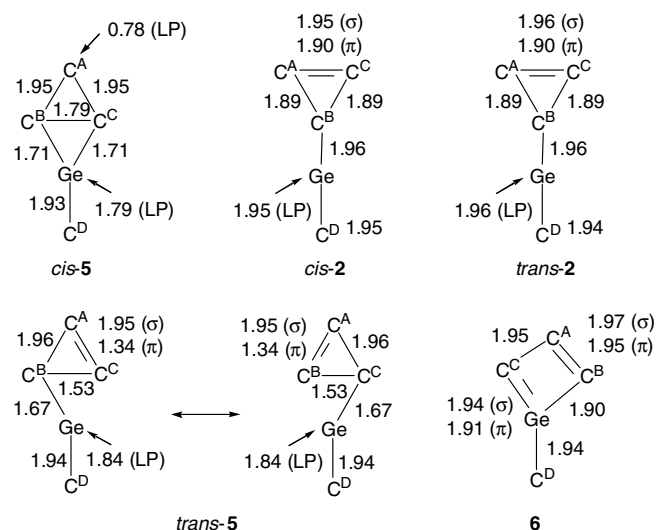
Fig. 3. Structures of *cis*-2, *trans*-2, *cis*-5, *trans*-5, and 6 described on the basis of the result of the NBO analysis. The values shown in the structures are the number of electrons assigned to each bond. LP represents a lone-pair orbital on an atom. All the *tert*-butyl groups and the *p*-anisyl group are omitted for clarity.

analysis also suggests that the electronic structure of both *cis*- and *trans*-2 can be regarded as a germylene. As shown in Fig. 3, the number of electrons assigned to the lone-pair orbital of the germanium atom is greater than 1.95 for both structures, which are very close to the value (1.99) for dimethylgermylene. For the C^A–C^C bond in *cis*-2, the number of electrons assigned on the σ and π bonds is 1.95 and 1.90, respectively. The number of electrons on the C^A–C^B, C^B–C^C, Ge–C^B, and Ge–C^D bonds in *cis*-2 is as many as 1.89, 1.89, 1.96, and 1.95, respectively. The result of the NBO analysis for *trans*-2 is very similar to *cis*-2.

For *cis*-5, the C^B–C^C distance is calculated to be 1.653 Å. This bond distance is longer than the normal C–C bond (ca. 1.5 Å). The C^A–C^B–C^C–Ge dihedral angle in *cis*-5 is as small as 115.6° and the plane containing the C^A–C^B–C^C triangle faces toward the plane containing the six carbon atoms of the benzene ring. It is noteworthy that re-optimization of *cis*-5 followed by a 90° rotation of the benzene ring along the Ge–C^D bond gave the initial structure of *cis*-5. The NBO analysis revealed that *cis*-5 has the bonding character of a bicyclobutane diradical derivative. As shown in Fig. 3, the valence electron of 0.78 is assigned to the 2p orbital of C^A perpendicular to the plane containing the C^A–C^B–C^C triangle, while the germanium atom has 1.79 electrons on the lone-pair orbital (70.7% s-character and 29.2% p-character). It seems interesting that a large number of electrons is assigned on the lone-pair orbital of the germanium atom, because a bicyclobutane structure should formally have one unpaired electron on each C^A and the germanium atom. The large electron occupancy on the lone-pair orbital of the germanium atom results in weak σ bonds between C^B, C^C and the germanium atom. The number of electrons on the C^B–C^C, Ge–C^B, and Ge–C^C bonds is calculated to be 1.79, 1.71 and 1.71, respec-

tively. Although the corresponding triplet structure is also a local minimum on the potential energy surface of *cis*-5, the triplet structure is 191.8 kJ/mol less stable than the singlet structure.

