

# Reaction of disilagermirenes with phenylacetylene: from a germasilene $-\text{Ge}=\text{Si}-$ to a metalladiene of the type $-\text{Si}=\text{Ge}-\text{C}=\text{C}-$

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Dedicated to Professor Oleg Nefedov on the occasion of his 70th birthday and for the recognition of his outstanding contribution in the field of Group 14 elements chemistry.

## Abstract

The reaction of tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene (**1b**) with phenylacetylene at room temperature produced highly air- and moisture-sensitive bright orange crystals of 1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-4-phenyl-1,2-disila-3-germacyclopenta-2,4-diene (**2b**), which represents a previously unknown metalladiene with one Si=Ge and one C=C double bond. The crystal structure of **2b** was determined by X-ray crystallography, which showed a *trans*-bent configuration around the Si=Ge double bond with a bond length of 2.250(1) Å. The reaction mechanism to form **2b**, the question of conjugation of the two double bonds in a cyclopentadiene ring of **2b**, as well as its reactivity are discussed. The reaction of tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene (**1a**), which is an isomer of **1b**, with phenylacetylene is also examined. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Conjugation; Cycloaddition; Germasilene; Metalladiene; Phenylacetylene; Silole

## 1. Introduction

It is well known that 1,3-dienes as well as their cyclic analogues constitute one of the most important classes of organic compounds, both from the fundamental and the practical points of view. Therefore, it is not surprising that after the discovery of the first stable metallenes and dimetallenes of heavier Group 14 elements (for reviews on metallenes and dimetallenes of Group 14 elements, see Ref. [1]), the experimental efforts of many research groups have been focused on the synthesis of the Group 14 elements containing metalladienes, which were expected to be very interesting because of their unusual structures and reactivity. Talking about such metalladienes, one can imagine several structures of the types:  $-\text{E}=\text{C}=\text{C}=\text{C}-$ ,  $-\text{C}=\text{E}=\text{C}=\text{C}-$ ,  $-\text{E}=\text{E}'=\text{C}=\text{C}-$ ,  $-\text{E}=\text{C}=\text{E}'=\text{C}-$ ,  $-\text{E}=\text{C}=\text{C}=\text{E}'-$ ,  $-\text{C}=\text{E}=\text{E}'=\text{C}-$ ,  $-\text{E}=\text{E}'=\text{E}''=\text{C}-$ ,  $-\text{E}=\text{E}'=\text{C}=\text{E}''-$  or  $-\text{E}=\text{E}'=\text{E}''=\text{E}'''-$  (E, E', E'' and E''' = heavier Group 14 elements). Such compounds are ex-

remely interesting objects for studying the degree of conjugation of the two double bonds and reactivity aspects, which can also be different from those of their carbon analogues. Nevertheless, in spite of the evidently great synthetic challenge, there are very few examples of such compounds, which can be explained by the difficulties in their preparation. Thus, among all of the possible structures, only two examples have been reported to the present time: symmetrical hexakis(2,4,6-triisopropylphenyl)tetrasilabuta-1,3-diene [2] and hexakis(2,4,6-triisopropylphenyl)tetragermabuta-1,3-diene [3].

Here we report the synthesis, full characterization, crystal structure and some aspects of the reactivity of the first metalladiene consisting of Group 14 elements of the type  $-\text{Si}=\text{Ge}-\text{C}=\text{C}-$ , in which the Si=Ge double bond was structurally characterized for the first time [4]. This compound also represents a previously unknown metallole with an unsymmetrically composed skeleton. The reaction mechanism to form the metalladiene, supported by theoretical calculations, and the question of conjugation of the two double bonds will also be discussed.

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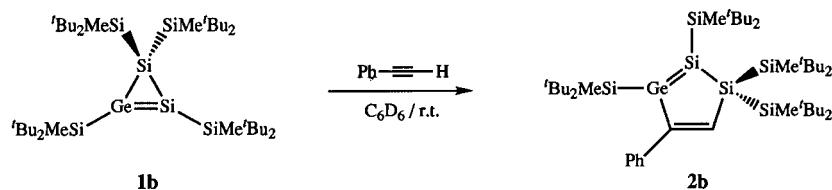
## 2. Results and discussion

Previously we have reported the synthesis of tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene (**1a**) with a Si=Si double bond as well as its isomerization to a tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene (**1b**) with a Si=Ge double bond [5]. The reactivity of both compounds was found to be very rich and interesting, especially regarding cycloaddition reactions across their double bonds, which gives access to new cyclic and bicyclic compounds. The most important results were obtained from the reaction of disilagermirenes with phenylacetylene. Thus, the reaction of disilagermirene **1b** with excess phenylacetylene in deuteriobenzene at room temperature quickly produced an orange-red reaction mixture, which showed a down-field signal in the  $^{29}\text{Si}$ -NMR at +124.2 ppm [6]. Monitoring of the reaction by NMR spectroscopy showed that the reaction proceeded cleanly and was completed in 5 h, at which time the  $^1\text{H}$ -NMR spectrum showed the absence of the starting compound **1b**. After evaporation of solvent and excess phenylacetylene, recrystallization of the residue from hexane gave bright orange crystals of 1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-4-phenyl-1,2-disila-3-germacyclopenta-2,4-diene (**2b**) in 42% yield (Scheme 1), whose structure has been established on the basis of  $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{29}\text{Si}$ -NMR and mass spectra.

