# Heavy cyclopropene analogues $R_4SiGe_2$ and $R_4Ge_3$ ($R = SiMe^tBu_2$) – New members of the cyclic digermenes family

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## Abstract

1$H$-Siladigermirene $R_4SiGe_2$ (**2a**) and 1$H$-trigermirene $R_4Ge_3$ (**2b**) ($R = SiMe^tBu_2$) with a Ge=Ge double bond were synthesized by the reaction of tetrachlorodigermane $RGeCl_2$–$GeCl_2R$ with dilithiosilane $R_2SiLi_2$ and dilithiogermane $R_2GeLi_2$, respectively. The skeletal Ge=Ge double bond of **2a** is *trans*-bent (51.0(2)°) with a bond distance of 2.2429(6) Å. The reaction of both **2a** and **2b** with $CH_2Cl_2$ resulted in the formation of unusual four-membered ring compounds **5a** and **5b** as a result of a ring expansion reaction. 1$H$-Trisilirene **7a** and 3$H$-disilagermirene **7b** with an Si=Si double bond also smoothly reacted with $CH_2Cl_2$ to yield the four-membered ring systems **8a** and **8b**, respectively.
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## 1. Introduction

The research area of the cyclopropene analogs of heavier group 14 elements of the type $cyclo$-[$R_2E'$–$E(R)$=$E(R)$] ($E$, $E' = $ Si, Ge, Sn; R = bulky silyl substituent) is becoming an increasingly attractive field of modern organometallic chemistry [1]. The major accomplishments in such chemistry have been made by the research groups of Sekiguchi, Kira, and Wiberg, who have reported the synthesis of heavy cyclopropenes of Si, Ge, and Sn atoms [2]: trigermirenes $Ge_3$ [2a–c], trisilirenes $Si_3$ [2d–g], and tristannirene $Sn_3$ [2h].

In 2000, we prepared the first hybrid compounds containing two *different* group 14 elements, 3$H$- and 1$H$-disilagermirenes $GeSi_2$ [3a], and studied their particularly attractive chemistry, a result of the favorable combination of high ring strain and exceeding reactivity of the endocyclic E=E bond, which opened new unprecedented possibilities for the synthesis of a number of novel cyclic and polycyclic organometallics [3b–k]. The recent fast progress in the field enabled us to claim the constitution of this new class of organometallic compounds, *heavy cyclopropenes*, in our preceding contribution [4]. However, until now no other representatives of heteronuclear heavy cyclopropenes (except for the above-mentioned 3$H$- and 1$H$-disilagermirenes $GeSi_2$ [3a]) have been synthesized, although these compounds are expected to possess unusual promising properties.

In this paper, we present the synthesis, full structural characterization, and unexpected reactivity of new representatives of the heavy cyclopropenes family, heteronuclear 1$H$-siladigermirene $SiGe_2$ and homonuclear trigermirene $Ge_3$, both featuring endocyclic Ge=Ge double bonds [5].

## 2. Results and discussion

Our first attempts to synthesize the new hybrid 1$H$-siladigermirene derivative $R_4SiGe_2$ ($R = SiMe^tBu_2$) by the identical synthetic procedure to that of the previously reported 3$H$-disilagermirene $R_4GeSi_2$ [3a] were unsuccessful, because it required the preparation of $^tBu_2MeSi$–

$GeX_3$ (X = Cl, Br) as one of the key starting materials (Scheme 1). We found that compounds of this type, $^tBu_2$-MeSi–$GeX_3$, are highly thermally unstable, in marked contrast to the stable $^tBu_2MeSi$–$SiBr_3$, because of the higher tendency of the former to undergo α-elimination of $^tBu_2MeSiX$ accompanied by the generation of dihalogermylenes $X_2Ge$: (Scheme 1).

This forced us to develop a new synthetic protocol for the synthesis of the desired 1H-siladigermirene derivative, using a 1,1,2,2-tetrahalodigermane unit as a starting building block for the subsequent design of the endocyclic Ge=Ge moiety. As such, $^tBu_2MeSi$–$GeCl_2$–$GeCl_2$–$SiMe^tBu_2$ (1a) was selected as the best candidate. The synthesis of 1a commenced from the preparation of (p-tolyl)$_3$GeCl (50%), which was converted to (p-tolyl)$_3$-GeH (80%) followed by its lithiation and coupling with $^tBu_2MeSiBr$ to form $^tBu_2MeSi$–Ge(p-tolyl)$_3$ (75%) (Scheme 2). The reaction of $^tBu_2MeSi$–Ge(p-tolyl)$_3$ and an equivalent amount of $CF_3SO_3H$ followed by subsequent treatment with $NH_4Cl$ produced $^tBu_2MeSi$–Ge(p-tolyl)$_2Cl$ (84%), which was reacted with Li resulting in the formation of the tetraaryldigermane derivative $^tBu_2MeSi$–Ge

(p-tolyl)$_2$–Ge(p-tolyl)$_2$–SiMe$^tBu_2$ (67%). The final dearylation–chlorination of $^tBu_2MeSi$–Ge(p-tolyl)$_2$–Ge(p-tolyl)$_2$–SiMe$^tBu_2$ with HCl/AlCl$_3$ provided the desired starting 1,1,2,2-tetrachlorodigermane 1a in 95% yield (Scheme 2). The corresponding 1,1,2,2-tetrabromodigermane $^tBu_2MeSi$–$GeBr_2$–$GeBr_2$–SiMe$^tBu_2$ (1b) was also synthesized by the bromination of $^tBu_2MeSi$–Ge(p-tolyl)$_2$–Ge(p-tolyl)$_2$–SiMe$^tBu_2$ with HBr/AlBr$_3$, albeit in a lower yield of 52% due to the partial decomposition of 1b at room temperature.