For *trans*-5, the C^B–C^C distance (1.854 Å) is 0.201 Å longer than that in *cis*-5. The geometric parameters for the GeC$_3$ skeleton in *trans*-5 are close to those in *cis*-5, except for the C^B–C^C distance. The benzene ring of the *p*-anisyl group in *trans*-5 locates nearly perpendicular to the C^A–C^B–C^C triangle in the GeC$_3$ skeleton unlike *cis*-5. The NBO structure of *trans*-5 is described as a pair of resonant structures, as shown in Fig. 3. For the resonant structure *trans*-5, the number of electrons on the C^A–C^B, C^B–C^C, Ge–C^B bonds is calculated to be 1.96, 1.53, and 1.67, respectively. The number of electrons accommodated on the σ and π bonds between C^A and C^C is 1.95 and 1.34, respectively. No unpair electron is assigned on the 2p orbital of C^A. The valence electrons of 1.84 on the germanium atom are assigned as the lone-pair electrons. Thus, the bonding character of *trans*-5 is close to that of a germylene with the cyclopropenyl ring, despite its germabicyclobutanediyl geometry.

Structure 6, in which the GeC$_3$ ring is fixed as planar, has the long Ge–C^B (2.008 Å) and C^A–C^C (1.622 Å) bonds as well as the short Ge–C^C (1.790 Å) and C^A–C^B (1.357 Å) bonds. The C^B–C^C distance is calculated to be 2.375 Å, implying that no bond exists between C^B and C^C unlike the case of *cis*- and *trans*-5. From the viewpoint of geometry, 6 is a germacyclobutadiene. Re-optimization of 6 without maintaining the planar GeC$_3$ skeleton gave *trans*-5. The NBO analysis result also indicates that 6 has a germacyclobutadiene character. Two double bonds and two single bonds are assigned to the GeC$_3$ skeleton of 6. The number of electrons assigned to each bond is greater than 1.9, which is high enough to confirm the presence of a chemical bond. Namely, structure 6 can be regarded as a germacyclobutadiene derivative.

To elucidate the substituent effects on the geometry of the GeC$_3$ skeleton, the structures of GeC$_3$H$_4$ were investigated. As shown in Fig. 4, five structures *cis*-7, *trans*-7, *cis*-8, *trans*-8, and 9 were optimized at the B3LYP/6-311+G(d,p) level. The *trans*-2-germabicyclo[1.1.0]butane-2,4-diyl structure *trans*-7 is the most stable of the five structures. The *cis*-germabicyclobutanediyl structure *cis*-7 is 28.8 kJ/mol less stable than *trans*-7. The germylene structures *cis*- and *trans*-8 are 32.5 and 31.0 kJ/mol higher in energy than *trans*-7, respectively. The planar germacyclobutadiene 9 is a transition-state structure. The result of the NBO analysis for *cis*-7, *trans*-7, *cis*-8, *trans*-8, and 9 is shown in Fig. 5. It is interesting that the NBO structures of *cis*- and *trans*-7 are almost identical and have a germylene character similar to *trans*-5. The NBO structures of *cis*-8, *trans*-8, and 9 are similar to those of *cis*-2, *trans*-2, and 6, respectively. Only *cis*-5 has an NBO structure different from the corresponding hydrogen-substituted structure (*cis*-7). Another finding to be pointed out is that *cis*-5 is more stable than *trans*-5, while the *trans* structure is energetically more favorable in the hydrogen-substituted compound. These results indicate that the *tert*-butyl groups
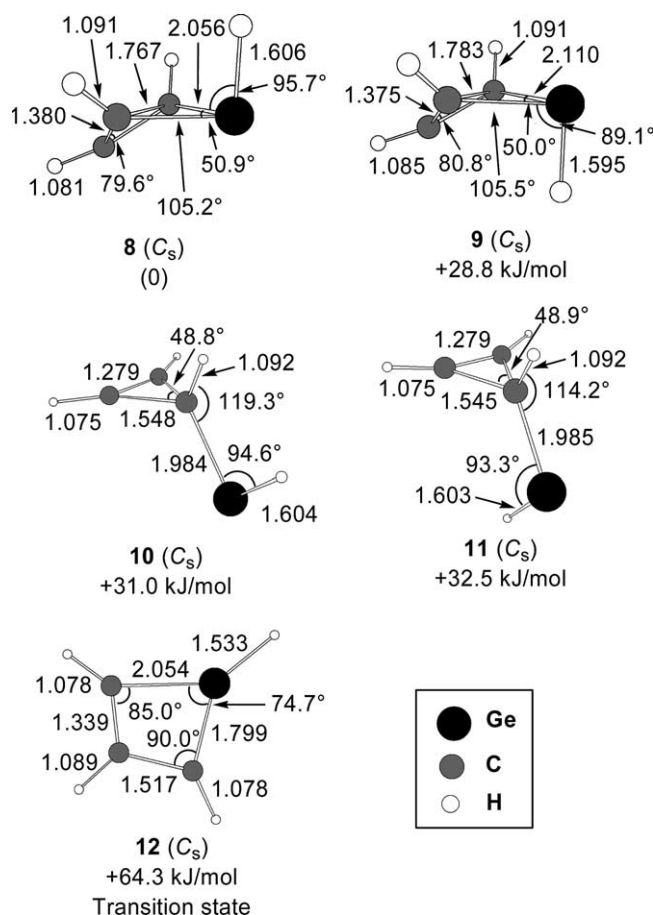
Fig. 4. Optimized structures and relative energies of isomers of GeC$_3$H$_4$ cis-7, trans-7, cis-8, trans-8, and 9 optimized at the B3LYP/6-311+G(d,p) level.