The  $^1\text{H}$ -NMR spectrum of **2b** showed three types of methyl groups and four different *tert*-butyl groups, whereas the  $^{13}\text{C}$ -NMR spectrum exhibited two signals for the methyl groups and four signals for the *tert*-butyl

groups. The  $^{29}\text{Si}$ -NMR spectrum revealed five resonances of which three belong to the silyl substituents: 19.4, 26.6 and 30.1 ppm. The down-field signal at +124.2 ppm is characteristic of the doubly bonded silicon atom, and the up-field signal at -45.6 ppm corresponds to the endocyclic  $\text{sp}^3$  Si atom. The chemical shift of such Si atoms in silole molecules depends on the substituents: +8.1 ppm for 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene [7], whereas -34.2 ppm for 1,1-bis(trimethylsilyl)-2,3,4,5-tetramethyl-1-silacyclopenta-2,4-diene [8]. The mass spectrum of **2b** showed the strong  $\text{M}^+$  parent ion cluster at 856–866, as well as the fragmentation peaks 803 [ $\text{M}^+ - \text{Bu}$ ] and 703 [ $\text{M}^+ - \text{SiMe}^t\text{Bu}_2$ ].

Compound **2b** is extremely air- and moisture-sensitive and even in the solid state quickly decomposes in air. The decomposition of **2b** in hexane solution in the presence of air caused the formation of a very complicated mixture. The molecular structure of compound **2b** was established by X-ray crystallography (Fig. 1). The five-membered ring is almost planar, which is normal for cyclopentadiene derivatives, although the Si=Ge double bond has a *trans*-bent configuration with a torsional angle Si(6)–Ge(1)–Si(2)–Si(5) of  $38.6(1)^\circ$ . The phenyl ring is almost perpendicular to the plane of the silole ring, which is usual for phenyl-substituted metalloles (for the reviews on metalloles chemistry see Ref. [9]). The large value for the Si(3)–Si(1)–Si(4) angle of  $124.7(5)^\circ$  indicates the significant steric repulsion of the two bulky  $\text{SiMe}^t\text{Bu}_2$  substituents in the geminal position. The length of the Si=Ge double bond is 2.250(1)



Scheme 1.

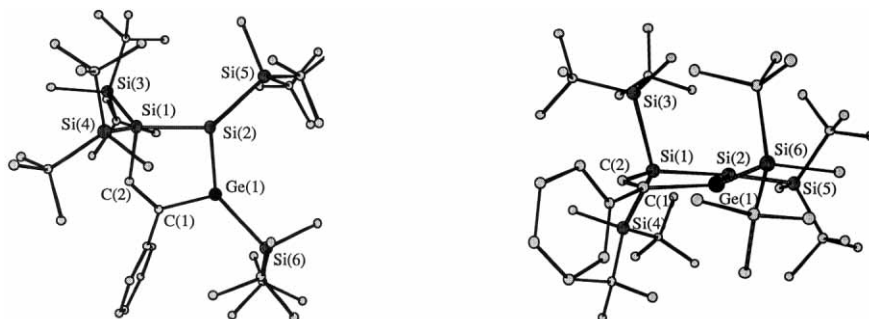
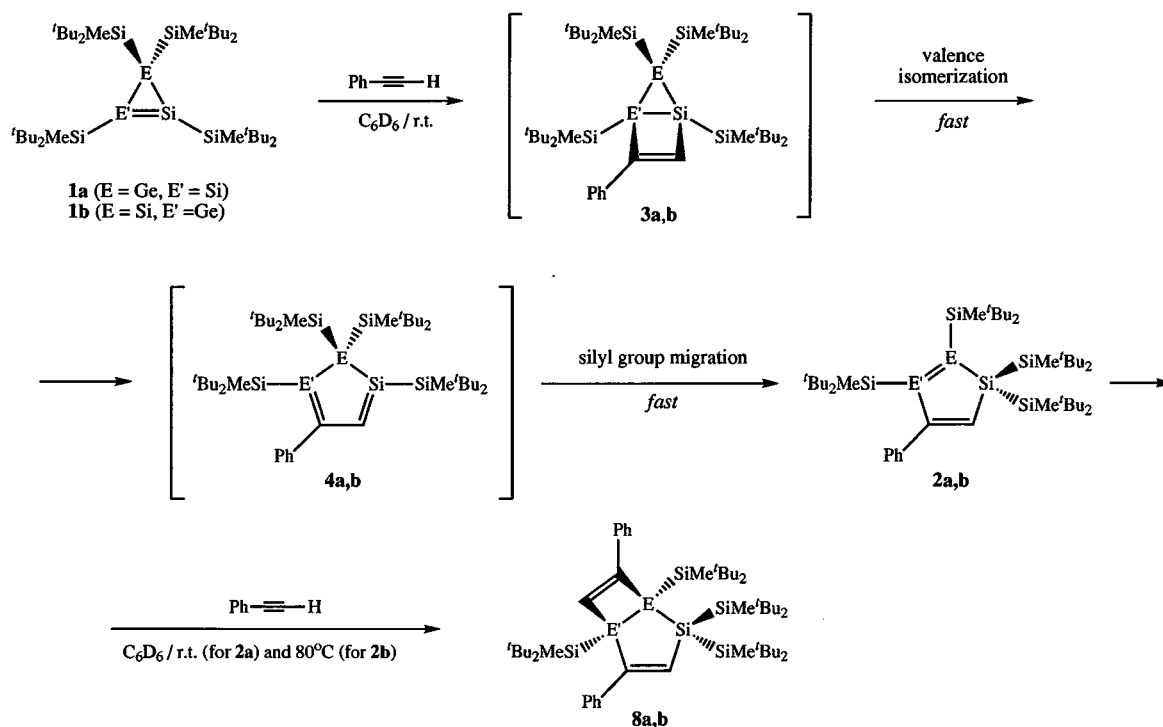


