Disilagermirenes: heavy cyclopropenes of Si and Ge atoms

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Dedicated to the 50th Anniversary of Polysilane Chemistry in 2003, and the pioneering work of Professor Makoto Kumada to this field and his outstanding contribution to silicon chemistry

Abstract

Tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene (**3**) was prepared by the reaction of 2,2,2-tribromo-1,1-di-*tert*-butyl-1-methyldisilane and dichlorobis[di-*tert*-butyl(methyl)silyl]germane with sodium in toluene. The molecular structure of **3** was established by X-ray crystallography, which showed a *trans*-bent configuration around the Si=Si double bond with a bond length of 2.146(1) Å. Thermal and photochemical isomerization of **3** to tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene (**4**) is also reported, as well as the reactions of **3** with MeI, PhCH$_2$OH, and PhCOCH$_3$.
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1. Introduction

Cyclopropene, the smallest unsaturated ring system, together with its derivatives, represents one of the most important classes of organic compounds because of its enhanced reactivity caused by the large ring strain [1]. Very recently, it was demonstrated that the heavy neighbors of carbon in Group 14 (Si, Ge, Sn) are also capable of forming such unsaturated three-membered ring systems [2]. Despite the much greater difficulties in the preparation of such compounds compared with their carbon analogue (cyclopropene), they are becoming increasingly available, constituting a new highly promising and quickly developing class of organometallic compounds: *heavy cyclopropenes*. Such compounds tend to occupy a rather important position in the chemistry of heavier Group 14 elements, as the high reactivity of heavy cyclopropenes is much more pro-

nounced than that of cyclopropene, because of the extreme reactivity of the endocyclic metal–metal double bond and the weakness of the endocyclic metal–metal single bonds [2].

Despite such great interest from the structural and synthetic viewpoints, the story of heavy cyclopropenes is very short, being only 8 years old: the first report on the germanium version, cyclotrigermenes, only appeared in 1995 (Sekiguchi et al.) [3]. After that report there was a period of extensive development of the chemistry of heavy cyclopropenes with an increase in the number of their representatives. Thus, the first silicon analogues, cyclotrisilenes, were synthesized in 1999 by the experimental efforts of two research groups—Kira et al. [4] and Sekiguchi et al. [5]. In the same year, the first and still the only example of a tin representative, cyclotristannene, was reported by Wiberg et al. [6], and finally, we have recently synthesized the first heavy cyclopropenes containing two different heavier Group 14 elements—isomeric 1- and 2-disilagermirenes, consisting of one germanium and two silicon atoms [7] and studied their reactivity [8]. In this paper we present the

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full description of their synthesis, structural peculiarities and some new aspects of their chemical reactivity.

2. Results and discussion

The synthesis of the first three-membered unsaturated ring compound consisting of different heavier Group 14 elements required the preliminary preparation of the two corresponding precursors: 1,1,1-tribromo-2,2-di-*tert*-butyl-2-methyldisilane (**1**) (silicon part) and dichlorobis[di-*tert*-butyl(methyl)silyl]germane (**2**) (germanium part) (Scheme 1). The silicon part, compound **1**, was prepared starting from SiF_4, which was reacted with ^tBuLi to produce $^tBu_2SiF_2$ in 83% yield. The last compound was then methylated with MeLi to form $^tBu_2MeSiF$ (80% yield), which was in turn treated with Ph_3SiLi to give $^tBu_2MeSiSiPh_3$ in 83% yield. Finally, the disilane $^tBu_2MeSiSiPh_3$ was subjected to a dephenylation–bromination reaction with gaseous HBr in the presence of $AlBr_3$ catalyst to form the final precursor, $^tBu_2MeSiSiBr_3$ (**1**), in 92% yield (Scheme 1). The germanium part, compound **2**, was synthesized starting from $MeHSiCl_2$ which was reacted with ^tBuLi in pentane to form $^tBu_2MeSiH$ in 83% yield. This hydrosilane was subsequently brominated with Br_2 in CH_2Cl_2 to form the corresponding bromide $^tBu_2MeSiBr$ (94% yield), which was then reacted with $(p\text{-tolyl})_2GeCl_2$ and Li in THF to form $(p\text{-tolyl})_2Ge(SiMe^tBu_2)_2$ in 62% yield. In the final step, the last compound was treated with gaseous HCl in the presence of catalytic $AlCl_3$ to form the second precursor, $(^tBu_2MeSi)_2GeCl_2$ (**2**), almost quantitatively (Scheme 1).

The final Würtz-type coupling reaction of precursors **1** and **2** with metallic sodium was carried out in toluene at room temperature. A dark red color quickly devel-

oped, the reaction being monitored by GC, which showed the disappearance of starting material **1** after 7–8 h. At this time the reaction mixture was filtered to remove excess sodium and inorganic salts, and the filtrate was evaporated in vacuum. The residue was recrystallized from hexane in a refrigerator at −30 °C to form the target tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene (**3**) as large hexagonal-shaped ruby crystals in 37% yield (Scheme 2). This compound is highly sensitive to atmospheric oxygen and moisture, being quickly decomposed in air even in the solid state.