and/or p-anisyl group in 5 would strongly influence their electronic structure and relative stability. What factors influence the electronic structure and relative stability of cis-5? The spatial distribution of the HOMO of cis-5 would provide a clue to answer this question.

The HOMOs of cis-5, trans-5, cis-7, and trans-7 are depicted in Fig. 6. For trans-5, cis-7, and trans-7, the HOMOs are comprised of the non-bonding orbital of the germanium atom and the π orbital delocalized over the C^A–C^B–C^C triangle in the GeC$_3$ skeleton. In the HOMO of cis-5, on the other hand, the π orbital of the benzene ring interacts with the orbitals of the GeC$_3$ skeleton. In the orbitals of the GeC$_3$ skeleton, the C^A atom has a larger lobe compared with C^B and C^C, implying that C^A possesses
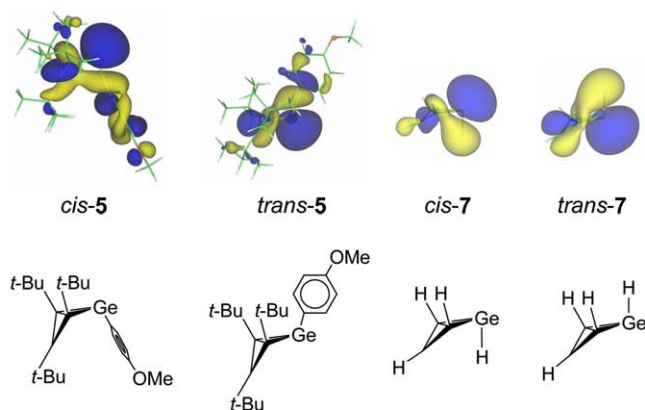
Fig. 6. Side view images of the HOMOs of cis-5, trans-5, cis-7, and trans-7. Hydrogen atoms are omitted for clarity.
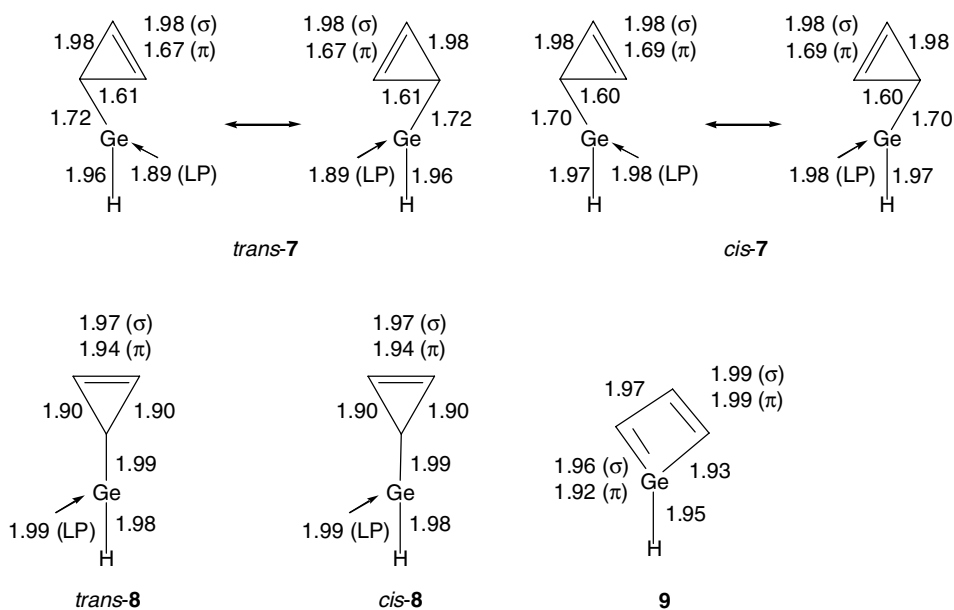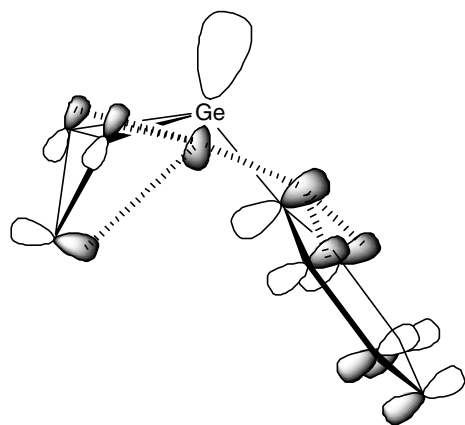