Fig. 1. Molecular structure of the silole **2b**; left (top view), right (side view). Selected bond lengths (Å): Ge(1)–Si(2) 2.250(1), Si(1)–Si(2) 2.364(1), Si(1)–C(2) 1.888(3), C(1)–C(2) 1.343(5), Ge(1)–C(1) 1.972(3), Si(1)–Si(3) 2.431(1), Si(1)–Si(4) 2.432(1), Si(2)–Si(5) 2.380(1), Ge(1)–Si(6) 2.418(1). Selected bond angles ( $^\circ$ ): C(1)–Ge(1)–Si(2) 101.8(1), Ge(1)–Si(2)–Si(1) 95.2(0), C(2)–Si(1)–Si(2) 98.1(1), C(1)–C(2)–Si(1) 126.9(2), C(2)–C(1)–Ge(1) 117.9(2), Si(3)–Si(1)–Si(4) 124.7(0).



Scheme 2.

Å, which lies between the typical values of Si=Si (2.138–2.289 Å) [1,10] and Ge=Ge (2.213–2.460 Å) [1] double bond lengths. This value is close to that of the theoretically predicted 2.180 Å (MP2) for **1b** [5]. It was quite interesting to estimate the degree of conjugation of the two double bonds in the silole ring system. In the case of such conjugation, one can expect a shortening of the Ge(1)–C(1) ordinary bond as well as an elongation of the Ge(1)=Si(2) and C(1)=C(2) double bonds. The length of the Ge(1)–C(1) bond is 1.972(3) Å, which lies in the normal range for Ge–C bond lengths of 1.95–2.00 Å [11]. We were not able to compare the Ge(1)=Si(2) double bond length with other examples, since no structural data regarding Si=Ge double bonds were available to date. The C(1)=C(2) double bond length is 1.343(5) Å, which also lies in the normal range for C=C double bond lengths of 1.34 Å. All of these data give no evidence for any real conjugation between the Si=Ge and the C=C double bonds in the cyclopentadiene moiety of **2b**, despite the planarity of the five-membered ring. The same conclusion came also from the UV–vis spectrum of **2b**, which showed no significant bathochromic shift in comparison with an isolated Si=Ge double bond in the compound **1b** (472 vs 467 nm, respectively). This seems to be curious since all the known cyclopentadiene compounds were described as fully conjugated systems, for which Diels–Alder cycloaddition reactions are typical [12]. Apparently, such unusual behavior of **2b** is caused by both the great energy difference and the difference in the size of the

atoms of the Si=Ge and C=C double bonds, which prevent the effective overlapping of molecular orbitals of the two  $\pi$ -bonds, which is necessary for real conjugation. In contrast, for the symmetrical heavier Group 14 elements containing 1,3-diene systems with two equal double bonds, such as 2,3-digerma-1,3-butadiene  $H_2C=GeH-GeH=CH_2$ , theoretical calculations have predicted about half the degree of conjugation compared with that of the parent 1,3-butadiene [13]. This was supported by the experimental results: symmetrical tetrasila- and tetragerma-1,3-butadienes were reported as highly conjugated systems, as evidenced by the X-ray and UV–vis data [2,3].

For the mechanism of formation of **2b**, the following reaction sequence can be considered (Scheme 2). In the first step [2 + 2] cycloaddition of one molecule of phenylacetylene occurred across the Si=Ge double bond to form bicyclic compound **3b**. The last compound then quickly undergoes valence isomerization to form a silole-type structure **4b** with one Ge=C and one Si=C double bond, which in turn rapidly isomerizes to give the thermodynamically more stable silole **2b** with one Si=Ge and one C=C double bond. Such a type of isomerization was found for the first time for 1-methyl-1-trimethylsilyl-2,5-diphenyl-1-silacyclopenta-2,4-diene, which undergoes isomerization at 150°C through the 1,5-migration of the silyl substituent to form 1-methyl-5-trimethylsilyl-2,5-diphenyl-1-silacyclopenta-1,3-diene. The last compound was unstable and evidenced only by trapping reactions [14]. A similar 1,5 H-migration was

also observed in unsubstituted silole systems to give finally the most stable 1-silacyclopenta-2,4-diene isomer [15]. The stability of the isomeric compounds **3b**, **4b** and **2b** was evaluated by ab initio calculations on the parent compounds (**5b** for **3b**, **6b** for **4b** and **7b** for **2b**) at B3LYP/6-31G\* level (Fig. 2). The theory predicted **7b** to be the most stable compound. Compound **5b** is less stable by 13.39 kcal mol<sup>-1</sup> and compound **6b** is the most unfavorable isomer by 14.29 kcal mol<sup>-1</sup>, which is in a good agreement with the experimental results [16]. Thus, compounds **3b** and **4b** are quite unstable, since it was impossible to isolate and even detect them by NMR monitoring of the reaction. In contrast, compound **2b** is stable in solution, and at room temperature there is only a very slow reaction between **2b** and excess phenylacetylene.