Taking into account the intrinsic inclination of halosilyl-germanes >Ge(X)SiR$_3$ to undergo easy α-elimination of R$_3$SiX to produce germylenes >Ge:, the stability of 1a is surprising. The composition of 1a was reliably established with a complete set of spectral and analytical data, and the crystal structure of 1a was determined by X-ray crystallography (Fig. 1). The Si1–Ge1–Ge1#–Si1# atom chain has the anticipated all-*trans* conformation resulting in a characteristic zigzag shape of the molecule with normal bond distances. One should note that only a couple of examples of R$_3$Si–$GeCl_2$–$GeCl_2$–SiR$_3$ type compounds have been prepared and structurally characterized:
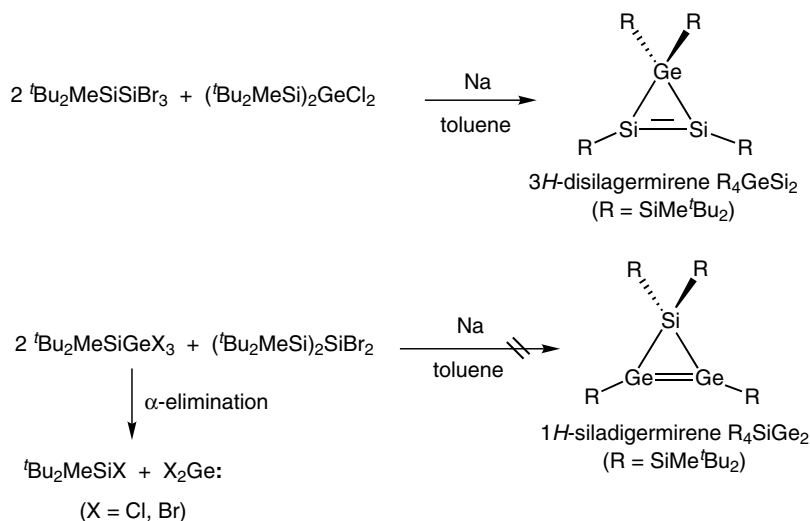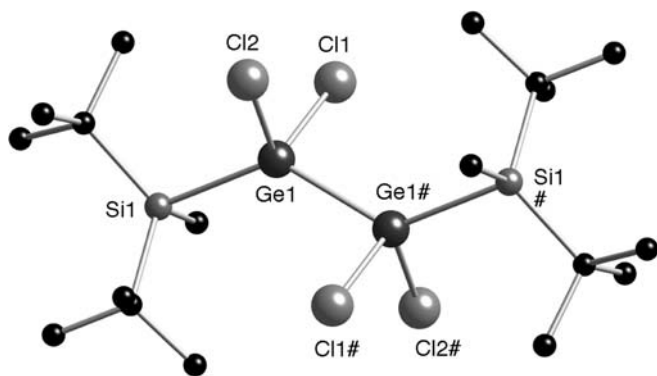


Scheme 1.
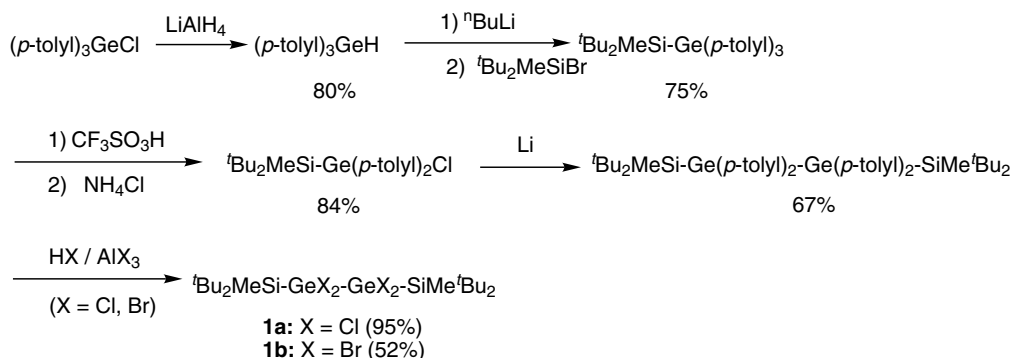


Scheme 2.

Fig. 1. Crystal maker view of **1a** (hydrogen atoms are not shown). Selected bond lengths (Å): Ge1–Ge1# = 2.448(2), Ge1–Cl1 = 2.205(3), Ge1–Cl2 = 2.186(3), Si1–Ge1 = 2.447(3). Selected bond angle (°): Si1–Ge1–Ge1# = 131.94(10).

$(Me_3Si)_3Si–GeCl_2–GeCl_2–Si(SiMe_3)_3$ [6] and $^tBu_3Si–GeCl_2–GeCl_2–Si^tBu_3$ [7]. However, in both these cases the structural refinement suffered from either disorder [6] or co-crystallization with other compounds [7].

The reaction of **1a** with 1,1-dilithiosilane $(^tBu_2MeSi)_2Si-Li_2$ [8] in toluene cleanly resulted in the formation of a couple of products, the desired tetrakis(di-*tert*-butylmethylsilyl)-1*H*-siladigermirene $(^tBu_2MeSi)_4SiGe_2$ (**2a**) (26%) and tetrakis(di-*tert*-butylmethylsilyl)disilene $(^tBu_2MeSi)_2Si=Si-(SiMe^tBu_2)_2$ (**3a**) [9] in a 2:1 ratio (Scheme 3).

Interestingly, among several possible products of this reaction, namely 1,4-disila-2,3-digermabuta-1,3-diene, 2,4-disila-1,3-digermabicyclo[1.1.0]butane, and 1*H*-siladigermirene, only the last compound was formed. The two compounds, dark-red 1*H*-siladigermirene **2a** and deep-blue disilene **3a** [9], were separated by column chromatography (SiO_2, hexane) in a glovebox followed by recrystallization from pentane. The possible reaction pathway might include the initial formation of 2,3-dichlorosiladigermirane (**4a**) followed by the fast Li–Cl exchange reaction between **4a**

and a second molecule of $(^tBu_2MeSi)_2SiLi_2$ [10], leading to formation of **2a** and **3a** in the experimentally observed 2:1 ratio (Scheme 3).

The 1*H*-siladigermirene **2a** is the first representative of hybrid heavy cyclopropenes of SiGe_2 composition featuring a skeletal Ge=Ge double bond; that is, **2a** belongs also to the class of the cyclic digermenes [2a–c,3i]. The NMR spectra of **2a** are rather simple, reflecting its symmetrical structure: only two sets of signals were observed for both Me and $^tBu$ groups in $^1H$ and $^{13}C$ NMR spectra. The $^{29}Si$ NMR spectrum revealed three resonances at −110.6, 5.8, and 40.8 ppm: the most upfield signal at −110.6 ppm was in the reasonable range for an $sp^3$-Si atom in the three-membered ring, whereas the other two signals were attributed to the substituent Si atoms. The large difference in the chemical shifts of substituent Si atoms bound to either skeletal Si (5.8 ppm) or Ge (40.8 ppm) atoms is evidently due to the different hybridization degree of these skeletal atoms: $sp^3$-Si vs. $sp^2$-Ge.

X-ray crystallography of **2a** revealed an isosceles SiGe_2 triangle structure, in complete accord with the symmetrical structure of **2a** in solution (*vide supra*). Both skeletal Ge=Ge (2.2429(6) Å) as well as Si–Ge (2.4168(10) and 2.4165(10) Å) bond lengths are typical for the heavy cyclopropene systems [1] (Fig. 2). As was expected for digermenes [11], the Ge=Ge bond in **2a** is highly *trans*-bent with the Si4–Ge1–Ge2–Si5 torsional angle of 51.0(2)°.