All NMR spectra of **3** were in complete accord with its symmetrical structure: two sets of signals for both methyl and *tert*-butyl group protons in the ^{1}H-NMR spectrum, and three resonances in the ^{29}Si-NMR spectrum, of which two belong to silyl substituents (18.7 and 25.6 ppm) and the most deshielded one (107.8 ppm) was attributed to sp^2-Si atoms. The mass-spectrum of **3** gave the parent ion peak at $m/z = 758$, together with a strong peak at 601, which corresponds to the elimination of one silyl substituent and formation of the cyclopropenylium ion in the gas phase. The UV
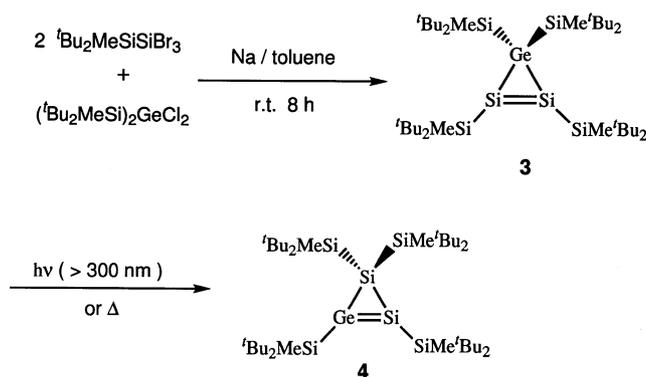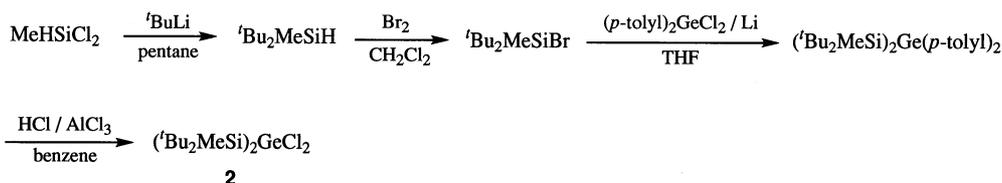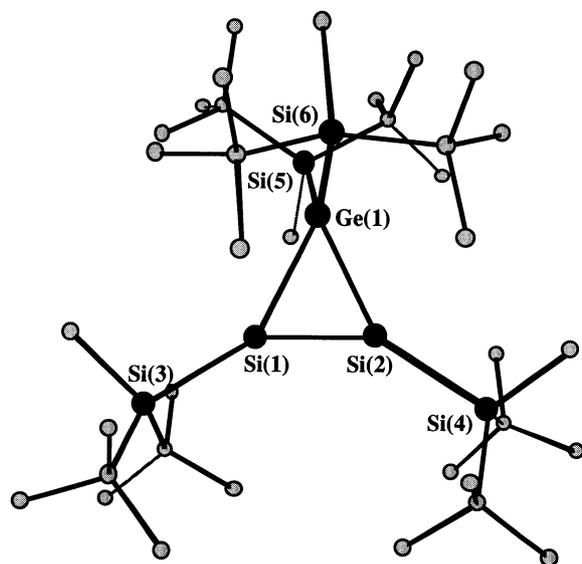

Scheme 2.
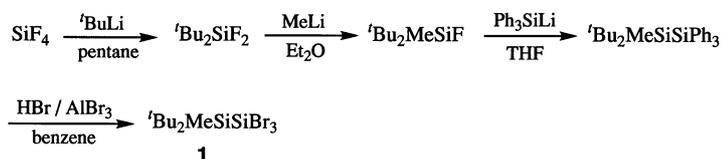
Scheme 1.

Fig. 1. Crystal designer view of **3**. Selected bond lengths (Å): Si(1)–Si(2) = 2.146(1), Ge(1)–Si(1) = 2.415(1), Ge(1)–Si(2) = 2.420(1), Ge(1)–Si(5) = 2.435(1), Ge(1)–Si(6) = 2.432(1), Si(1)–Si(3) = 2.361(1), Si(2)–Si(4) = 2.367 (1). Selected bond angles (°): Ge(1)–Si(1)–Si(2) = 63.76(3), Ge(1)–Si(2)–Si(1) = 63.53(3), Si(1)–Ge(1)–Si(2) = 52.71(3), Si(5)–Ge(1)–Si(6) = 123.33(3). Selected torsion angle (°): Si(3)–Si(1)–Si(2)–Si(4) 37.0(2).

spectrum of **3** showed a long wavelength absorption band at 469 nm, corresponding to the $\pi-\pi^*$ electronic transition due to the Si=Si double bond. The crystal structure of **3** was determined by X-ray diffraction analysis, which showed a triangular skeleton composed of one sp^3-Ge atom and two sp^2-Si atoms (Fig. 1). The endocyclic Si–Ge bond lengths of 2.415 and 2.420 Å are in the normal range for such bonds (2.384–2.457 Å) [9], and they are intermediate between the typical Si–Si and Ge–Ge bond lengths. The most important feature is the Si=Si double bond distance of 2.146(1) Å, which is one of the shortest Si=Si bond lengths reported thus far (2.138–2.289 Å) [10]. The geometry of substituents at the Si=Si double bond has a *trans*-bent character with the bending angle of 37°. This may be the result of the eclipsed conformation of the two silyl substituents on the sp^2-Si atoms, which can repulsively interact with the silyl substituents on the Ge atom, causing the highly pronounced *trans* bending geometry.