Such cycloaddition of the second molecule of phenylacetylene to the Si=Ge double bond of silole **2b** can be achieved only at elevated temperatures. Thus, heating at 80°C for 6 h caused the complete disappearance of **2b** and formation of the new bicyclic compound 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diphenyl-1,2-disila-5-germabicyclo[3.2.0]hepta-3,6-diene **8b**, which was isolated by recrystallization from hexane in 55% yield. The structure of compound **8b** was established by means of all spectral data and finally confirmed by X-ray analysis.

It is quite interesting that the regiochemistry of the PhC=CH cycloaddition to the Si=Ge double bond of **2b**

is different from the expected one: the phenyl-group substituted carbon atom is attached to the silicon atom, although according to the polarity of the Si=Ge double bond one can expect the opposite regioselectivity. Recently, the cycloaddition of phenylacetylene to the transient germasilenes was found to be regioselective to form only one isomer, in which the phenyl-group substituted carbon atom is attached to a germanium atom, which is in accordance with the polarity of the Si=Ge double bond [17]. Apparently, in our case the reaction is governed by steric effects, rather than electronic; i.e. kinetic control takes place. As was established above, there is no real conjugation in a silole ring system; therefore, it is not surprising that **2b** and a second molecule of phenylacetylene react in a [2 + 2], but not [4 + 2], cycloaddition manner. That is, silole **2b** represents an unusual system with two formally conjugated, but actually isolated, double bonds in which one (Si=Ge) possesses a much higher reactivity than the other (C=C). This is in sharp contrast with a previously reported transient silole such as 1-methyl-2,5-diphenyl-5-trimethylsilyl-1-silacyclopenta-1,3-diene, which reacted with acetylenes and alkenes as a conjugated diene to give the corresponding Diels–Alder adducts [14].

The bicyclic compound **8b** has no symmetry, which causes the complicated NMR spectra. Thus, in the <sup>1</sup>H-NMR spectrum of **8b** all methyl and *tert*-butyl groups appeared to be non-equivalent, exhibiting four signals for Me and eight signals for <sup>t</sup>Bu groups. The

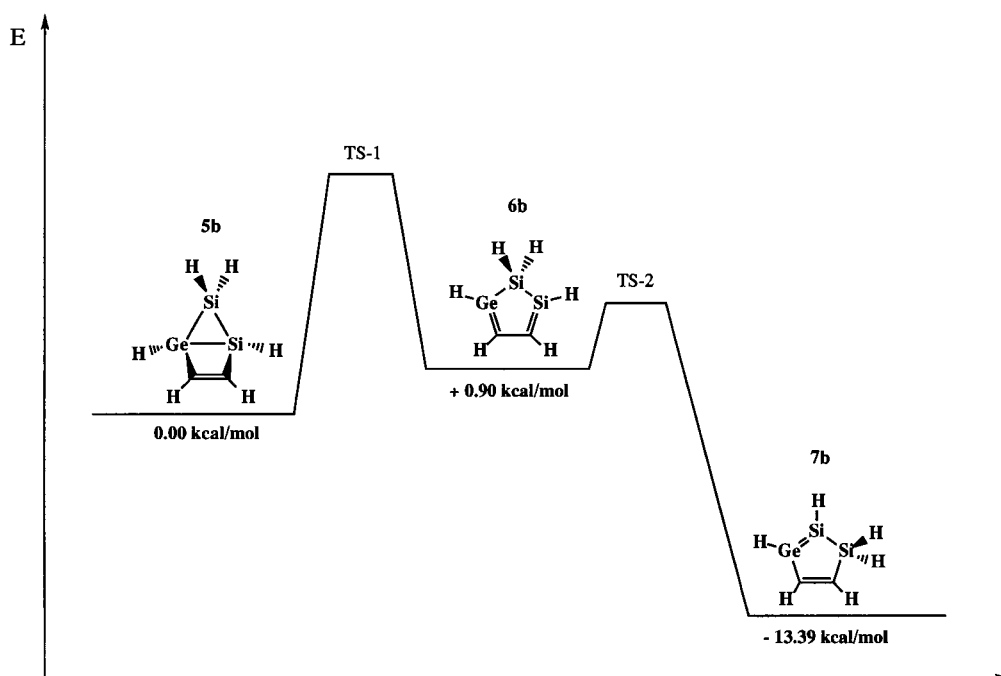


Fig. 2. Energy profile of the reaction of 2-disilagermirene GeSi<sub>2</sub>H<sub>4</sub> with acetylene by ab initio calculations (B3LYP/6-31G\* level).