Using dilithiogermane $(^tBu_2MeSi)_2GeLi_2$ [12] instead of 1,1-dilithiosilane $(^tBu_2MeSi)_2SiLi_2$, we synthesized a germanium analogue of **2a**, a novel trigermirene derivative tetrakis(di-*tert*-butylmethylsilyl)-1*H*-trigermirene (**2b**) (22%) by the reaction of $(^tBu_2MeSi)_2GeLi_2$ and **1a** in toluene (Scheme 3). Quite similar to the case of 1*H*-siladigermirene **2a**, the formation of **2b** was accompanied with the production of half an equivalent of digermene $(^tBu_2MeSi)_2-Ge=Ge(SiMe^tBu_2)_2$ (**3b**). Both products were separated employing the same experimental procedure: column chromatography in a glove-box followed by the recrystalli-
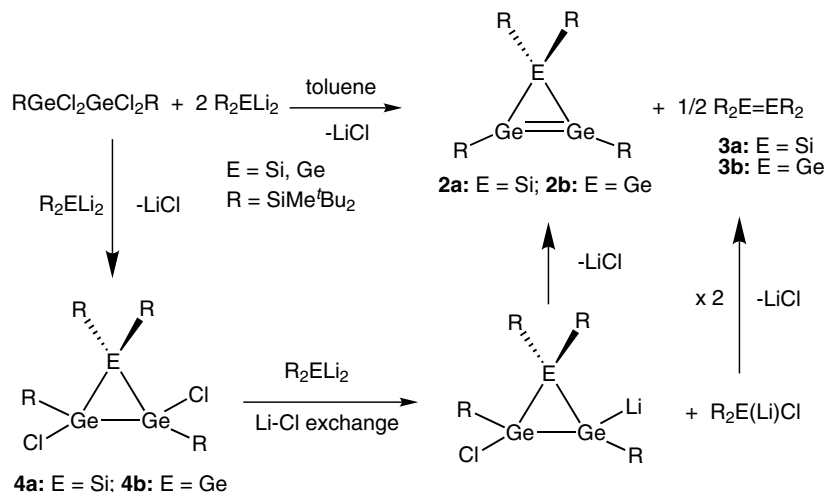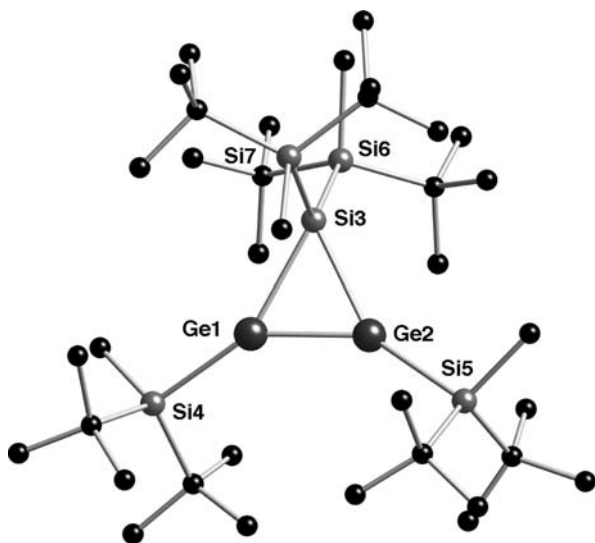


Scheme 3.

Fig. 2. Crystal maker view of **2a** (hydrogen atoms are not shown). Selected bond lengths (Å): Ge1–Ge2 = 2.2429(6), Si3–Ge1 = 2.4168(10), Si3–Ge2 = 2.4165(10), Ge1–Si4 = 2.3995(11), Ge2–Si5 = 2.3943(11), Si3–Si6 = 2.3993(13), Si3–Si7 = 2.4033(13). Selected bond angles (°): Ge2–Ge1–Si3 = 62.34(11), Ge1–Ge2–Si3 = 62.36(3), Ge1–Si3–Ge2 = 55.30(2). Torsional angle (°): Si4–Ge1–Ge2–Si5 = 51.0(2).

zation from pentane to afford dark-red crystals of **2b** and deep-blue crystals of the previously unknown digermene **3b** [13]. The 1H-trigermirene **2b** was completely isostructural to 1H-siladigermirene **2a** crystallizing in the same monoclinic $P2_1/c$ space group with very similar bond distances and bond angles [14]. However, the degree of trans-bending of Ge=Ge double bond in **2b** is more pronounced than that in **2a**: 60.5(2)° vs. 51.0(2)°. From this structural viewpoint, the comparison of both **2a** and **2b** with 1H-trisilirene (tBu2MeSi)4Si3 (**7a**) [2e] and 3H-disilagermirene (tBu2MeSi)4GeSi2 (**7b**) [3a] (both previously synthesized by us) is particularly instructive, because all these compounds have the same substituents, distinguish-

ing from each other only by the skeletal atoms (Si or Ge, or their combinations) (Fig. 3).

Comparing the structures of **2a** and **7a** (or **2b** and **7b**), one can easily recognize that the Ge=Ge bond is more trans-bent than the Si=Si bond in both cases: 51.0(2)° vs. 31.9(2)° (or 60.5(2)° vs. 37.0(2)°), which is quite normal because of the well-known tendency for increasing trans-bending on descending a group 14 [11]. On the other hand, comparing cyclic digermenes **2a** and **2b** (or cyclic disilenes **7a** and **7b**), another tendency becomes apparent: the trans-bending of the same bond Ge=Ge (or Si=Si) is more pronounced when the sp³-skeletal atom is Ge but not Si. This should be ascribed to the immediate influence of the electronegativity difference of Si and Ge atoms (Ge is more electronegative), because the electronegative substituents R increase the pyramidalization degree of doubly-bonded atoms E (E = heavier group 14 element) in compounds of the type $R_2E = ER_2$ [11]. Thus, 1H-trigermirene **2b** should be recognized as the most highly trans-bent (60.5(2)°) heavy cyclopropene known to date.