As is expected, and similar to the case of other disilenes, the Si=Si double bond in **3** is highly reactive, despite the bulky environment around it. The most significant result is the allylic-type rearrangement of **3** to form an isomeric tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene (**4**), which no longer has a Si=Si double bond, but instead has a Si=Ge double bond. This isomerization may proceed either photochemically or thermally (Scheme 2). Thus, photolysis of the solution of **3** in C_6D_6 with a high-pressure Hg lamp with light of wavelength longer than 300 nm produced **4** nearly

quantitatively, and this isomerization could be easily monitored by either ^{1}H-NMR or UV spectroscopy, which showed the disappearance of starting material **3** and clean formation of **4** in 6–8 h. Alternatively, **3** can be isomerized quantitatively under thermal conditions: heating a solution of **3** in mesitylene at 120 °C for 12 h caused the complete conversion of **3** to **4**. However, the best way to achieve isomerization is the thermolysis of **3** without solvent in a sealed evacuated tube at 215 °C, which is slightly above the melting point of **3** (205–207 °C). Surprisingly, under such drastic conditions isomeric 2-disilagermirene **4** was formed almost quantitatively without formation of any side or decomposition products. Nevertheless, both isomerization conditions (either thermal or photochemical) gave an equilibrium mixture of **4** ($\sim$98–99%) and **3** ($\sim$1–2%), and from this ratio it was estimated that **4** is more stable than **3** by $\sim$3 kcal mol^{-1}. This corresponds well to the results of theoretical calculations on the model H_3Si-substituted disilagermirenes at the B3LYP/DZd level [11], which also showed that 2-disilagermirene is more stable than 1-disilagermirene by $\sim$2.3 kcal mol^{-1}.

The NMR spectral data of **4** are more complicated due to its unsymmetrical structure. In the ^{1}H-NMR spectrum of **4** there are three distinct resonances for the methyl groups and four for the *tert*-butyl groups, whereas in the ^{13}C-NMR spectrum there are three sets of signals for both the methyl and *tert*-butyl groups. The ^{29}Si-NMR spectrum showed a total of five resonances: three belong to silyl substituents, and the other two to skeletal Si atoms: −120.1 ppm for the sp^3-Si atom and +100.7 ppm for the sp^2-Si atom.

The crystal structure of **4** was determined by X-ray diffraction analysis. This showed the expected cyclopropene-type skeleton consisting of one sp^3-hybridized Si atom and two sp^2 hybridized Si and Ge atoms, which form the Si=Ge double bond. Unfortunately, owing to the disorder problem between Si and Ge atoms (nearly 50:50% probability for each position), it was not possible to determine the Si=Ge double bond length, although the geometry of the Si=Ge double bond was found to be *trans*-bent with a bending angle of 40.3°. Calculations on the model H_3Si-substituted 2-disilagermirene at the B3LYP/DZd level gave the length of the Si=Ge double bond as 2.178 Å, almost the same as that of 2.184 Å for $H_2Si=GeH_2$ previously reported by Grev et al. [12].

We have investigated other examples of the reactivity of **3**, first of all 1,2-addition and cycloaddition reactions [8]. 1,2-Addition of a variety of reagents to Si=Si double bonds is well documented [13]. Our case was not exceptional, and 1-disilagermirene **3** easily undergoes addition across the Si=Si double bond, despite the presence of very bulky substituents. This method gave us the unique opportunity for easy and fast access to a number of saturated three-membered ring compounds

of different heavier Group 14 elements. In this paper, we describe the new reactions of 1-disilagermirene **3** with methyl iodide and benzyl alcohol. Reaction of **3** with MeI in benzene solution proceeds very quickly to give the corresponding 1,2-adduct, *trans*-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]-1-iodo-2-methyldisilagermirane (**5**), isolated quantitatively as yellow crystals (Scheme 3). The crystal structure analysis of **5** showed a disilagermirane skeleton with the anticipated *trans* arrangement of methyl group and iodine atom (Fig. 2). The reaction of benzyl alcohol with 1-disilagermirene **3** proceeded more slowly and was complete after stirring overnight at room temperature in benzene solution (Scheme 3). The structure of the single product **6**, *trans*-1-benzyloxy-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]disilagermirane, isolated as yellow crystals in 70% yield, was determined by NMR and X-ray diffraction analysis, which showed that in this case the reaction also proceeded stereospecifically as *trans* addition across the Si=Si double bond. It is worth mentioning here that earlier mechanistic studies of the reaction of transient disilenes with simple alcohols established the *syn* addition pathway [14]. In the present case the predominant *trans* addition of PhCH₂OH to the Si=Si bond should be definitely ascribed to steric reasons, which favor the formation of the less sterically hindered *trans* isomer [15].

Cycloaddition of unsaturated compounds and 1-disilagermirene **3** provides effective access to bicyclic fused compounds having a disilagermirane fragment. We have previously reported reactions of **3** with carbonyl compounds (such as PhCHO), which proceed as the expected [2+2] cycloadditions stereospecifically to form bicyclic compounds as a single stereoisomer [16]. We have observed another reaction mode in the case of enolizable carbonyl compounds having α-hydrogen atoms [17]. Thus, acetophenone smoothly reacts with **3** in benzene solution at room temperature to form
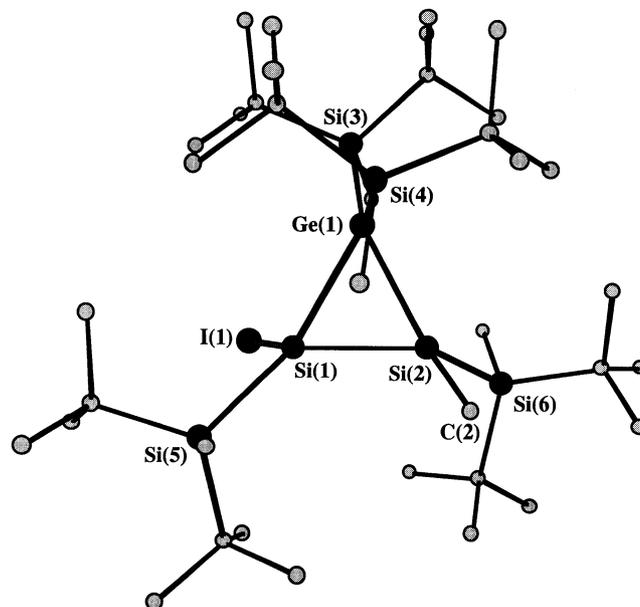