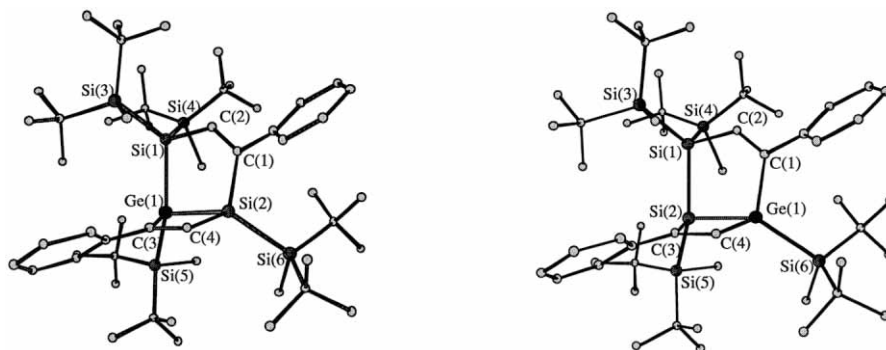


Fig. 3. Molecular structures of **8a** (left) and **8b** (right). **8a**: selected bond lengths (Å): Ge(1)–Si(2) 2.432(1), Ge(1)–Si(1) 2.509(1), Ge(1)–C(3) 2.035(5), Si(1)–C(2) 1.898(5), C(2)–C(1) 1.348(6), C(1)–Si(2) 1.925(4), Si(2)–C(4) 1.897(5), C(4)–C(3) 1.351(6). Selected bond angles (°): Si(1)–Ge(1)–Si(2) 92.1(0), Ge(1)–Si(2)–C(1) 101.1(1), Si(2)–Ge(1)–C(3) 71.6(1), Ge(1)–Si(2)–C(4) 76.5(1). Folding angle between the planes of four- and five-membered rings: 109.1°. **8b**: selected bond lengths (Å): Ge(1)–Si(2) 2.432(1), Si(1)–Si(2) 2.481(2), Ge(1)–C(1) 1.993(6), Si(1)–C(2) 1.897(6), C(1)–C(2) 1.345(8), Ge(1)–C(4) 1.968(7), Si(2)–C(3) 1.967(6), C(3)–C(4) 1.374(8). Selected bond angles (°): Si(1)–Si(2)–Ge(1) 93.1(0), Ge(1)–Si(2)–C(3) 75.1(1), Si(2)–Ge(1)–C(1) 99.8(1), Si(2)–Ge(1)–C(4) 73.7(2). Folding angle between the planes of four- and five-membered rings: 109.0°.

olefinic proton in the cyclobutene ring has a very characteristic down-field shifted signal at 8.15 ppm. For example, the chemical shifts of the olefinic proton in 1,1,2,2-tetramesityl-3-phenyl-1,2-disilacyclobut-3-ene are reported to be 8.08 [18] and 8.07 ppm in 1,1,2,2-tetramesityl-3-phenyl-1,2-digermacyclobut-3-ene [19]. The  $^{29}\text{Si}$ -NMR spectrum revealed six resonances for six non-equivalent silicon atoms; four of them belong to the silyl substituents: 16.5, 19.3, 21.4 and 21.8 ppm, and two of them belong to the endocyclic bridgehead silicon atoms:  $-52.8$  and  $-13.9$  ppm. According to the X-ray data (Fig. 3, right) compound **8b** has a highly distorted structure with a folding angle between the planes of the four- and five-membered rings of 109.0°. Both four- and five-membered rings are nearly planar, whereas phenyl rings are out of these planes by 29.9 and 54.1°, respectively.

The reaction of disilagermirene **1a**, which is a structural isomer of **1b**, with phenylacetylene proceeds in a similar way, to give finally the bicyclic compound 1,2,2,5-tetrakis[di-*tert*-butyl-(methyl)silyl]-4,7-diphenyl-2,5-disila-1-germabicyclo[3.2.0]hepta-3,6-diene (**8a**) (structural isomer of **8b**) in 63% yield (Scheme 2). Both **8a** and **8b** have very similar NMR spectra, which gives evidence of their structural similarities. X-ray analysis of **8a** (Fig. 3, left) has confirmed such a conclusion, showing the molecular structure of **8a** to be almost identical to that of **8b**, with very similar structural characteristics; for example, with the same folding angle between the two planes of 109.1°. The only difference in the structures of **8a** and **8b** is the position of the bridgehead Si and Ge atoms, which is opposite to each other in these two compounds.

In contrast to the previous case, the existence of the initially formed bicyclic compound **3a** can be detected by NMR spectroscopy. Six resonances can be seen in

the  $^{29}\text{Si}$ -NMR: four of them (21.9, 23.5, 26.8 and 28.3 ppm) belong to substituents, and two of them ( $-84.1$  and  $-65.0$  ppm) can be assigned to the endocyclic Si atoms. The intermediate compounds **4a** and **2a** cannot be detected by NMR, apparently because **4a** quickly isomerizes to **2a**, which in turn easily and rapidly undergoes cycloaddition with a second molecule of phenylacetylene, even at room temperature, to give finally the bicyclic compound **8a**. The cycloaddition of the second molecule of phenylacetylene to the silole **2a** is also regioselective, as in the above case of **2b**, but having an opposite direction: the phenyl-group substituted carbon atom is attached to a germanium atom, which can be well explained by electronic reasons. Apparently, in the former case of compound **2b**, the cycloaddition of the second molecule of phenylacetylene is significantly hindered because of great steric problems and therefore, even upon heating, steric control of the reaction is predominant over thermodynamic control.