Apart from their particular structures, both **2a** and **2b** exhibited an interesting reactivity toward halogenated hydrocarbons, especially $CH_2Cl_2$. Thus, both **2a** and **2b** smoothly reacted with an excess of dry $CH_2Cl_2$ to form unexpected products, trans-2,4-dichloro-1,1,2,4-tetrakis(di-tert-butylmethylsilyl)-1,2,4-siladigermetane (**5a**) and trans-1,3-dichloro-1,2,2,3-tetrakis(di-tert-butylmethylsilyl)-1,2,3-trigermetane (**5b**), respectively, as the result of the ring enlargement reaction (Scheme 4). Both **5a** and **5b** were isolated in 71% and 69% yield and fully characterized by spectral and crystallographic data. The most diagnostic feature of both **5a** and **5b** was the markedly low-field signals of the methylene unit of the four-membered ring: 2.79 and 2.98 ppm (1H NMR spectrum), 42.6 and 44.9 ppm (13C NMR spectrum). Such an observation is in evident contrast to other known cyclobutane derivatives featuring the RR′Si–CH2–SiRR′– fragment, which characteristically exhibit the 1H NMR resonances of methylene
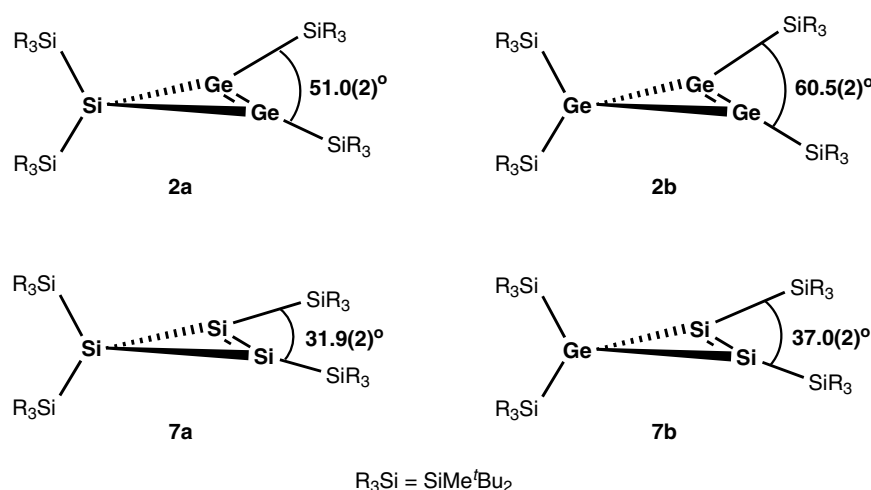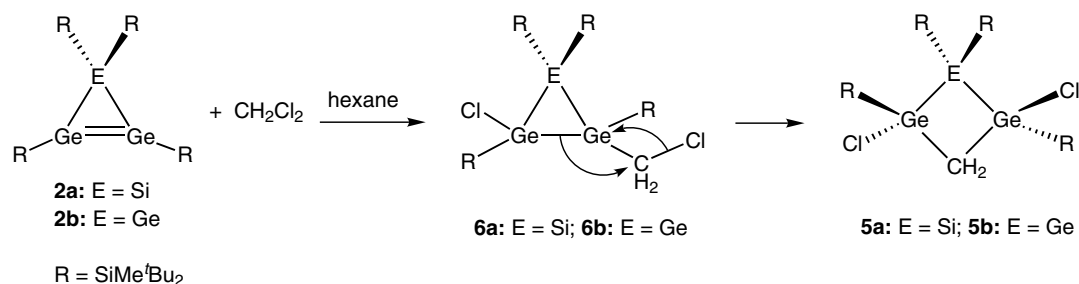


$R_3Si = SiMe^tBu_2$

Fig. 3. Schematic representation of heavy cyclopropene analogs **2a**, **2b**, **7a**, **7b** and torsional angles.

Scheme 4.

protons in the high-field region of 0.18–0.89 ppm [15]. Such a remarkable spectral feature of **5a** and **5b** might be attributed to the hyperconjugative mixing of σ(C–H)–σ*(Ge–Cl) orbitals, definitely resulting in the deshielding of both H and C nuclei of the CH$_2$-moiety.

The crystal structure analysis of **5a** disclosed a folded SiGe$_2$C-four-membered ring (folding angle 33°) with the *trans*-arrangement of the two Cl atoms bound to the skeletal Ge atoms. The skeletal Si–Ge bonds of 2.475(2) and 2.547(3) Å significantly exceeded the normal values of Si–Ge bond distances (2.384–2.462 Å [16]), which was explained by the great steric congestion around the Ge1–Si2–Ge3 fragment of the cyclic skeleton (Fig. 4). The exocyclic Ge–Cl bonds of 2.229(2) and 2.236(2) Å are considerably longer than the typical values of 2.08–2.15 Å [16], a fact that can also be taken as another manifestation of the σ(C–H)–σ*(Ge–Cl) hyperconjugative interaction.

The mechanism for the formation of the four-membered rings **5a** and **5b** starting from the three-membered



Fig. 4. Crystal maker view of **5a** (hydrogen atoms are not shown). Selected bond lengths (Å): Si2–Ge1 = 2.547(3), Si2–Ge3 = 2.475(2), Ge1–C1 = 1.998(10), Ge3–C1 = 1.956(10), Ge1–Cl1 = 2.229(2), Ge3–Cl2 = 2.236(2), Ge1–Si5 = 2.443(3), Ge3–Si8 = 2.490(3), Si2–Si6 = 2.449(4), Si2–Si7 = 2.450(4). Selected bond angles (°): Ge1–Si2–Ge3 = 73.88(6), Si2–Ge3–C1 = 90.0(3), Ge3–C1–Ge1 = 99.5(4), C1–Ge1–Si2 = 87.0(3).

rings **2a** and **2b** is of particular interest. Although we do not have direct spectroscopic evidence for formation of any detectable intermediates, we can suggest the following reaction scheme. The initial 1,2-addition of CH$_2$Cl$_2$ across the Ge=Ge double bond to form the intermediate cyclopropane derivatives **6a**, **6b** can be assumed as the reasonable first step of the reaction. The analogous 1,2-addition of the simple chloroalkanes (CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$) to the stable tetrasilyldisilenes [17a] and transient digermenes [17b,c] has been recently reported. The next step of the reaction is assumed to be a formal intramolecular insertion of the CH$_2$-unit into the skeletal Ge–Ge bond accompanied by the migration of Cl atom from C to Ge. One of the evident driving forces for the ring expansion step should be release of the ring strain on going from a three- to a four-membered ring. Indeed, our calculations at the B3LYP/6-31G(d) level of theory with the GAUSSIAN 98 program package on the model compounds **5a**, **5b** (R = SiH$_3$) revealed that the final four-membered rings **5a** and **5b** are much more stable than the transient three-membered rings **6a** and **6b** by 41.7 and 41.8 kcal/mol, respectively.

We found that the ring expansion reaction with CH$_2$Cl$_2$ is general for *all* heavy cyclopropenes of the type ($^t$Bu$_2$MeSi)$_4$EE$'_2$ (E, E' = Si, Ge). Thus, 1*H*-trisilirene **7a** and 3*H*-disilagermirene **7b** (previously prepared by us) also smoothly reacted with CH$_2$Cl$_2$ to yield the four-membered ring systems **8a** and **8b**, totally isostructural to the above described **5a** and **5b** (Scheme 5). The new compounds **8a** and **8b** were isolated in a pure form and characterized by NMR spectral and X-ray crystallography data.

It should be noted that CH$_2$Cl$_2$ is quite a unique reagent toward **2** and **7** to give the ring enlargement products. Thus, CCl$_4$ reacted with both **2a** and **2b** to produce the corresponding dichlorocyclopropane derivatives, *trans*-2, 3-dichloro-1,1,2,3-tetrakis(di-*tert*-butylmethylsilyl)siladigermirane (**9a**) and *trans*-1,2-dichloro-1,2,3,3-tetrakis(di-*tert*-butylmethylsilyl)trigermirane (**9b**), respectively, instead of the four-membered ring compounds (Scheme 6). That is, carbon tetrachloride in these reactions acts purely as a chlorinating reagent.