Fig. 5. Structures of cis-7, trans-7, cis-8, trans-8, and 9 described on the basis of the NBO analysis results. The values shown in the structures are the number of electrons assigned to each bond. LP represents a lone-pair orbital on an atom. All the tert-butyl groups and the p-anisyl group are omitted for clarity.

Fig. 7. Schematic diagram of the through-space interaction in the HOMO of cis-5.

Fig. 8. Absorption wavelengths of cis-2, trans-2, cis-5, trans-5, and 7 calculated at the TD-B3LYP/6-311+G(d,p) level.

an unpaired electron as suggested by the NBO analysis. A schematic diagram of the through-space interaction in the HOMO of cis-5 is presented in Fig. 7. This interaction plays an essential role in the high stability of cis-5. Of course, the steric repulsion between the p-anisyl group and the tert-butyl groups on C^B and C^C would be an important factor in determining the relative stability of cis- and trans-5. Also, the presence of this interaction reasonably explains the optimized structure of cis-5, in which the plane containing the C^A–C^B–C^C triangle faces toward the plane containing the six carbon atoms of the benzene ring. The optimized structure of trans-5 might be governed by the steric repulsion, because the C^AC^D distance in trans-5 (4.257 Å) is much longer than that in cis-5 (3.105 Å).

In conclusion, the GeC_3 skeleton tends to adopt a 2-germabicyclo[1.1.0]butane-2,4-diyl structure. The germabicyclobutanediyl structures basically have the bonding character of a cyclopropenyl-substituted germylene. However, introducing an aryl substituent on the germanium atom dramatically changes the relative stability and the bonding character of the germabicyclobutanediyl structure.

2.4.2. Spectroscopic properties

We describe the spectroscopic properties of cis-2, trans-2, cis-5, trans-5, and 6 based on the time-dependent DFT (TD-DFT) calculation. Recently, the applicability of the TD-DFT method has been proved for unsaturated silicon [7,9,17] and germanium [18] compounds. To evaluate the electron transition energies of cis-2, trans-2, cis-5, trans-5, and 6, the TD calculations were carried out at the B3LYP/6-311+G(d,p) level. The results of the calculations are shown in Fig. 8. The TD calculations predict quite different spectral patterns for the five structures. The absorption wavelengths of cis-5 and trans-5 for the HOMO–LUMO transition are calculated to be 393 nm and 347 nm, respectively. In contrast, cis-2 has the HOMO–LUMO transition at 671 nm, which is significantly red-shifted relative to dimethylgermylene (430 nm) [19] and diphenylgermylene (466 nm) [20]. Another germylene structure trans-2 also has a red-shifted HOMO–LUMO
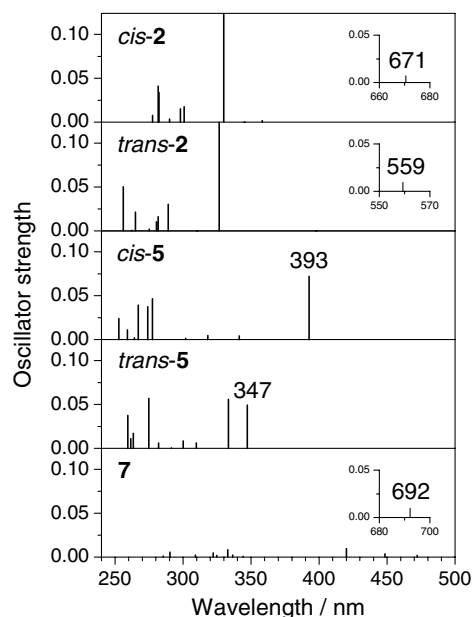
transition at 559 nm. The TD calculation predicts the longest-wavelength absorption of 6 at 692 nm.

