Organometallic Chemistry

DOI: 10.1002/ange.200501885

$SiGe_2$ and Ge_3: Cyclic Digermenes that Undergo Unexpected Ring-Expansion Reactions[**]

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The chemistry of cyclic compounds composed of heavier Group 14 elements represents one of the most fascinating topics of modern organometallic chemistry. Since the first reports on the preparation of heavy cyclopropane analogues by Masamune et al. in 1982–1983,[1] the chemistry of these unusual compounds has been greatly developed in all respects, including synthesis, structure, and reactivity. The first examples of heavy cyclopropene analogues were synthesized only recently, during the last decade.[2] Since then, several representatives of these highly challenging compounds, which combine the properties of heavy cyclopropanes and heavy alkenes in one molecule, have been reported.[3]

Apart from the homonuclear heavy cyclopropenes, consisting of identical Group 14 elements, several heteronuclear analogues containing different heavier Group 14 elements can also be imagined. However, of all the possible combinations only two heteronuclear heavy cyclopropenes have been synthesized by the Würtz-type coupling reaction, namely 3*H*- and 1*H*-disilagermirenes, which feature endocyclic Si=Si and Si=Ge bonds, respectively.[4] Herein, we report the synthesis of two cyclic, three-membered-ring digermenes: the first 1*H*-siladigermirene, a heteronuclear cyclopropene with one Si and two Ge atoms, and a novel 1*H*-trigermirene derivative.

As the target compound 1*H*-siladigermirene, in contrast to 3*H*-disilagermirene,[4] could not be prepared by the Würtz coupling reaction, we developed a new synthetic protocol that involves a coupling reaction of 1,1-dilithiosilane R_2SiLi_2[5] with tetrachlorodigermane $RCl_2Ge{-}GeCl_2R$ in toluene ($R = SiMe\textit{t}Bu_2$). This reaction quickly results in the formation of two products, tetrakis(di-*tert*-butylmethylsilyl)-1*H*-siladigermirene (R_4SiGe_2, **1a**) and disilene $R_2Si{=}SiR_2$ (**2a**),[6] in a 2:1 ratio (Scheme 1). It is interesting that among the various compounds that one can imagine as the 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 isolation of disilene **2a** as the side product provides evidence for the

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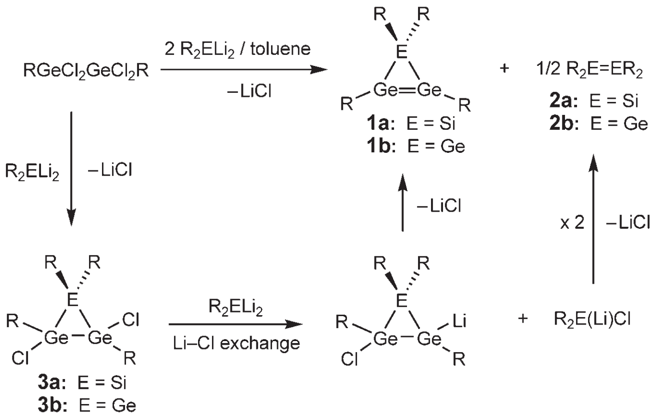
[**] This work was supported by Grants-in-Aid for Scientific Research (Nos. 14078204, 16205008, 17655014) from the Ministry of Education, Culture, Sports, Science, and Technology, and the COE (Center of Excellence) program.



Scheme 1. Synthesis of the 1*H*-siladigermirene **1a** and the 1*H*-trigermirene **1b**. E = Si, Ge; R = SiMe*t*Bu$_2$.

initial formation of the intermediate cyclic 2,3-dichlorosiladigermirane (**3a**) followed by a rapid lithium–chlorine exchange reaction between **3a** and a second equivalent of R_2SiLi_2, finally resulting in the formation of **1a** and **2a** in a 2:1 ratio.[7] The 1H-siladigermirene **1a** represents the first $SiGe_2$ hybrid heavy analogue of cyclopropene featuring a skeletal Ge=Ge double bond.

Compound **1a** exhibits very simple ^{1}H and ^{13}C NMR spectra with only two sets of signals for the protons of the Me and *t*Bu groups. In the ^{29}Si NMR spectrum of **1a**, the skeletal Si atom resonates at high field ($\delta = -110.6$ ppm), as expected for tetrahedral Si atoms incorporated in a three-membered-ring system. Dark red crystals of **1a** were isolated that were highly sensitive to air and moisture. The X-ray crystal structure analysis[8] proved that **1a** was an unsaturated three-membered ring with a Ge=Ge double bond length of 2.2429(6) Å (Figure 1). The remaining two sides of the $SiGe_2$ isosceles triangle are made up of Si–Ge single bonds (2.4167(10) Å). These skeletal bond lengths are characteristic for three-membered rings of heavier Group 14 elements. As expected, the Ge=Ge double bond has a highly pronounced *trans*-bent configuration with a bending angle of 51.0(2)°.[9]