The striking difference in the reactivity of CH$_2$Cl$_2$ and CCl$_4$ toward the Ge=Ge double bond of **2a** and **2b** might be caused by the greater steric bulk of the ·CCl$_3$ radical compared with that of the ·CH$_2$Cl radical, which precludes

Scheme 5.



Scheme 6.

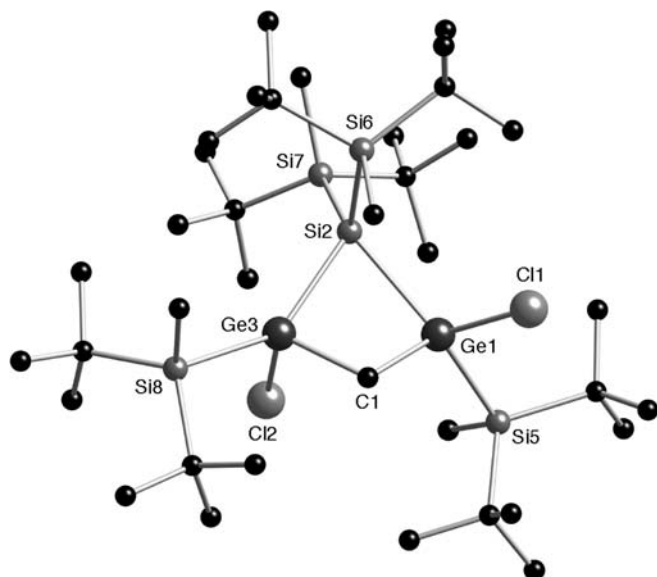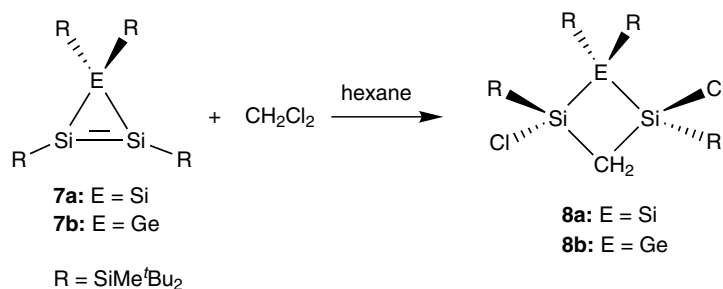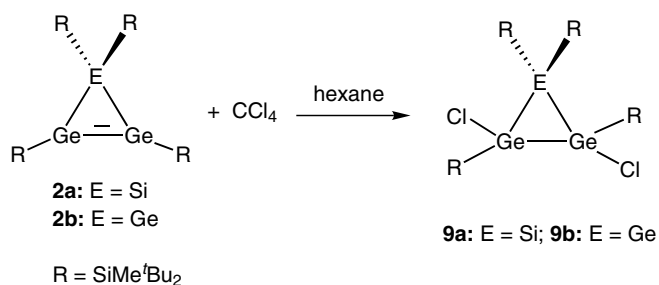the formation of the CCl₃-adduct. The same reaction course was previously observed in the reaction of 1$H$-trisilirene **7a** and 3$H$-disilagermirene **7b** with CCl₄, resulting in the quantitative formation of dichloro derivatives analogous to **9a**, **b** [3c]. The reaction of both **2a** and **2b** with CHCl₃ produced complicated reaction mixtures, probably due to the operation of several competing reaction pathways.

## 3. Experimental

### 3.1. General procedures

All experiments were carried out using high-vacuum line techniques or in an argon atmosphere of MBRAUN MB 150B-G glove box. The solvents were predried over sodium benzophenone ketyl and finally dried and degassed over potassium mirror in vacuum immediately prior to use. NMR spectra were recorded on Bruker AC-300FT NMR ($^1$H NMR at 300.13 MHz; $^{13}$C NMR at 75.47 MHz; $^{29}$Si NMR at 59.63 MHz) and Bruker ARX-400FT NMR ($^1$H NMR at 400.23 MHz; $^{13}$C NMR at 100.64 MHz; $^{29}$Si NMR at 79.52 MHz) spectrometers. MS spectra were measured on Shimadzu GCMS-QP5000 instrument and on JEOL JMS SX-102 instrument. UV-spectra were recorded on Shimadzu UV-3150 UV–Vis spectrophotometer in hexane.

### 3.2. Synthesis of (p-tolyl)₃GeCl

A solution of $p$-tolylMgCl [prepared from $p$-tolylCl (192.0 g, 1.51 mol) and Mg (36.50 g, 1.5 mol) in THF

(700 ml)] was slowly added to the solution of GeCl₄ (105.2 g, 0.49 mol) in THF (600 ml) over a period of 2 h at 0 °C. Then the temperature was raised to room temperature and the reaction mixture was refluxed overnight. THF (600 ml) was distilled off and dry hexane (600 ml) was added. After the usual work-up (filtration, evaporation of solvents) the residue was recrystallized from hexane to give ($p$-tolyl)₃GeCl as a colorless solid (93.8 g, 50%). $^1$H NMR (C₆D₆) δ 2.30 (s, 9H, $Me$–C₆H₄–), 6.99 (d, $^3J$ = 7.5 Hz, 6H, H$_{arom}$), 7.66 (d, $^3J$ = 7.5 Hz, 6H, H$_{arom}$); $^{13}$C NMR (C₆D₆) δ 21.4, 129.7, 132.3, 134.6, 140.6.

### 3.3. Synthesis of (p-tolyl)₃GeH

A solution of ($p$-tolyl)₃GeCl (61.5 g, 0.16 mol) in Et₂O (400 ml) was slowly added to a suspension of LiAlH₄ (6 g, 0.16 mol) in Et₂O (200 ml), and the reaction mixture was refluxed for 4 h. After usual water work-up, ($p$-tolyl)₃GeH was isolated by Kugelrohr distillation as a colorless solid (45.0 g, 80%). $^1$H NMR (C₆D₆) δ 2.09 (s, 9H, $Me$–C₆H₄–), 5.93 (s, 1H, Ge–H), 7.02 (d, $^3J$ = 7.5 Hz, 6H, H$_{arom}$), 7.54 (d, $^3J$ = 7.5 Hz, 6H, H$_{arom}$); $^{13}$C NMR (C₆D₆) δ 21.4, 129.6, 132.8, 135.6, 139.0.