3. Conclusion

We succeeded in generating the first example of a cyclopropenylgermylene, p-anisyl(1,2,3-tri-tert-butylcyclo-prop-2-en-1-yl)germylene (2), by reduction of the corresponding dichlorogermane 1. The intermediary 2 was trapped by tert-butyldimethylsilane to give the corresponding tert-butyldimethylsilyl(hydro)germane 4. DFT calculations revealed that the cis-2-p-anisyl-1,3,4-tri-tert-butyl-2-germabicyclo[1.1.0]butane-2,4-diyl structure cis-5 is 8.0 kJ/mol more stable than cis-2. The NBO analysis revealed that cis-5 has a diradical character, although the germanium atom possesses 1.78 electrons in its lone-pair orbital. The electronic structure of the trans-germabicyclobutanediyl structure trans-5 can be described by two resonance structures, which have a germylene character. For GeC_3H_4, on the other hand, the trans-germabicyclobutanediyl structure trans-7 is more stable than cis-7 and both structures have a germylene character. The high stability of cis-5 can be rationalized by a through-space interaction in the HOMO between the π orbital of the benzene ring in the p-anisyl group and the orbitals of the GeC_3 ring. Introduction of the p-anisyl group on the divalent germanium atom dramatically changes the electronic structure of the GeC_3 skeleton from a germylene character to a diradical character. The TD-DFT calculation for the five structures predicts that their longest-wavelength absorptions strongly depend on the geometry around the germanium atom. This structure dependence of the absorption wavelengths would provide useful infor-

mation on the structure of germylene **2** and its related compounds, if the UV–vis spectral data for the compounds are available.

4. Experimental

4.1. General methods

The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded using a Varian INOVA 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The mass spectra were recorded using Shimadzu GCMS-QP5050A and Hitachi M-2500 mass spectrometers. Gel permeation chromatography (GPC) was conducted using a LC908 recycling high-performance liquid chromatography (Japan Analytical Instruments Co., Ltd.) using JAIGEL-1H (20 mm × 600 mm) and JAIGEL-2H (20 mm × 600 mm) columns, using toluene as the eluent.

4.2. Materials

Toluene, *tert*-BuLi, triphenylchlorogermane, lithium, HCl gas, aluminum chloride, potassium, trimethylchlorosilane, $CHCl_3$, and $CDCl_3$ were commercially available and used as supplied. THF, hexane, C_6D_6 and *tert*-butyldimethylsilane were freshly distilled over potassium. Tri-*tert*-butylcyclopropenium tetrafluoroborate [21], tri-*p*-anisylgermane [22], and tris[*o*-(dimethylamino)phenyl]germane [23] were prepared according to the reported procedures.