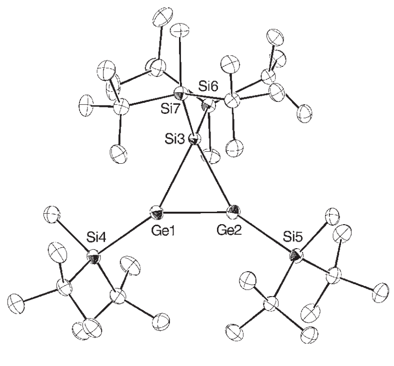
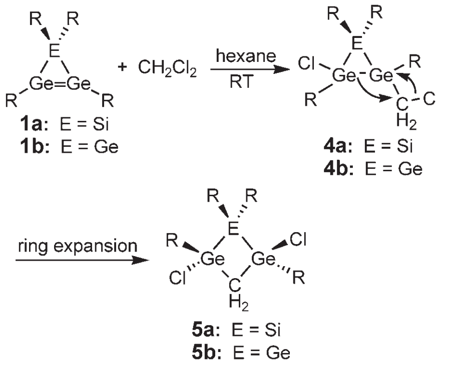


Figure 1. ORTEP plot of the crystal structure of **1a**; the thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Ge1-Ge2 2.2429(6), Si3-Ge1 2.4168(10), Si3-Ge2 2.4165(10), Ge1-Si4 2.3995(11), Ge2-Si5 2.3943(11), Si3-Si6 2.3993(13), Si3-Si7 2.4033(13); Ge2-Ge1-Si3 62.34(11), Ge1-Ge2-Si3 62.36(3), Ge1-Si3-Ge2 55.30(2). The torsional angle Si4-Ge1-Ge2-Si5 is 51.0(2)°.

By employing the same synthetic approach, we were able to prepare the corresponding Ge_3 analogue, tetrakis(di-*tert*-butylmethylsilyl)-1*H*-trigermirene (**1b**), by the reaction of dilithiogermane R_2GeLi_2[10] and tetrachlorodigermane $RCl_2Ge{-}GeCl_2R$ in toluene (Scheme 1). As with **1a**, compound **1b** was formed along with $R_2Ge{=}GeR_2$ (**2b**) in a 2:1 ratio.

The reactivity of the new cyclic digermenes **1a** and **1b** proved to be very interesting. Compounds **1a** and **1b** readily react with an excess of CH_2Cl_2 at room temperature to produce the new four-membered-ring compounds, *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 ring expansion (Scheme 2).



Scheme 2. Reaction of **1a** and **1b** with CH_2Cl_2 along with the proposed mechanism for the formation of [1,2,4]siladigermetane **5a** and [1,2,3]trigermetane **5b**. R = SiMe*t*Bu$_2$.

Surprisingly, the ^{1}H NMR spectra of **5a** and **5b** display markedly downfield-shifted resonances for the skeletal methylene protons: $\delta = 2.79$ and 2.98 ppm, respectively.[11] This unusual feature might be attributed to a hyperconjugative σ(C–H)–σ^*(Ge–Cl) interaction, which would result in a downfield shift of the signal of the CH_2 protons. The crystal structure analysis of **5a**[8] demonstrates a folded $SiGe_2C$ four-membered ring (folding angle 33°) with long skeletal Si–Ge bonds of 2.475(2) and 2.547(3) Å (typical values 2.384–2.462 Å[12]), which could be due to steric congestion around the Ge1-Si2-Ge3 unit (Figure 2). The long Ge–Cl bonds of 2.229(2)–2.236(2) Å are another interesting feature, as they exceed the normal values of 2.08–2.15 Å.[12] The formation of **5a** and **5b** may involve initial 1,2-addition of a molecule of CH_2Cl_2 across the Ge=Ge bond of **1a** and **1b** to form the intermediate cyclopropane-type derivatives **4a** and **4b**,[13] followed by intramolecular insertion of the methylene unit into the neighboring endocyclic Ge–Ge bond (Scheme 2). Indeed, calculations at the B3LYP/6-31G(d) level with the GAUSSIAN 98 program on model compounds of **5a** and **4a** with R=SiH_3 showed that the final four-membered ring **5a** is 41.7 kcal mol^{-1} more stable than the intermediate three-membered ring **4a**.