### 3.4. Synthesis of $^t$Bu₂MeSi–Ge(p-tolyl)₃

A 1.6 M solution of $^n$BuLi in hexane (82 ml, 0.13 mol) was slowly added to a solution of ($p$-tolyl)₃GeH (45.0 g, 0.13 mol) in Et₂O (250 ml), and the reaction mixture was stirred for 1 h at room temperature. The resulting solution of ($p$-tolyl)₃GeLi in Et₂O was added dropwise to the solution of $^t$Bu₂MeSiBr (31.4 g, 0.13 mol) in THF (250 ml), and the reaction mixture was stirred overnight at room temperature. After usual water work-up, $^t$Bu₂MeSi–Ge($p$-tolyl)₃ was isolated by Kugelrohr distillation as a colorless solid (52.4 g, 80%). Bp 200–220 °C/0.2 mm Hg, mp 106–107 °C; $^1$H NMR (C₆D₆) δ 0.49 (s, 3H, Me), 1.07 (s, 18H, $^t$Bu), 2.09 (s, 9H, $Me$–C₆H₄–), 7.05 (d, $^3J$ = 7.5 Hz, 6H, H$_{arom}$), 7.74 (d, $^3J$ = 7.5 Hz, 6H, H$_{arom}$); $^{13}$C NMR (C₆D₆) δ 4.69, 21.3, 21.8, 30.0, 129.3, 136.5, 137.6, 137.9; $^{29}$Si NMR (C₆D₆) δ 11.6; MS (m/z): 504 (M$^+$), 447 (M$^+$–$^t$Bu), 347 (M$^+$–SiMe$^t$Bu₂).

### 3.5. Synthesis of $^tBu_2MeSi$–$Ge(p$-tolyl$)_2Cl$

CF$_3$SO$_3$H (5.3 ml) was slowly added to the solution of $^tBu_2MeSi$–Ge($p$-tolyl)$_3$ (30 g, 59.5 mmol) in CH$_2$Cl$_2$ (150 ml) at 0 °C. The reaction was complete in 1 h, then the fine powder of dry NH$_4$Cl (32 g, 598 mmol) was added at room temperature, and the reaction mixture was stirred for 54 h. Then excess of NH$_4$Cl was filtered off and CH$_2$Cl$_2$ was evaporated. $^tBu_2MeSi$–Ge($p$-tolyl)$_2$Cl was isolated by Kugelrohr distillation as a colorless oil (22.4 g, 84%). Bp 150–170 °C/0.07 mmHg; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.45 (s, 3H, Me), 1.03 (s, 18H, $^tBu$), 2.03 (s, 6H, $Me$–C$_6$H$_4$–), 7.01 (d, $^3J = 8$ Hz, 4H, H$_{arom}$), 7.81 (d, $^3J = 8$ Hz, 4H, H$_{arom}$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 6.2, 21.3, 21.8, 29.4, 129.6, 134.0, 137.9, 139.2; $^{29}$Si NMR (C$_6$D$_6$) $\delta$ 16.1; MS ($m/z$): 448 (M$^+$), 413 (M$^+$–Cl), 291 (M$^+$–SiMe$^tBu_2$).

### 3.6. Synthesis of $^tBu_2MeSi$–$Ge(p$-tolyl$)_2$–$Ge(p$-tolyl$)_2$–$SiMe^tBu_2$

A solution of $^tBu_2MeSi$–Ge($p$-tolyl)$_2$Cl (22.4 g, 50 mmol) in THF (150 ml) was added to the suspension of Li (710 mg, 101 mmol) in THF (50 ml), and the reaction mixture was refluxed overnight. After usual work-up the solvent was evaporated, and the residue was recrystallized from toluene to give $^tBu_2MeSi$–Ge($p$-tolyl)$_2$–Ge($p$-tolyl)$_2$–SiMe$^tBu_2$ as a colorless solid (13.8 g, 67%). Mp 235–238 °C; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.18 (s, 6H, Me), 0.95 (s, 36H, $^tBu$), 2.16 (s, 12H, $Me$–C$_6$H$_4$–), 7.11 (d, $^3J = 7.7$ Hz, 8H, H$_{arom}$), 7.91 (d, $^3J = 7.7$ Hz, 8H, H$_{arom}$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ −4.0, 21.4, 23.0, 30.3, 128.7, 137.7, 137.9, 138.1; $^{29}$Si NMR (C$_6$D$_6$) $\delta$ 19.3.

### 3.7. Synthesis of $^tBu_2MeSi$–$GeCl_2$–$GeCl_2$–$SiMe^tBu_2$ (1a)

Dry gaseous HCl was bubbled into a solution of $^tBu_2MeSi$–Ge($p$-tolyl)$_2$–Ge($p$-tolyl)$_2$–SiMe$^tBu_2$ (5.5 g, 6.66 mmol) in benzene (70 ml), containing AlCl$_3$ (200 mg, 1.49 mmol). Reaction progress was monitored by $^1$H NMR spectroscopy, which showed that the reaction was complete in 1 h at room temperature. The solvent was then evaporated, dry hexane was added to the residue, and the resulting suspension was filtered through Celite. After evaporation of hexane $^tBu_2MeSi$–GeCl$_2$–GeCl$_2$–SiMe$^tBu_2$ was obtained as a white solid (3.8 g, 95%). Mp 92–95 °C; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.45 (s, 6H, Me), 1.14 (s, 36H, $^tBu$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ −6.1, 22.9, 29.2; $^{29}$Si NMR (C$_6$D$_6$) $\delta$ 42.6.

### 3.8. Synthesis of $^tBu_2MeSi$–$GeBr_2$–$GeBr_2$–$SiMe^tBu_2$ (1b)

Dry gaseous HBr was bubbled into a solution of $^tBu_2MeSi$–Ge($p$-tolyl)$_2$–Ge($p$-tolyl)$_2$–SiMe$^tBu_2$ (0.3 g, 0.36 mmol) in benzene (10 ml), containing AlBr$_3$ (60 mg, 0.22 mmol). The reaction progress was monitored by $^1$H NMR spectroscopy, which showed that the reaction was

complete in 10 h at room temperature. Then solvent was evaporated, dry hexane was added to the residue and the resulting suspension was filtered through Celite. After evaporation of hexane $^tBu_2MeSi$–GeBr$_2$–GeBr$_2$–SiMe$^tBu_2$ was obtained as a white solid (0.15 g, 52%). Mp 74–79 °C; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.52 (s, 6H, Me), 1.19 (s, 36H, $^tBu$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ −4.7, 23.7, 29.5; $^{29}$Si NMR (C$_6$D$_6$) $\delta$ 43.7.

### 3.9. Synthesis of tetrakis(di-tert-butylmethylsilyl)-1H-siladigermirene ($^tBu_2MeSi)_4SiGe_2$ (2a)

A mixture of ($^tBu_2MeSi)_2SiLi_2$ [prepared from 1,1-bis(di-$tert$-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene (500 mg, 0.98 mmol) and Li (35 mg, 5.0 mmol) in THF (4 ml)] and 1a (200 mg, 0.33 mmol) was placed in a reaction tube with a magnetic stirring bar. Dry oxygen-free toluene (4 ml) was introduced by vacuum transfer, and the dark-green reaction mixture was stirred for 1 h at room temperature. After evaporation of solvent and filtration of inorganic salts, the reaction mixture was separated by column chromatography on silica gel (hexane eluent) in a glove box, followed by the recrystallization from pentane at −30 °C to produce pure 2a as dark-red crystals (68 mg, 26%). Mp 193–195 °C; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.43 (s, 6H, Me), 0.53 (s, 6H, Me), 1.21 (s, 36H, $^tBu$), 1.30 (s, 36H, $^tBu$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ −3.9, −2.1, 22.8, 23.4, 29.8, 31.2; $^{29}$Si NMR (C$_6$D$_6$) −110.6 (skeletal Si), 5.8 and 40.8 (substituent Si); UV (hexane) $\lambda_{max}$ nm ($\varepsilon$) 236 (21800), 311 (2400), 403 (1000), 470 (1200); Anal. Found: C, 54.06; H, 10.33. Calc. for C$_{36}$H$_{84}$Ge$_2$Si$_5$: C, 53.87; H, 10.55%.