4.2.1. Preparation of tri-p-anisyl(1,2,3-tri-tert-butylcyclo-prop-2-en-1-yl)germane (3a)

A solution of tri-*p*-anisylgermyllithium [prepared by mixing *tert*-BuLi (1.45 N, 7.7 ml, 11.2 mmol) and tri-*p*-anisyl-germane (4.24 g, 10.7 mmol) in THF (100 ml) at −40 °C] was added to a mixture of tri-*tert*-butylcyclopropenyl tetrafluoroborate (3.13 g, 10.6 mmol) and THF (200 ml) at −40 °C. After stirring at −40 °C for 2 h and at room temperature for 21 h, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel using toluene as the eluent. The eluate was concentrated under reduced pressure to give **3a** (4.89 g, 8.13 mmol, 77%). **3a**: Colorless crystals; m.p. 178.2–179.8 °C; ^1H NMR (CDCl$_3$, δ) 0.93 (s, 9H), 1.06 (s, 18H), 3.78 (s, 9H), 6.83 (d, $J = 8$ Hz, 6H), 7.43 (d, $J = 8$ Hz, 6H); ^{13}C NMR (CDCl$_3$, δ) 30.69 (CH$_3$), 31.38 (C), 31.43 (CH$_3$), 38.40 (C), 41.87 (C), 54.93 (CH$_3$), 113.14 (CH), 127.07 (C), 131.81 (C), 137.77 (CH), 159.46 (C); MS (70 eV) *m/z* (%) 545 (M$^+$ − 56, 1) 207 (100). Anal. Calc. for C$_{36}$H$_{48}$GeO$_3$: C, 71.90; H, 8.04%. Found: C, 71.72; H, 8.12%.

4.2.2. Preparation of triphenyl(1,2,3-tri-tert-butylcycloprop-2-en-1-yl)germane (3b)

A solution of triphenylgermyllithium [prepared by mixing lithium (2.90 g, 417 mmol) and triphenylchlorogermane (6.46 g, 19.0 mmol) in THF (200 ml) at room temperature] was added to a mixture of tri-*tert*-butylcyclopropenyl tetrafluoroborate (4.56 g, 15.5 mmol) and THF (200 ml) at 0 °C. After stirring at 0 °C for 1 h, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel using hexane as the eluent. The eluate was concentrated under reduced pressure to give **3b** (6.72 g, 13.1 mmol, 85%). **3b**: Colorless crystals; m.p. 262–263 °C; ^1H NMR (CDCl$_3$, δ) 0.95 (s, 9H), 1.06 (s, 18H), 7.25–7.3 (m, 9H), 7.5–7.6 (m, 6H); ^{13}C NMR (CDCl$_3$, δ) 30.63 (CH$_3$), 31.39 (C), 31.48 (CH$_3$), 38.58 (C), 42.24 (C), 127.23 (C), 127.48 (CH), 128.00 (CH), 136.67 (CH), 140.57 (C); MS (70 eV) *m/z* (%) 455 (M$^+$ − 57, 2), 207 (100). Anal. Calc. for C$_{32}$H$_{42}$Ge: C, 77.51; H, 8.28%. Found: C, 77.12; H, 8.34%.

4.2.3. Preparation of tris[o-(dimethylamino)phenyl](1,2,3-tri-tert-butylcycloprop-2-en-1-yl)germane (3c)

A pentane solution of *tert*-BuLi (1.45 N, 5.8 ml, 8.41 mmol) was added to a THF (30 ml) solution of tris[(o-dimethylamino)phenyl]germane (3.00 g, 6.91 mmol) at −40 °C. After stirring at −40 °C for 3 h, tri-*tert*-butylcyclopropenyl tetrafluoroborate (2.56 g, 8.70 mmol) was added to the mixture at −40 °C. After stirring overnight at room temperature, the solvents were concentrated under reduced pressure. Dry hexane was added, and the resulting salt was removed by filtration. The filtrate was concentrated under reduced pressure (200 °C/0.05 mmHg), and **3c** (2.50 g, 3.90 mmol, 56%) was obtained as colorless solid. **3c**: m.p. 216–219 °C; ^1H NMR (C$_6$D$_6$, δ) 1.166 (s, 9H), 1.169 (s, 18H), 2.18 (s, 18H), 6.98–7.20 (m, 9H), 8.28–8.31 (m, 3H); ^{13}C NMR (C$_6$D$_6$, δ) 31.40 (CH$_3$), 32.12 (C), 33.11 (CH$_3$), 40.48 (C), 46.03 (CH$_3$), 47.56 (C), 121.14 (CH), 122.40 (CH), 128.95 (CH), 129.30 (C), 141.04 (CH), 141.76 (C), 159.12 (C); MS (30 eV) 640 (M$^+$). Anal. Calc. for C$_{39}$H$_{57}$GeN$_3$: C, 73.14; H, 8.97; N, 6.56. Found: C, 73.35; H, 9.00; N, 6.59%.