There is no reaction of 1-disilagermirene **1a** with diphenylacetylene or bis(trimethylsilyl)acetylene even upon prolonged heating at 80°C in  $\text{C}_6\text{D}_6$  for 2 days. This gives evidence that the cycloaddition reactions of disilagermirenes proceed mainly by the polar mechanism rather than the concerted one: no reaction with non-polar internal alkynes ( $\text{PhC}\equiv\text{CPh}$ ), relatively smooth reaction with slightly polarized terminal alkynes ( $\text{PhC}\equiv\text{CH}$ ), and very easy reaction with carbonyl compounds [20]. It is interesting that there is also no reaction of 1-disilagermirene **1a** with styrene at 80°C in  $\text{C}_6\text{D}_6$  for 2 days, in contrast to the phenylacetylene case. This seems to be understandable since, in the case of  $\text{PhCH}=\text{CH}_2$ , formation of the conjugated system (like **2a, 2b**) is impossible.

### 3. Experimental

#### 3.1. General procedures

All experiments were performed in an Ar atmosphere of MBRAUN MB 150B-G glove-box and by using high-vacuum line techniques. All solvents were dried and degassed over potassium mirror in vacuum prior to use. NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer ( $^1\text{H}$ -NMR at 300.13 MHz;  $^{13}\text{C}$ -NMR at 75.47 MHz;  $^{29}\text{Si}$ -NMR at 59.63 MHz). Mass spectra were obtained on JEOL JMS SX-102 instrument. UV-vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Elemental analysis was performed in the Analytical Center at Tohoku University. 1- and 2-Disilagermirenes, **1a** and **1b**, were prepared according to the literature [5a].

#### 3.2. Synthesis of 1,1,2,3-tetrakis[di-tert-butyl(methyl)silyl]-4-phenyl-1,2-disila-3-germacyclopenta-2,4-diene (**2b**)

Tetrakis[di-tert-butyl(methyl)silyl]-2-disilagermirene (**1b**) was prepared from tetrakis[di-tert-butyl(methyl)silyl]-1-disilagermirene (**1a**) (93 mg, 0.12 mmol) by heating at 215°C for 25 min. Then compound **1b** was reacted with a six-fold excess of phenylacetylene (74.5 mg, 0.73 mmol) in a dry  $\text{O}_2$ -free  $\text{C}_6\text{D}_6$  (0.55 ml) in a sealed NMR tube at room temperature (r.t.). Reaction progress was monitored by NMR spectra, which showed the reaction was completed in 5 h. After evaporation of the solvent and excess phenylacetylene in vacuum, the residue was recrystallized from a dry hexane to give **2b** as bright orange crystals (44 mg, 42%); m.p. 161–163°C —  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.37 (s, 6H), 0.40 (s, 3H), 0.59 (s, 3H), 0.99 (s, 18H), 1.15 (s, 18H), 1.19 (s, 18H), 1.31 (s, 18H), 7.06–7.09 (m, 1H, ArH), 7.19–7.24 (m, 2H, ArH), 7.34 (s, 1H, C=CH), 7.42 (dd,  $J$  = 8.2 Hz,  $J$  = 8.2 Hz, 2H, ArH) —  $^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = -2.9 (Me), -2.3 (3Me), 22.1 (CMe<sub>3</sub>), 22.5 (CMe<sub>3</sub>), 23.2 (CMe<sub>3</sub>), 23.7 (CMe<sub>3</sub>), 29.9 (CMe<sub>3</sub>), 30.96 (CMe<sub>3</sub>), 31.12 (CMe<sub>3</sub>), 31.4 (CMe<sub>3</sub>), 126.3, 126.8, 128.6, 149.8 (C=CH), 151.7 (*ipso* C), 173.3 (C=CH) —  $^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = -45.6, 19.4, 26.6, 30.1, 124.2 — EIMS (70 eV): 856–866 [ $\text{M}^+$  cluster, 31], 803 [ $\text{M}^+$  - 'Bu, 2], 703 [ $\text{M}^+$  - SiMe'Bu<sub>2</sub>, 4], 73 (100) — UV-vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ) (hexane) 243 (37 330), 307 (6570), 472 (5540).

#### 3.3. Synthesis of 1,2,2,5-tetrakis[di-tert-butyl(methyl)silyl]-4,7-diphenyl-1,2-disila-5-germabicyclo[3.2.0]hepta-3,6-diene (**8b**)