We found that CH_2Cl_2 is a unique reagent with respect to its reactivity toward the heavy cyclopropene analogues **1a** and **1b**. For example, CCl_4 reacts with **1a** and **1b** to form the

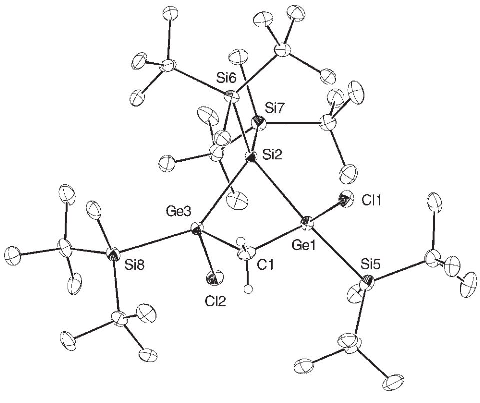
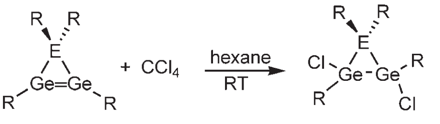


Figure 2. ORTEP plot of the crystal structure of **5a**; the thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Si2-Ge1 2.547(3), Si2-Ge3 2.475(2), Ge1-C1 1.998(10), Ge3-C1 1.956(10), Ge1-Cl1 2.229(2), Ge3-Cl2 2.236(2); Ge1-Si2-Ge3 73.88(6), Si2-Ge3-C1 90.0(3), Ge3-C1-Ge1 99.5(4), C1-Ge1-Si2 87.0(3).

corresponding dichloro derivatives 2,3-dichloro-1,1,2,3-tetrakis(di-*tert*-butylmethylsilyl)siladigermirane (**3a**) and 1,2-dichloro-1,2,3,3-tetrakis(di-*tert*-butylmethylsilyl)trigermirane (**3b**), instead of the ring-expansion products (Scheme 3).[14]



1a: E = Si
1b: E = Ge

3a: E = Si
3b: E = Ge

Scheme 3. Reaction of **1a** and **1b** with CCl_4 with formation of 2,3-dichlorosiladigermirane **3a** and 1,2-dichlorotrigermirane **3b**. R = SiMe*t*Bu$_2$.

The reaction with $CHCl_3$ results in complicated product mixtures. The ring-expansion reaction with CH_2Cl_2 is general for all heavy cyclopropene analogues of the type $R_4EE'_2$ (R = SiMe*t*Bu$_2$; E, E′ = Si, Ge). Thus, the previously reported 1*H*-trisilirene R_4Si_3[2b] as well as the 3*H*- and 1*H*-disilagermirenes R_4GeSi_2[4] smoothly react with CH_2Cl_2 to produce four-membered rings that are isostructural to **5a** and **5b**.

Experimental Section

1a: A mixture of (*t*Bu$_2$MeSi)$_2$SiLi$_2$—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, 5.00 mmol) in THF (4 mL)—and *t*Bu$_2$MeSi-GeCl$_2$-GeCl$_2$-SiMe*t*Bu$_2$ (200 mg, 0.33 mmol) was placed in a reaction tube with a magnetic stirrer 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 the inorganic salts were removed by filtration and the solvent was removed under vacuum, the residue was taken up in hexane and separated by column chromatography on silica gel (eluent: hexane) in a glove box. Recrystallization of the appropriate fraction from pentane at −30 °C produced pure **1a** as dark red crystals (68 mg, 26%), m.p.: 193–195 °C; ^{1}H NMR (300.1 MHz, [D$_6$]benzene, TMS): $\delta = 0.43$ (s, 6H), 0.53 (s, 6H), 1.21 (s, 36H), 1.30 ppm (s, 36H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene, TMS): $\delta = -3.9$, −2.1, 22.8, 23.4, 29.8, 31.2 ppm; ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene, TMS): $\delta = -110.6$ (cyclic Si), 5.8 and 40.8 ppm (substituent Si); UV/Vis (hexane): λ_{max} (ε) = 470 (1200), 403 (1000), 311 (2400), 236 nm (21 800 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{36}H_{84}Ge_2Si_5$: C 53.87, H 10.55; found: C 54.06, H 10.33.

1b: Compound **1b** was prepared from (*t*Bu$_2$MeSi)$_2$GeLi$_2$ and *t*Bu$_2$MeSi-GeCl$_2$-GeCl$_2$-SiMe*t*Bu$_2$ in 22% yield as dark red crystals; m.p.: 188–190 °C; ^{1}H NMR (300.1 MHz, [D$_6$]benzene, TMS): $\delta = 0.46$ (s, 6H), 0.54 (s, 6H), 1.23 (s, 36H), 1.29 ppm (s, 36H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene, TMS) $\delta = -3.8$, −1.9, 22.7, 23.7, 29.8, 31.0 ppm; ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene, TMS): $\delta = 17.0$, 39.1 ppm; UV/Vis (hexane): λ_{max} (ε) = 457 (700), 407 (700), 324 (2400), 234 nm (13 600 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{36}H_{84}Ge_3Si_4$: C 51.04, H 9.99; found: C 50.71, H 9.77.