### 3.10. Synthesis of tetrakis(di-tert-butylmethylsilyl)-1H-trigermirene ($^tBu_2MeSi)_4Ge_3$ (2b)

Compound 2b was prepared by the procedure analogues to that of 2a, starting from ($^tBu_2MeSi)_2GeLi_2$ [prepared from 1,1-bis(di-$tert$-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-germacycloprop-2-ene (200 mg, 0.36 mmol) and Li (20 mg, 2.86 mmol) in a mixture of solvents THF (0.3 ml) + Et$_2$O (1.2 ml)] and 1a (83 mg, 0.14 mmol) in toluene (1.5 ml). 2b was isolated as dark-red crystals (75 mg, 22%). Mp 188–190 °C; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.46 (s, 6H, Me), 0.54 (s, 6H, Me), 1.23 (s, 36H, $^tBu$), 1.29 (s, 36H, $^tBu$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ −3.8, −1.9, 22.7, 23.7, 29.8, 31.0; $^{29}$Si NMR (C$_6$D$_6$) $\delta$ 17.0 and 39.1 (substituent Si); UV (hexane) $\lambda_{max}$ nm ($\varepsilon$) 234 (13600), 324 (2400), 407 (700), 457 (700); Anal. Found: C, 50.71; H, 9.77. Calc. for C$_{36}$H$_{84}$Ge$_3$Si$_4$: C, 51.04; H, 9.99%.

### 3.11. Synthesis of trans-2,4-dichloro-1,1,2,4-tetrakis(di-tert-butylmethylsilyl)-1,2,4-siladigermetane (5a)

1H-siladigermirene 2a (244 mg, 0.30 mmol) was placed in a reaction tube and dry oxygen-free hexane (1 ml) and CH$_2$Cl$_2$ (1 ml) were introduced by vacuum transfer, then

the reaction mixture was stirred for 3 h at room temperature. After the evaporation of solvents the residue was recrystallized from pentane to give **5a** as colorless crystals (183 mg, 71%). Mp 152–154 °C; $^1$H NMR ($C_6D_6$) $\delta$ 0.46 (s, 6H, Me), 0.79 (s, 6H, Me), 1.20 (s, 18H, $^t$Bu), 1.21 (s, 18H, $^t$Bu), 1.24 (s, 18H, $^t$Bu), 1.31 (s, 18H, $^t$Bu), 2.79 (s, 2H, CH$_2$); $^{13}$C NMR ($C_6D_6$) $\delta$ −4.8, 1.1, 22.5, 23.1, 23.5, 24.3, 29.8, 30.0, 31.4, 31.8, 42.6 (CH$_2$), $^{29}$Si NMR ($C_6D_6$) $\delta$ 21.5 (skeletal Si), 28.6, 30.7; Anal. Found: C 49.81, H 9.82. Calc. for $C_{37}H_{86}Cl_2Ge_2Si_5$: C 50.07, H 9.77%.

### 3.12. Synthesis of trans-1,3-dichloro-1,2,2,3-tetrakis(di-tert-butylmethylsilyl)-1,2,3-trigermetane (5b)

Trigermirene **2b** (100 mg, 0.12 mmol) was placed in a reaction tube and dry oxygen-free hexane (0.5 ml) and $CH_2Cl_2$ (0.5 ml) were introduced by vacuum transfer, then the reaction mixture was stirred for 3 h at room temperature. After the evaporation of solvents the residue was recrystallized from pentane to give **5b** as colorless crystals (68 mg, 69%). Mp 149–152 °C; $^1$H NMR ($C_6D_6$) $\delta$ 0.46 (s, 6H, Me), 0.84 (s, 6H, Me), 1.201 (s, 18H, $^t$Bu), 1.203 (s, 18H, $^t$Bu), 1.23 (s, 18H, $^t$Bu), 1.30 (s, 18H, $^t$Bu), 2.98 (s, 2H, CH$_2$); $^{13}$C NMR ($C_6D_6$) $\delta$ −4.9, 1.3, 22.9, 23.3, 23.5, 24.2, 29.8, 30.0, 31.2, 31.6, 44.9 (CH$_2$); $^{29}$Si NMR ($C_6D_6$) $\delta$ 27.7, 31.0; Anal. Found: C 47.74, H 9.32. Calc. for $C_{37}H_{86}Cl_2Ge_3Si_4$: C 47.68, H 9.30%.

### 3.13. Synthesis of trans-1,3-dichloro-1,2,2,3-tetrakis(di-tert-butylmethylsilyl)-1,2,3-trisiletane (8a)

Trisilirene **7a** (500 mg, 0.702 mmol) was placed in a reaction tube and dry oxygen-free hexane (1 ml) and $CH_2Cl_2$ (1 ml) were introduced by vacuum transfer, then the reaction mixture was stirred for 4 h at room temperature. After the evaporation of solvents the residue was recrystallized from pentane to give **8a** as colorless crystals (420 mg, 75%). Mp 161–163 °C; $^1$H NMR ($C_6D_6$) $\delta$ 0.41 (s, 6H, Me), 0.71 (s, 6H, Me), 1.22 (s, 36H, $^t$Bu), 1.24 (s, 18H, $^t$Bu), 1.35 (s, 18H, $^t$Bu), 2.20 (s, 2H, CH$_2$); $^{13}$C NMR ($C_6D_6$) $\delta$ −5.0, 1.6, 22.6 (2C), 22.9, 23.8, 30.2, 30.4, 31.0 (CH$_2$), 31.7, 32.0; $^{29}$Si NMR ($C_6D_6$) $\delta$ −16.8 (skeletal Si), 11.2, 21.5, 31.0 (skeletal Si–Cl).