Fig. 2. Crystal designer view of **5**. Selected bond lengths (Å): Si(1)–Si(2) = 2.3696(13), Ge(1)–Si(1) = 2.4749(10), Ge(1)–Si(2) = 2.4762(10), Si(1)–Si(5) = 2.4239(14), Si(2)–Si(6) = 2.4220(14), Ge(1)–Si(3) = 2.4713(11), Ge(1)–Si(4) = 2.4813(11), I(1)–Si(1) = 2.5198(10). Selected bond angles (°): Si(1)–Ge(1)–Si(2) = 57.19(3), Si(2)–Si(1)–Ge(1) = 61.43(3), Si(1)–Si(2)–Ge(1) = 61.38(3).

stereospecifically the *cis*-1,2-adduct **7**, *cis*-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]-1-(1-phenylvinyloxy)disilagermirane, which was identified by NMR spectroscopy (Scheme 4). This product is the result of 1,2-addition of 1-phenylvinyl alcohol (the enol form of acetophenone) to the Si=Si double bond. As can be seen, such *cis* addition is consistent with the aforementioned *syn* addition of simple alcohols to transient disilenes [14]. Nevertheless, the *cis* isomer is not stable under the reaction conditions, and gradually isomerized in a benzene solution during 2 days at room temperature to the thermodynamically more stable *trans* isomer **7**, which was isolated as pale yellow crystals (Scheme 4).
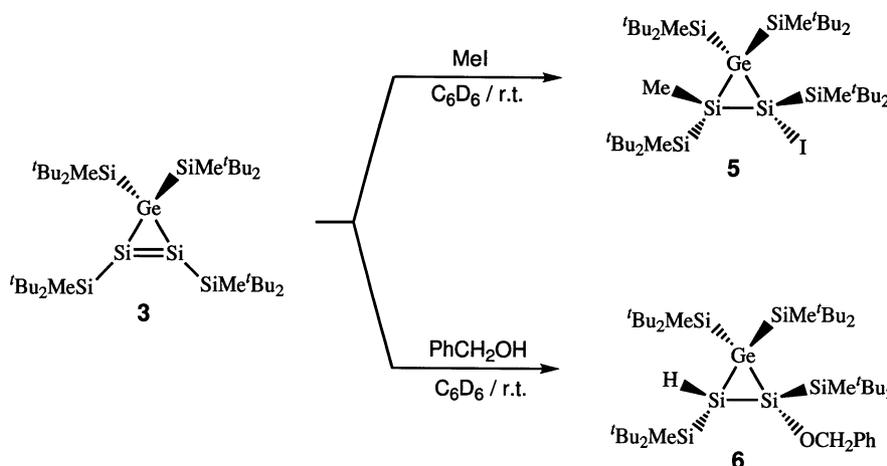
Scheme 3.
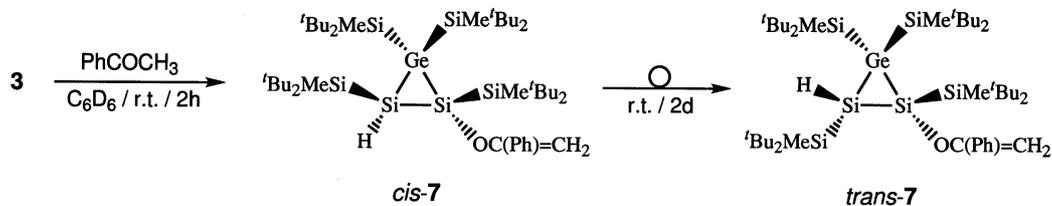
Scheme 4.

The reason for such an isomerization seems to be a decrease in steric hindrance on going from *cis* to *trans* isomers. As can be seen, similar to the case of the reaction of **3** with benzyl alcohol, the final formation of the *trans* isomer is always favorable. The structure of *trans*-**7** was determined by means of all spectral data and X-ray analysis (Fig. 3), which showed the disilagermirane skeleton with the *trans* arrangement of H and $H_2C=C(Ph)O$ substituents. Thus, the reaction of **3** with acetophenone represents a new reaction mode for the interaction of disilenes with carbonyl compounds: an 'ene'-type reaction resulting in the formation of the corresponding enol ether products instead of the only previously known and commonly recognized [2+2] cycloaddition pathway [13a–d].

3. Experimental

3.1. General procedures

All experiments were performed using high-vacuum line techniques or in an argon atmosphere of MBRAUN
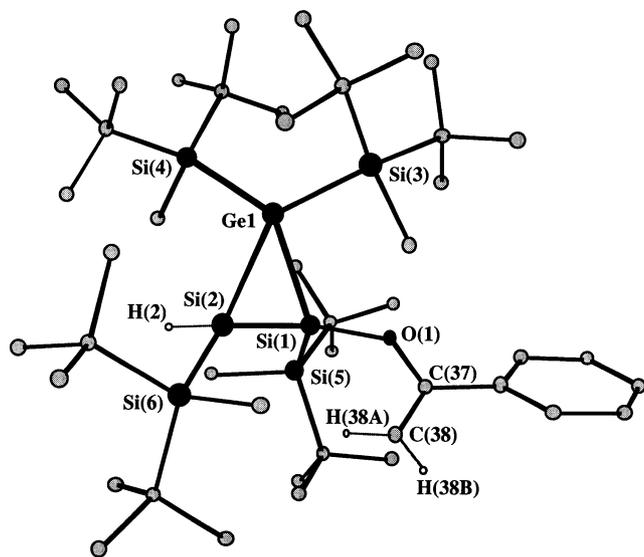