Tetrakis[di-tert-butyl(methyl)silyl]-2-disilagermirene (**1b**), prepared from **1a** (52 mg, 0.07 mmol) by the

photolysis ( $\lambda > 300$  nm) for 7 h, was reacted with a six-fold excess of phenylacetylene (43 mg, 0.42 mmol) in a dry  $\text{O}_2$ -free  $\text{C}_6\text{D}_6$  (0.55 ml) in a sealed NMR tube at r.t. In 5 h the starting material disappeared, and compound **2b** was cleanly formed. After heating at 80°C for 6 h compound **2b** was completely transformed to **8b**. After evaporation of the solvent and excess phenylacetylene in vacuum, the residue was recrystallized from a dry hexane to give **8b** as colorless crystals (36 mg, 55%); m.p. (dec.) 215–217°C —  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.16 (s, 3H), 0.30 (s, 3H), 0.50 (s, 3H), 0.66 (s, 3H), 0.88 (s, 9H), 0.97 (s, 9H), 1.06 (s, 9H), 1.13 (s, 9H), 1.19 (s, 9H), 1.28 (s, 9 H), 1.29 (s, 9 H), 1.39 (s, 9 H), 7.06–7.09 (m, 2H), 7.22 (t,  $J$  = 8.1 Hz, 4 H), 7.31 (s, 1 H), 7.52 (d,  $J$  = 7.1 Hz, 2H), 7.68 (d,  $J$  = 7.1 Hz, 2H), 8.15 (s, 1 H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = -3.8 (Me), -2.0 (Me), -1.3 (Me), -0.7 (Me), 22.1 (CMe<sub>3</sub>), 22.3 (CMe<sub>3</sub>), 22.5 (CMe<sub>3</sub>), 22.57 (CMe<sub>3</sub>), 22.60 (CMe<sub>3</sub>), 23.6 (CMe<sub>3</sub>), 23.7 (CMe<sub>3</sub>), 23.9 (CMe<sub>3</sub>), 29.7 (CMe<sub>3</sub>), 30.1 (CMe<sub>3</sub>), 31.3 (CMe<sub>3</sub>), 31.6 (3 CMe<sub>3</sub>), 31.7 (CMe<sub>3</sub>), 31.9 (CMe<sub>3</sub>), 125.8, 126.6, 127.3, 127.5, 128.1, 128.3, 142.6 (*ipso* C), 149.0 (C=CH), 150.8 (*ipso* C), 158.3 (C=CH), 163.6 (C=CH), 167.5 (C=CH) —  $^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = -52.8, -13.9, 16.5, 19.3, 21.4, 21.8 — EIMS (70 eV): 958–968 [ $\text{M}^+$  cluster, 1], 905 [ $\text{M}^+$  - 'Bu, 2], 805 [ $\text{M}^+$  - SiMe'Bu<sub>2</sub>, 2], 73 (100) — Anal. Found: C, 64.58; H, 9.74. Calc. for  $\text{C}_{52}\text{H}_{96}\text{GeSi}_6$ : C, 64.89; H, 10.05%.

#### 3.4. Synthesis of 1,2,2,5-tetrakis[di-tert-butyl(methyl)silyl]-4,7-diphenyl-2,5-disila-1-germabicyclo[3.2.0]hepta-3,6-diene (**8a**)

Tetrakis[di-tert-butyl(methyl)silyl]-1-disilagermirene (**1a**) (50 mg, 0.06 mmol) was reacted with a seven-fold excess of phenylacetylene (48 mg, 0.47 mmol) in a dry  $\text{O}_2$ -free  $\text{C}_6\text{D}_6$  (0.6 ml) in a sealed tube at r.t. In 1 day the reaction was completed, and the red color of the starting material disappeared. After evaporation of the solvent and excess phenylacetylene in vacuum, the residue was recrystallized from a dry hexane to give **8a** as colorless crystals (40 mg, 63%); m.p. (dec.) 213–214°C —  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.15 (s, 3H), 0.26 (s, 3H), 0.47 (s, 3H), 0.69 (s, 3H), 0.91 (s, 9H), 0.99 (s, 9H), 1.05 (s, 9H), 1.15 (s, 9H), 1.16 (s, 9H), 1.28 (s, 18H), 1.36 (s, 9H), 7.06 (d,  $J$  = 7.4 Hz, 2H), 7.16–7.18 (m, 2H), 7.22 (t,  $J$  = 7.4 Hz, 2H), 7.55 (s, 1 H), 7.56 (d,  $J$  = 7.0 Hz, 2H), 7.70 (d,  $J$  = 7.0 Hz, 2H), 8.05 (s, 1H) —  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = -3.9 (Me), -2.3 (Me), -1.2 (Me), -1.1 (Me), 21.6 (CMe<sub>3</sub>), 22.0 (CMe<sub>3</sub>), 22.3 (CMe<sub>3</sub>), 22.5 (CMe<sub>3</sub>), 23.2 (CMe<sub>3</sub>), 23.6 (2 CMe<sub>3</sub>), 24.1 (CMe<sub>3</sub>), 29.9 (CMe<sub>3</sub>), 30.3 (CMe<sub>3</sub>), 31.2 (CMe<sub>3</sub>), 31.5 (5 CMe<sub>3</sub>), 126.0, 126.7, 127.5, 128.2, 128.5, 142.5 (*ipso* C), 149.6 (C=CH), 150.2 (*ipso* C), 155.1 (C=CH), 162.4 (C=CH), 170.8 (C=CH) —  $^{29}\text{Si}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = -45.3, -18.4, 9.4, 18.6, 21.1,