4.2.4. Preparation of p-anisyl(1,2,3-tri-tert-butylcycloprop-2-en-1-yl)dichlorogermane (1)

Dry HCl gas was bubbled through a mixture of **3a** (1.57 g, 2.60 mmol), aluminum chloride (0.126 g, 0.948 mmol), and dry toluene (30 ml) for 2.5 h. After adding acetone (0.05 ml, 1.09 mmol), the resulting mixture was concentrated under reduced pressure, followed by the addition of hexane and decantation. The mixture was concentrated under reduced pressure. Bulb-to-bulb distillation [140–180 °C/0.05 mmHg (bath temp.)] gave **1** (750 mg, 1.93 mmol, 74%). **1**: Colorless crystals; m.p. 98.2–99.6 °C;

^{1}H NMR (CDCl$_3$, δ) 0.93 (s, 9H), 1.33 (s, 18H), 3.82 (s, 3H), 6.96 (d, $J = 8.7$ Hz, 2H), 7.71 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (CDCl$_3$, δ) 30.33 (CH$_3$), 30.78 (CH$_3$), 31.40 (C), 37.90 (C, overlapping), 55.19 (CH$_3$), 114.23 (CH), 125.60 (C), 132.58 (C), 134.22 (CH), 161.27 (C). Anal. Calc. for C$_{22}$H$_{34}$Cl$_2$GeO: C, 57.69; H, 7.48%. Found: C, 58.08; H, 7.56%.

4.2.5. Reduction of *1a* with potassium in the presence of tert-butyldimethylsilane

A mixture of **1** (51.3 mg, 1.1×10^{-4} mol), potassium (47.6 mg, 1.2 mmol), *tert*-butyldimethylsilane (379 mg, 3.3 mmol), and benzene (10 ml) was stirred for 6 h under reflux. After removing potassium by filtration, the filtrate was concentrated under reduced pressure. After adding hexane, the resulting salt was removed by filtration. After evaporating the solvent, separation of the residue using recycling GPC (toluene as an eluent) gave *p*-anisyl(*tert*-butyldimethylsilyl)(1,2,3-tri-*tert*-butylcycloprop-2-en-1-yl) germane (**4**, 8.4 mg, 1.7×10^{-5} mol, 15%). **4**: Colorless oil; ^{1}H NMR (C$_6$D$_6$, δ) 0.34 (s, 3H), 0.45 (s, 3H), 0.92 (s, 9H), 1.11 (s, 9H), 1.13 (s, 9H), 1.19 (s, 9H), 3.26 (s, 3H), 4.25 (s, 1H), 6.82 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (C$_6$D$_6$, δ) −3.59 (CH$_3$), −2.62 (CH$_3$), 19.27 (C), 27.51 (CH$_3$), 30.80 (CH$_3$), 30.93 (CH$_3$), 31.23 (C), 31.71 (CH$_3$), 31.83 (C), 37.86 (C), 44.12 (C), 54.32 (CH$_3$), 113.98 (CH), 130.12 (C), 130.57 (C), 133.63 (C), 138.44 (CH), 159.93 (C); ^{29}Si NMR (C$_6$D$_6$, δ) 0.1; MS (40 eV) m/z (%) 504 (M$^+$, 0.2), 447 (7), 341 (7), 207 (100), 151 (10). Anal. Calc. for C$_{28}$H$_{50}$GeOSi: C, 66.80; H, 10.01%. Found: C, 66.47; H, 9.60%.

4.3. Theoretical calculations

All calculations were carried out using the GAUSSIAN 98 program package [10,11]. The structures of **2**, **5**, and **6** were optimized using the B3LYP hybrid functional [24] with the 6-31G(d) basis sets. The 6-311+G(d,p) basis sets were used for **7**–**9**. For all the compounds, the relative energies were calculated at the B3LYP/6-311+G(d,p), including the zero-point energy correction obtained at the B3LYP/6-31G(d) level. The NBO analysis was performed at the B3LYP/6-311+G(d,p) level.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.09.041.

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