### 3.14. Synthesis of trans-1,3-dichloro-1,2,2,3-tetrakis(di-tert-butylmethylsilyl)[1,3,2]disilagermetane (8b)

3$H$-disilagermirene **7b** (500 mg, 0.660 mmol) was placed in a reaction tube and dry oxygen-free hexane (1 ml) and $CH_2Cl_2$ (1 ml) were introduced by vacuum transfer, then the reaction mixture was stirred for 4 h at room temperature. After the evaporation of solvents the residue was recrystallized from pentane to give **8b** as colorless crystals (392 mg, 70%). Mp 157–159 °C; $^1$H NMR ($C_6D_6$) $\delta$ 0.40

(s, 6H, Me), 0.75 (s, 6H, Me), 1.21 (s, 36H, $^t$Bu), 1.23 (s, 18H, $^t$Bu), 1.28 (s, 18H, $^t$Bu), 2.35 (s, 2H, CH$_2$); $^{13}$C NMR ($C_6D_6$) $\delta$ −5.2, 1.8, 22.3, 22.9, 23.3, 23.7, 30.1, 30.3, 31.3, 31.9, 32.7 (CH$_2$); $^{29}$Si NMR ($C_6D_6$) $\delta$ 10.3, 30.2, 32.5 (skeletal Si).

### 3.15. Synthesis of trans-2,3-dichloro-1,1,2,3-tetrakis(di-tert-butylmethylsilyl)siladigermirane (9a)

1$H$-siladigermirene **2a** (50 mg, 0.062 mmol) was reacted with an excess of dry $CCl_4$ (0.5 ml). Reaction immediately occurred upon melting of $CCl_4$, and the color of the reaction mixture was changed from dark-red to yellow. **9a** was isolated by the recrystallization from hexane as yellow crystals (38.7 mg, 71%). Mp 131–133 °C (dec.); $^1$H NMR ($C_6D_6$) $\delta$ 0.50 (s, 6H, Me), 0.57 (s, 6H, Me), 1.27 (s, 18H, $^t$Bu), 1.29 (s, 18H, $^t$Bu), 1.31 (s, 18H, $^t$Bu), 1.35 (s, 18H, $^t$Bu); $^{13}$C NMR ($C_6D_6$) $\delta$ −2.8, 2.5, 22.8, 23.7, 23.8, 24.1, 29.9, 30.1, 30.9, 31.4; $^{29}$Si NMR ($C_6D_6$) $\delta$ −83.0, 26.0, 39.1.

### 3.16. Synthesis of trans-1,2-dichloro-1,2,3,3-tetrakis(di-tert-butylmethylsilyl)trigermirane (9b)

Trigermirene **2b** (50 mg, 0.059 mmol) was reacted with an excess of dry $CCl_4$ (0.5 ml). Reaction immediately occurred upon melting of $CCl_4$, and the color of the reaction mixture was changed from dark-red to yellow. **9b** was isolated by the recrystallization from hexane as yellow crystals (35.2 mg, 65%). Mp 125–127 °C (dec.); $^1$H NMR ($C_6D_6$) $\delta$ 0.49 (s, 6H, Me), 0.63 (s, 6H, Me), 1.26 (s, 18H, $^t$Bu), 1.30 (s, 36H, 2 $^t$Bu), 1.35 (s, 18H, $^t$Bu); $^{13}$C NMR ($C_6D_6$) $\delta$ −3.1, 2.6, 23.2, 23.6, 24.0, 24.1, 29.9, 30.0, 30.7, 31.3; $^{29}$Si NMR ($C_6D_6$) $\delta$ 35.6, 36.9.

### 3.17. Crystal structure analyses of the compounds 1a, 2a and 5a

The single crystals of compounds **1a**, **2a** and **5a** for X-ray diffraction study were grown from the saturated 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 [18], and refined by the full-matrix least-squares method by SHELXL-97 program [19]. The crystal data and experimental parameters for the X-ray analysis of **1a**, **2a**, and **5a** are listed in Table 1. Crystallographic data of **1a**, **2a** and **5a** have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 298969 (**1a**), CCDC No. 273374 (**2a**) and CCDC No. 273375 (**5a**). Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or 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 **1a**, **2a** and **5a**

|  | 1a | 2a | 5a |
|---|---|---|---|
| Empirical formula | $C_{18}H_{42}Cl_4Ge_2Si_2$ | $C_{36}H_{84}Ge_2Si_5$ | $C_{37}H_{86}Cl_2Ge_2Si_5$ |
| Formula mass (g mol$^{-1}$) | 601.68 | 802.66 | 887.59 |
| Collection temperature (K) | 120 | 120 | 120 |
| $\lambda$ (Mo-K$\alpha$) (Å) | 0.71070 | 0.71070 | 0.71070 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P\,21/n$ | $P\,21/c$ | $Cc$ |
| Unit cell parameters |  |  |  |
| $a$ (Å) | 7.925(3) | 24.1020(6) | 23.1270(16) |
| $b$ (Å) | 14.864(3) | 11.6190(9) | 12.4550(14) |
| $c$ (Å) | 12.013(5) | 17.7300(16) | 17.8730(19) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 94.091(16) | 110.206(4) | 109.567(6) |
| $\gamma$ (°) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 1411.5(8) | 4659.6(6) | 4850.9(8) |
| $Z$ | 2 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.416 | 1.144 | 1.215 |
| $\mu$ (mm$^{-1}$) | 2.597 | 1.440 | 1.496 |
| $F(0\,0\,0)$ | 620 | 1736 | 1904 |
| Crystal dimensions (mm) | $0.30 \times 0.01 \times 0.01$ | $0.30 \times 0.25 \times 0.05$ | $0.15 \times 0.10 \times 0.02$ |
| $\theta$ Range (°) | 2.18–28.05 | 2.14–28.00 | 2.06–28.02 |
| Index ranges | $0 \leqslant h \leqslant 10$ | $-31 \leqslant h \leqslant 29$ | $0 \leqslant h \leqslant 30$ |
|  | $0 \leqslant k \leqslant 18$ | $-15 \leqslant k \leqslant 0$ | $0 \leqslant k \leqslant 16$ |
|  | $-15 \leqslant l \leqslant 15$ | $0 \leqslant l \leqslant 22$ | $-23 \leqslant l \leqslant 22$ |
| Collected reflections | 13 749 | 44 850 | 24 669 |
| Independent reflections | 3039 | 10 257 | 5764 |
| $R_{int}$ | 0.1470 | 0.0620 | 0.0970 |
| Reflections used | 3039 | 10 257 | 5764 |
| Parameters | 119 | 389 | 416 |
| $S^a$ | 1.069 | 1.008 | 0.999 |
| Weight parameters $a/b^b$ | 0.1235/0.0000 | 0.0967/3.3310 | 0.0821/0.0000 |
| $R_1^c$ [$I > 2\sigma(I)$] | 0.0817 | 0.0544 | 0.0580 |
| $wR_2^d$ (all data) | 0.2547 | 0.1611 | 0.1548 |
| Maximum/minimum residual electron density (e Å$^{-3}$) | 0.994/$-1.237$ | 1.087/$-1.224$ | 0.756/$-0.936$ |

[a] $S = \{\sum[w(F_0^2 - F_c^2)^2]/(n-p)\}^{0.5}$, $n$ = no. of reflections; $p$ = no. of parameters.
[b] $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, with $P = (F_0^2 + 2F_c^2)/3$.
[c] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$.
[d] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{0.5}$.

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