5a: A mixture (319 mg) of 2-siladigermirene **1a** and disilene **2a** (2:1) was placed in a reaction tube with a magnetic stirrer bar. Dry, oxygen-free CH_2Cl_2 (1 mL) and hexane (1 mL) were introduced by vacuum transfer, and the reaction mixture was stirred for 3 h at room temperature to give a dark blue solution. After removal of the solvents under vacuum, the residue was separated by column chromatography on silica gel (eluent: hexane) in a glove box. Two fractions were collected: the first blue fraction (**2a**) and the second pale yellow fraction (**5a**). After removal of the solvent under vacuum, the second fraction was recrystallized from hexane at −30 °C to give pure **5a** as colorless crystals (173 mg, 71%), m.p.: 152–154 °C; ^{1}H NMR (300.1 MHz, [D$_6$]benzene, TMS): $\delta = 0.46$ (s, 6H), 0.79 (s, 6H), 1.20 (s, 18H), 1.21 (s, 18H), 1.24 (s, 18H), 1.31 (s, 18H), 2.79 ppm (s, 2H, CH$_2$); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene, TMS): $\delta = -4.8$, 1.1, 22.5, 23.1, 23.5, 24.3, 29.8, 30.0, 31.4, 31.8, 42.6 ppm; ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene, TMS): $\delta = 21.5$ and 28.6 (substituent Si), 30.7 ppm (cyclic Si); elemental analysis (%) calcd for $C_{37}H_{86}Cl_2Ge_2Si_5$: C 50.07, H 9.77; found: C 49.81, H 9.82.

5b: Compound **5b** was prepared from a mixture of **1b** and **2b** in 69% yield as colorless crystals; m.p.: 149–152 °C; ^{1}H NMR (300.1 MHz, [D$_6$]benzene, TMS): $\delta = 0.46$ (s, 6H,), 0.84 (s, 6H), 1.201 (s, 18H), 1.203 (s, 18H), 1.23 (s, 18H), 1.30 (s, 18H), 2.98 ppm (s, 2H, CH$_2$); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene, TMS): $\delta = -4.9$, 1.3, 22.9, 23.3, 23.5, 24.2, 29.8, 30.0, 31.2, 31.6, 44.9 ppm; ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene, TMS): $\delta = 27.7$, 31.0 ppm; elemental analysis (%) calcd for $C_{37}H_{86}Cl_2Ge_3Si_4$: C 47.68, H 9.30; found: C 47.74, H 9.32.

Received: May 31, 2005

Keywords: germanium · group 14 elements · ring expansion · silicon · small ring systems

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[7] The dichloride **3a**, independently synthesized by the reaction of **1a** with CCl_4, immediately reacts with an equivalent amount of R_2SiLi_2 to form exclusively **1a** and **2a** in a 2:1 ratio.

[8] Crystal structure analyses of **1a** and **5a**: The single crystals were grown from saturated solutions in hexane. The diffraction data were collected at 120 K on a MacScience DIP2030 Image Plate Diffractometer employing graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystal data for **1a** ($C_{36}H_{84}Ge_2Si_5$): $M_r = 802.66$, monoclinic, space group $P21/c$, $a = 24.1020(6)$, $b = 11.6190(9)$, $c = 17.7300(16)$ Å, $\beta = 110.206(4)°$, $V = 4659.6(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.144$ g cm^{-3}, GOF = 1.008. The final R factor was 0.0544 ($R_w = 0.1611$ for all data) for 7455 reflections with $I_o > 2\sigma(I_o)$. Crystal data for **5a** ($C_{37}H_{86}Cl_2Ge_2Si_5$): $M_r = 887.59$, monoclinic, space group Cc, $a = 23.1270(16)$, $b = 12.4550(14)$, $c = 17.8730(19)$ Å, $\beta = 109.567(6)°$, $V = 4850.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.215$ g cm^{-3}, GOF = 0.999. The final R factor was 0.0580 ($R_w = 0.1548$ for all data) for 3834 reflections with $I_o > 2\sigma(I_o)$. The structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXL-97 program. CCDC 273374 (**1a**) and 273375 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] Similar dichloro derivatives were formed upon reaction of 1*H*-trisilirene R_4Si_3[2b] as well as the 3*H*- and 1*H*-disilagermirenes R_4GeSi_2[4] (R = SiMe*t*Bu_2) with CCl_4: V. Ya. Lee, T. Matsuno, M. Ichinohe, A. Sekiguchi, *Heteroat.Chem.* **2001**, *12*, 223.