Table 1  
Crystallographic data and experimental parameters for the crystal structure analysis of **2b**, **8a** and **8b**

|  | <b>2b</b>  | <b>8a</b>  | <b>8b</b>  |
|--|--|--|--|
| Empirical formula  | C <sub>44</sub> H <sub>90</sub> GeSi <sub>6</sub>              | C <sub>52</sub> H <sub>96</sub> GeSi <sub>6</sub>              | C <sub>52</sub> H <sub>96</sub> GeSi <sub>6</sub>              |
| Formula weight (g mol <sup>-1</sup> )                            | 860.29   | 962.42   | 962.42   |
| Temperature (K)  | 120  | 120  | 120  |
| Wavelength (Å)   | 0.71070  | 0.71070  | 0.71070  |
| Crystal system   | Triclinic  | Triclinic  | Triclinic  |
| Space group  | <i>P</i> $\bar{1}$ (2)   | <i>P</i> $\bar{1}$ (2)   | <i>P</i> $\bar{1}$ (2)   |
| Unit cell dimensions   |  |  |  |
| <i>a</i> (Å)   | 12.2070(8)   | 13.721(1)  | 13.772(3)  |
| <i>b</i> (Å)   | 13.214(1)  | 14.662(1)  | 14.580(3)  |
| <i>c</i> (Å)   | 18.815(1)  | 15.746(1)  | 15.746(3)  |
| $\alpha$ (°)   | 74.551(4)  | 99.642(5)  | 99.798(9)  |
| $\beta$ (°)  | 73.514(5)  | 114.978(5)   | 114.94(1)  |
| $\gamma$ (°)   | 64.841(5)  | 92.283(5)  | 92.097(9)  |
| <i>V</i> (Å <sup>-3</sup> )                                      | 2596.7(4)  | 2809.1(5)  | 2804.2(9)  |
| <i>Z</i>   | 2  | 2  | 2  |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )                   | 1.100  | 1.138  | 1.140  |
| Absorption coefficient (mm <sup>-1</sup> )                       | 0.755  | 0.705  | 0.706  |
| <i>F</i> (000)   | 940  | 1048   | 1048   |
| Crystal size (mm)  | 0.3 × 0.3 × 0.1  | 0.2 × 0.2 × 0.1  | 0.15 × 0.15 × 0.15   |
| Theta range for data collection (°)                              | 3.51–27.99   | 2.63–28.00   | 2.63–27.99   |
| Index ranges   | 0 ≤ <i>h</i> ≤ 14, -15 ≤ <i>k</i> ≤ 17,<br>-23 ≤ <i>l</i> ≤ 24 | 0 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 19,<br>-20 ≤ <i>l</i> ≤ 18 | 0 ≤ <i>h</i> ≤ 18, -19 ≤ <i>k</i> ≤ 19,<br>-20 ≤ <i>l</i> ≤ 18 |
| Reflections collected  | 22 573   | 27 484   | 26 584   |
| Independent reflections  | 10 815 [ <i>R</i> <sub>int</sub> = 0.0560]                     | 11 932 [ <i>R</i> <sub>int</sub> = 0.0680]                     | 11 971 [ <i>R</i> <sub>int</sub> = 0.0890]                     |
| Reflections used   | 10 815   | 11 932   | 11 971   |
| Parameters   | 551  | 532  | 533  |
| <i>S</i> <sup>a</sup>  | 1.015  | 1.032  | 1.044  |
| Weight parameters <i>a/b</i> <sup>b</sup>                        | 0.0362/3.3161  | 0.1403/3.1257  | 0.1383/8.2043  |
| Final <i>R</i> indices <sup>c</sup> [ <i>I</i> > 2σ( <i>I</i> )] | 0.0562   | 0.0832   | 0.0974   |
| <i>wR</i> <sub>2</sub> <sup>d</sup> (all data)                   | 0.1119   | 0.2402   | 0.2806   |
| Largest difference peak and hole<br>(e Å <sup>-3</sup> )         | +0.408 and -0.575  | +1.912 and -1.615  | +2.907 and -1.313  |

<sup>a</sup>  $S = \{\sum w[F_o^2 - F_c^2]^2 / (n - p)\}^{0.5}$ , *n* = no. of reflections; *p* = no. of parameters.

<sup>b</sup>  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ , with  $P = (F_o^2 + 2F_c^2) / 3$ .

<sup>c</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum ||F_o|$ .

<sup>d</sup>  $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{0.5}$ .

27.4 — EIMS (70 eV): 958–968 [*M*<sup>+</sup> cluster, 3], 905 [*M*<sup>+</sup> - *t*Bu, 5], 805 [*M*<sup>+</sup> - SiMe<sup>t</sup>Bu<sub>2</sub>, 93], 73 (100) — Anal. Found: C, 64.82; H, 10.21. Calc. for C<sub>52</sub>H<sub>96</sub>GeSi<sub>6</sub>: C, 64.89; H, 10.05%.

### 3.5. Crystal structure analyses of the compounds **2b**, **8a** and **8b**

The single crystals of **2b**, **8a** and **8b** for X-ray diffraction study were grown from the hexane solutions. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71070$  Å). The structures were solved by the direct method, using SIR-92 program [21], and refined by the full-matrix least-squares method by SHELXL-97 program [22]. The crystal data and experimental parameters for the X-ray analysis of **2b**, **8a** and **8b** are listed in Table 1.

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