Fig. 3. Crystal designer view of *trans*-**7**. Selected bond lengths (Å): Si(1)–Si(2) = 2.3383(6), Ge(1)–Si(1) = 2.4901(5), Ge(1)–Si(2) = 2.4524(5), Ge(1)–Si(3) = 2.4612(5), Ge(1)–Si(4) = 2.4586(5), Si(1)–Si(5) = 2.3978(6), Si(2)–Si(6) = 2.3944(6), Si(1)–O(1) = 1.6929(12). Selected bond angles (°): Si(2)–Ge(1)–Si(1) = 56.467(14), Si(2)–Si(1)–Ge(1) = 60.951(15), Si(1)–Si(2)–Ge(1) = 62.582(16).

MB 150B-G glove-box. All solvents were predried over sodium benzophenone ketyl and finally dried and degassed over potassium mirror in vacuum prior to use. NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (^{1}H-NMR at 300.13 MHz; ^{13}C-NMR at 75.47 MHz; ^{29}Si-NMR at 59.63 MHz). GC–MS spectra were obtained using Shimadzu GCMS-QP5000 instrument and direct mass-spectra were obtained on JEOL JMS SX-102 instrument. UV-spectra were recorded on a Shimadzu UV-3150 UV–Vis spectrophotometer in hexane. Elemental analysis was performed at the Analytical Center of Tohoku University (Sendai, Japan).

(p-Tolyl)$_2$GeCl$_2$ was synthesized by the reaction of (p-tolyl)MgCl (prepared from p-CH$_3$C$_6$H$_4$Cl and Mg in THF) and GeCl$_4$ in THF by the slightly modified experimental procedure [18]. ^{t}Bu$_2$SiF$_2$ was prepared by the reaction of SiF$_4$ with ^{t}BuLi in pentane according to Ref. [19], ^{t}Bu$_2$MeSiF by the methylation of ^{t}Bu$_2$SiF$_2$ with MeLi in Et$_2$O, ^{t}Bu$_2$MeSiH by the reaction of MeSiHCl$_2$ with ^{t}BuLi according to Ref. [20], and ^{t}Bu$_2$MeSiBr by the bromination of ^{t}Bu$_2$MeSiH with Br$_2$ in CH$_2$Cl$_2$ according to Ref. [21].

3.2. Synthesis of ^{t}Bu$_2$MeSiSiPh$_3$

A solution of Ph$_3$SiCl (40 g, 0.13 mol) in THF (80 ml) was slowly added at room temperature to a suspension of Li (9.5 g, 1.36 mol) in THF (240 ml) and reaction mixture was stirred overnight at room temperature. The resulting Ph$_3$SiLi was added dropwise to the solution of ^{t}Bu$_2$SiMeF (24 g, 0.14 mol) in THF (150 ml). The reaction was complete in 2 days refluxing and after usual work-up, Kugelrohr distillation gave 47 g (83%) of ^{t}Bu$_2$MeSiSiPh$_3$. B.p. 170–175 °C/0.2 mmHg; ^{1}H-NMR (C$_6$D$_6$) δ 0.44 (s, 3H, Me), 1.00 (s, 18H, ^{t}Bu), 7.14–7.16 and 7.77–7.80 (m, 15H, Ph); ^{13}C-NMR (C$_6$D$_6$) δ −4.7, 21.6, 30.2, 128.1, 129.1, 137.3, 137.6; ^{29}Si-NMR (C$_6$D$_6$) δ −20.1, 1.2; GC–MS (m/z) 416 [M$^+$], 359 (M$^+$ −^{t}Bu).

3.3. Synthesis of ^{t}Bu$_2$MeSiSiBr$_3$ (**1**)

Gaseous HBr was slowly bubbled at room temperature into the solution of ^{t}Bu$_2$MeSiSiPh$_3$ (9.5 g, 22.9 mmol) in benzene (40 ml) containing catalytic amount of AlBr$_3$. After the reaction was complete (2 h), the

solvent was evaporated and the residue was distilled by Kugelrohr distillation to give 8.9 g (92%) of $^tBu_2MeSi\text{-}SiBr_3$ (**1**) as colorless solids. B.p. 80–110 °C/0.2 mmHg; ^{1}H-NMR (C_6D_6) δ 0.11 (s, 3H, Me), 1.06 (s, 18H, ^tBu); ^{13}C-NMR (C_6D_6) δ -8.2, 22.0, 29.3; ^{29}Si-NMR (C_6D_6) δ -7.5, 10.3; GC–MS (m/z): 371 (M$^+$ $-^tBu$).

3.4. Synthesis of $(^tBu_2MeSi)_2Ge(p\text{-}tolyl)_2$

A mixture of $^tBu_2SiMeBr$ (3.02 g, 12.7 mmol) and $(p\text{-}tolyl)_2GeCl_2$ (1.4 g, 4.3 mmol) in THF (15 ml) was slowly added at -10 °C to a suspension of Li (0.18 g, 25.7 mmol) in THF (50 ml). After stirring overnight at room temperature an additional amount of $^tBu_2SiMeBr$ (2.03 g, 8.6 mmol) in THF (7 ml) was added and the reaction mixture was refluxed for 1 day. After usual work-up, Kugelrohr distillation gave 1.52 g (62%) of $(^tBu_2MeSi)_2Ge(p\text{-}tolyl)_2$ as a colorless glass solidifying upon standing. B.p. 200–220 °C/0.2 mmHg, m.p. 129–131 °C; ^{1}H-NMR (C_6D_6) δ 0.60 (s, 6H, Me), 1.01 (s, 36H, ^tBu), 2.11 (s, 6H, $Me\text{-}C_6H_4$), 7.06 (d, $J = 7.9$ Hz, 4H, H_{arom}) and 7.99 (d, $J = 7.9$ Hz, 4H, H_{arom}); ^{13}C-NMR (C_6D_6) δ -2.4, 21.4, 23.7, 30.7, 128.8, 137.4, 137.9, 138.4; ^{29}Si-NMR (C_6D_6) δ 14.5; MS (m/z): 413 (M$^+$ $-SiMe^tBu_2$).

3.5. Synthesis of $(^tBu_2MeSi)_2GeCl_2$ (**2**)

Gaseous HCl was bubbled into a solution of $(^tBu_2MeSi)_2Ge(p\text{-}tolyl)_2$ (0.5 g, 0.88 mmol) in benzene (10 ml), containing catalytic amount of AlCl$_3$, at room temperature. In 2.5 h the reaction was complete. Benzene was evaporated and the residue was extracted with dry hexane and filtered through Celite. After evaporation of filtrate practically pure product $(^tBu_2MeSi)_2GeCl_2$ (**2**) was obtained in nearly quantitative yield. ^{1}H-NMR (C_6D_6) δ 0.31 (s, 6H, Me), 1.17 (s, 36H, ^tBu); ^{13}C-NMR (C_6D_6) δ -6.1, 23.3, 29.7; ^{29}Si-NMR (C_6D_6) δ 26.0. MS (m/z): 458 [M$^+$], 423 (M$^+$ $-Cl$), 266 [($^tBu_2MeSi)GeCl$].

3.6. Synthesis of 1,2,3,3-tetrakis[di-tert-butyl(methyl)silyl]-1-disilagermirene (**3**)

A mixture of $^tBu_2MeSiSiBr_3$ (7.85 g, 18.5 mmol) and $(^tBu_2MeSi)_2GeCl_2$ (3.90 g, 8.5 mmol) in dry toluene (50 ml) was slowly added dropwise to a finely cutted pieces of sodium (4.3 g, 187 mmol) in dry toluene (50 ml) at room temperature. During the addition the exothermic reaction took place and the reaction mixture became dark-red. The reaction progress was monitored by GC-analysis, which showed disappearance of the starting $^tBu_2MeSiSiBr_3$ in 7 h stirring at room temperature. At that time the reaction was stopped and the reaction mixture was filtered off from the excess of sodium and inorganic salts through Celite. After evaporation of

solvent in vacuum the residue was recrystallized from hexane at -30 °C to give **3** as dark-ruby hexagonal-shaped crystals (2.36 g, 37% yield). M.p. 205–207 °C; ^{1}H-NMR (C_6D_6) δ 0.46 (s, 6H, Me), 0.49 (s, 6H, Me), 1.22 (s, 36H, ^tBu), 1.28 (s, 36H, ^tBu); ^{13}C-NMR (C_6D_6) δ -4.5, -2.2, 22.2, 23.6, 30.0, 31.0; ^{29}Si-NMR (C_6D_6) δ 18.7, 25.6, 107.8 (Si=Si); MS (m/z) 758 (M$^+$, 0.1), 701 (M$^+$ $-^tBu$, 0.05), 601 (M$^+$ $-SiMe^tBu_2$, 2.6), 73 (100); UV (hexane) λ_{max} nm^{-1} (ε) 230 (33 400), 259 (18 200), 308 (6300), 469 (1900). Anal. Found: C, 57.42; H, 10.75. Calc. for $C_{36}H_{84}GeSi_6$: C, 57.03; H, 11.17%.

3.7. Synthesis of 1,1,2,3-tetrakis[di-tert-butyl(methyl)silyl]-2-disilagermirene (**4**)

1-Disilagermirene **3** (50 mg, 0.07 mmol) was heated at 215 °C for 30 min in a sealed evacuated tube to form quantitatively 2-disilagermirene **4** as a pure compound. M.p. 194–196 °C; ^{1}H-NMR (C_6D_6) δ 0.43 (s, 6H, 2Me), 0.48 (s, 3H, Me), 0.53 (s, 3H, Me), 1.20 (s, 18H, ^tBu), 1.22 (s, 18H, ^tBu), 1.29 (s, 18H, ^tBu), 1.30 (s, 18H, ^tBu); ^{13}C-NMR (C_6D_6) δ -4.6, -3.9, -2.2, 22.2, 22.8, 23.4, 29.9, 30.0, 31.3; ^{29}Si-NMR (C_6D_6) δ -120.1, 6.9, 27.8, 39.5, 100.7; MS (m/z) 758 (M$^+$, 3), 701 (M$^+$ $-^tBu$, 1.5), 601 (M$^+$ $-SiMe^tBu_2$, 32), 73 (100); UV (hexane) λ_{max} nm^{-1} (ε) 235 (58 100), 263 (27 000), 301 (11 600), 395 (1600), 467 (4200). Anal. Found: C, 56.53; H, 10.84. Calc. for $C_{36}H_{84}GeSi_6$: C, 57.03; H, 11.17%.

3.8. Reaction of 1,2,3,3-tetrakis[di-tert-butyl(methyl)silyl]-1-disilagermirene (**3**) with methyl iodide

Dry methyl iodide (0.2 ml, 50-fold excess) was vacuum transferred to a solution of **3** (48 mg, 0.06 mmol) in dry deuterobenzene (0.5 ml) in NMR tube, and then NMR tube was sealed under vacuum. The reaction progress was monitored by NMR spectroscopy, which showed that the reaction was complete in 1 h at room temperature to form a single product **5**. This product was quantitatively isolated as bright-yellow crystals after evaporation of solvent and excess methyl iodide. M.p. 189–191 °C; ^{1}H-NMR (C_6D_6) δ 0.29 (s, 3H, Me), 0.34 (s, 3H, Me), 0.47 (s, 3H, Me), 0.75 (s, 3H, Me), 0.92 (s, 3H, Me), 1.21 (s, 18H, 2^tBu), 1.25 (s, 9H, ^tBu), 1.27 (s, 9H, ^tBu), 1.32 (s, 9H, ^tBu), 1.34 (s, 9H, ^tBu), 1.37 (s, 9H, ^tBu), 1.40 (s, 9H, ^tBu); ^{13}C-NMR (C_6D_6) δ -2.8, -2.0, 3.1, 3.2, 5.8, 23.1, 23.2, 23.36, 23.44, 23.7, 23.9, 24.0, 24.3, 30.6, 30.76, 30.83, 30.9, 31.1, 31.3, 31.5, 32.5; ^{29}Si-NMR (C_6D_6) δ -92.2, -80.3, 13.7, 16.3, 32.9, 35.9.

3.9. Reaction of 1,2,3,3-tetrakis[di-tert-butyl(methyl)silyl]-1-disilagermirene (3) with benzyl alcohol

Dry benzyl alcohol (9 mg, 0.08 mmol) and **3** (56 mg, 0.07 mmol) were placed in a glove-box to the glass tube with a magnetic stirring bar, then dry deuterobenzene (0.6 ml) was vacuum-transferred into this tube and tube was sealed under vacuum. After 1 day stirring at room temperature the reaction was complete to form nearly quantitatively one product **6**. This product was isolated after evaporation of solvent by the recrystallization from hexane as yellow crystals (45 mg, 70%). M.p. 79–81 °C; ^{1}H-NMR (C_6D_6) δ 0.31 (s, 3H, Me), 0.33 (s, 3H, Me), 0.35 (s, 3H, Me), 0.46 (s, 3H, Me), 1.20 (s, 9H, ^{t}Bu), 1.24 (s, 9H, ^{t}Bu), 1.27 (s, 18H, 2^{t}Bu), 1.28 (s, 18H, 2^{t}Bu), 1.30 (s, 9H, ^{t}Bu), 1.35 (s, 9H, ^{t}Bu), 2.90 (s, 1H, Si–H), 4.74 (d, $J = 13.0$ Hz, 1H, PhCH_2O), 5.09 (d, $J = 13.0$ Hz, 1H, PhCH_2O), 7.07 (t, $J = 7.7$ Hz, 1H, H_{para}), 7.21 (t, $J = 7.7$ Hz, 2H, H_{meta}), 7.46 (d, $J = 7.7$ Hz, 2H, H_{ortho}); ^{13}C-NMR (C_6D_6) δ −4.6, −4.3, −0.6, 0.1, 22.0, 22.4, 22.6, 22.7, 22.9, 23.0, 23.3, 24.7, 30.4 (2C), 30.5, 30.7, 30.9, 31.2 (2C), 31.8, 73.0 (PhCH_2O), 126.7, 127.4, 128.5, 141.0; ^{29}Si-NMR (C_6D_6) δ −148.9 (Si–H), −7.4 (Si–OCH$_2$Ph), 15.3, 20.8, 28.6, 32.1; MS (m/z) 866 (M$^+$, 0.2%), 775 (M$^+$ −CH$_2$Ph, 1%), 617 (M$^+$ − SiMe^{t}Bu$_2$−PhCH$_3$, 3.5%), 91 (PhCH$_2$, 100%).

3.10. Reaction of 1,2,3,3-tetrakis[di-tert-butyl(methyl)silyl]-1-disilagermirene (3) with acetophenone

Dry acetophenone (20.6 mg, 0.17 mmol) was vacuum transferred to a solution of **3** (110 mg, 0.15 mmol) in dry deuterobenzene (0.7 ml) in NMR tube, and then NMR tube was sealed under vacuum. The reaction progress was monitored by NMR spectroscopy. In 2 h at room temperature the reaction was complete and exclusively one product (*cis*-adduct) **7** was detected. NMR spectra of *cis*-isomer in the reaction mixture: ^{1}H-NMR (C_6D_6) δ 0.28 (s, 3H, Me), 0.29 (s, 3H, Me), 0.36 (s, 3H, Me), 0.45 (s, 3H, Me), 1.16 (s, 9H, ^{t}Bu), 1.18 (s, 9H, ^{t}Bu), 1.20 (s, 9H, ^{t}Bu), 1.24 (s, 9H, ^{t}Bu), 1.26 (s, 9H, ^{t}Bu), 1.29 (s, 18H, 2^{t}Bu), 1.34 (s, 9H, ^{t}Bu), 3.44 (s, 1H, Si–H), 5.07 (unresolved doublet, 1H, C=CH_2), 5.14 (unresolved doublet, 1H, C=CH_2), 7.03–7.15 (m, 3H, H_{para}+H_{meta}), 7.65 (d, $J = 7.6$ Hz, 2H, H_{ortho}); ^{13}C-NMR (C_6D_6) δ −3.9, −3.6, −1.9, 1.4, 22.25, 22.32, 22.4, 22.66, 22.69, 23.0, 23.5, 23.8, 30.2, 30.5, 30.7, 30.8, 31.0, 31.1, 31.3, 32.0, 94.1 (C=CH$_2$), 126.7, 128.2, 128.5, 138.8, 157.3 (C=CH$_2$); ^{29}Si-NMR (C_6D_6) δ −145.6 (Si–H), −19.0 (Si–O), 19.2, 24.1, 29.3, 31.5.

cis-Isomer **7** gradually isomerized to a *trans*-isomer **7**; in 1 day at room temperature the ratio *cis*-isomer:*trans*-isomer = 50:50%, in 2 days at room temperature only *trans*-isomer **7** was detected by NMR spectroscopy. This *trans*-isomer was quantitatively isolated by the recrystallization from hexane as pale-yellow crystals. M.p. 179–181 °C; ^{1}H-NMR (C_6D_6) δ 0.23 (s, 3H, Me), 0.39 (s, 3H, Me), 0.41 (s, 3H, Me), 0.47 (s, 3H, Me), 1.22 (s, 9H, ^{t}Bu), 1.23 (s, 9H, ^{t}Bu), 1.26 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 1.30 (s, 9H, ^{t}Bu), 1.31 (s, 18H, 2^{t}Bu), 3.01 (s, 1H, Si–H), 5.07 (d, $J = 1.6$ Hz, 1H, C=CH_2), 5.14 (d, $J = 1.6$ Hz, 1H, C=CH_2), 7.06 (t, $J = 7.2$ Hz, 1H, H_{para}), 7.19 (t, $J = 7.2$ Hz, 2H, H_{meta}), 7.69 (d, $J = 7.2$ Hz, 2H, H_{ortho}); ^{13}C-NMR (C_6D_6) δ −4.24, −4.21, −0.2, 0.1, 22.3 (2C), 22.5 (2C), 22.7, 23.1, 23.5, 25.0, 30.4, 30.5, 30.6, 30.7, 31.1, 31.3, 31.5, 32.0, 94.1 (C=CH$_2$), 126.8, 128.3, 128.6, 138.5, 159.3 (C=CH$_2$); ^{29}Si-NMR (C_6D_6) δ −142.2 (Si–H), −17.6 (Si–O), 17.2, 23.0, 28.8, 32.4; MS (m/z) 878 (M$^+$, 11%), 758 (M$^+$ −CH$_3$COPh, 5%). Anal. Found: C, 60.50; H, 10.45. Calc. for $C_{44}H_{92}GeOSi_6$: C, 60.17; H, 10.56%.

3.11. Crystal structure analyses of the compounds 3, 5, and trans-7

The single crystals of compounds **3** and *trans*-**7** for X-ray diffraction study were grown from the saturated hexane solutions, single crystals of compound **5** were grown from the saturated benzene solution. Diffraction data were collected at 150 K for **3**, 120 K for **5** and *trans*-**7** 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 [22], and refined by the full-matrix least-squares method by SHELXL-97 program [23]. The crystal data and experimental parameters for the X-ray analysis of **3**, **5**, and *trans*-**7** are listed in Table 1. Crystallographic data of **3** have been deposited with the American Chemical Society (see Ref. [7]). This material is available free of charge via the Internet at http://www.pubs.acs.org. Crystallographic data of *trans*-**7** have been deposited with the Cambridge Crystallographic Data Centre. CCDC No. 170581. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystallographic data and experimental parameters for the crystal structure analysis of **3,5**, and *trans*-**7**

	3	**5**	*trans*-**7**
Empirical formula	$C_{36}H_{84}GeSi_6$	$C_{37}H_{87}GeISi_6$	$C_{44}H_{92}GeOSi_6$
Formula mass (g mol^{-1})	758.16	987.20	878.31
Collection temperature (K)	150	120	120
λ (Mo$-K_\alpha$) (Å)	0.71070	0.71070	0.71070
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell parameters			
a (Å)	24.131(1)	13.0950(4)	11.0980(2)
b (Å)	11.6630(6)	20.2620(6)	20.9340(5)
c (Å)	17.760(1)	20.1520(3)	22.8640(6)
α (°)	90	90	90
β (°)	110.362(4)	93.974(2)	96.8960(10)
γ (°)	90	90	90
V (Å^3)	4686.0(5)	5334.1(2)	5273.5(2)
Z	4	4	4
D_{calc} (g cm^{-3})	1.075	1.218	1.106
μ (mm^{-1})	0.829	1.314	0.746
$F(0\,0\,0)$	1664	2080	1920
Crystal dimensions (mm)	$0.4 \times 0.3 \times 0.3$	$0.2 \times 0.2 \times 0.2$	$0.4 \times 0.3 \times 0.3$
θ Range (°)	2.29–27.93	2.06–27.89	2.09–27.93
Index ranges	$0 \le h \le 31$	$0 \le h \le 17$	$0 \le h \le 13$
	$0 \le k \le 15$	$0 \le k \le 26$	$0 \le k \le 27$
	$-23 \le l \le 21$	$-26 \le l \le 26$	$-30 \le l \le 29$
Collected reflections	46 096	53 594	52 312
Independent reflections	10 779	12 709	11 951
R_{int}	0.101	0.0520	0.0290
Reflections used	10 779	12 709	11 951
Parameters	389	467	471
S [a]	1.044	1.068	1.028
Weight parameters a/b [b]	0.0907/4.6977	0.0860/25.1640	0.0547/2.7170
R_1 [c] $[I > 2\sigma(I)]$	0.0589	0.0630	0.0348
wR_2 [d] (all data)	0.1691	0.1763	0.0953
Maximum/minimum residual electron density (e Å^{-3})	1.278/-0.987	2.121/-2.359	0.405/-0.794

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

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

[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

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