



## Article

# Synthesis of a Dichlorodigermasilane: Double Si–Cl Activation by a Ge=Ge Unit

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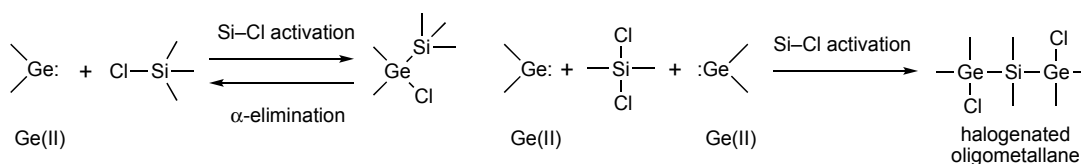
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**Abstract:** Halogenated oligosilanes and oligogermanes are interesting compounds in oligosilane chemistry from the viewpoint of silicon-based-materials. Herein, it was demonstrated that a 1,2-digermacyclobutadiene derivative could work as a bis-germylene building block towards double Si–Cl activation to give a halogenated oligometallane, a bis(chlorogermeryl)dichlorosilane derivative.

**Keywords:** Si–Cl activation; germylene; digermene; digermacyclobutadiene

## 1. Introduction

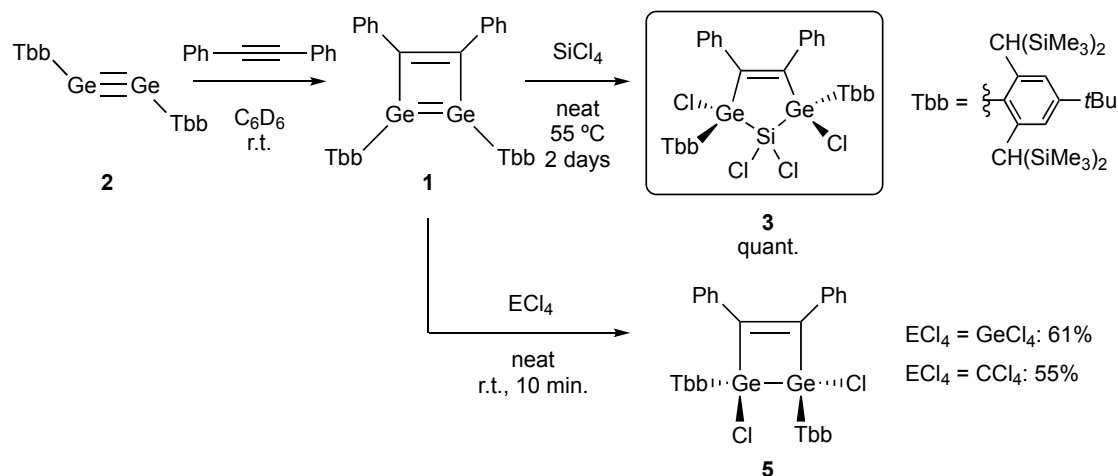
Halogenated oligosilanes and oligogermanes are attractive compounds as functionalized oligometallanes from the standpoint of oligosilane material chemistry [1–7]. In this regard, Si(II) or Ge(II) species should be an important building block for creating such halogenated oligosilanes/germanes because silylenes (divalent Si(II) species) or germynes (divalent Ge(II) species) have been known to undergo ready Si–Cl insertion reactions, i.e., Si–Cl activation reactions [8–11]. For example, Iwamoto and Kira reported the facile Si–Cl insertion of the isolable dialkylmetallylenes towards SiCl<sub>4</sub> under mild conditions [10]. However, especially in the germanium cases, it is difficult to isolate the insertion products, >Ge(Cl)SiR<sub>3</sub>, because the insertion reaction of a germylene toward a Si–Cl bond would be reversible in some cases [12]. Thus, the substituents on the Si atom (R of the R<sub>3</sub>Si–Cl species) should be bulky and/or electropositive to avoid the α-elimination of R<sub>3</sub>Si–Cl from the Ge moiety [8,12–22]. The requirement for the bulkiness on the Si–Cl moiety could make it difficult to create halogenated oligometallanes, such as >Ge(Cl)–SiCl<sub>2</sub>–Ge(Cl)< with utilizing the double Si–Cl activation of the Ge(II) species towards SiCl<sub>4</sub>, because of two unfavorable factors: (i) entropy, two Ge(II) moieties should react with one SiCl<sub>4</sub> species; and (ii) the stability of the product, the Cl atoms on the Si atom should promote the α-Si–Cl elimination, i.e., the retro reaction (Scheme 1). In this paper, we chose a 1,2-digermacyclobutadiene derivative [23] as a suitable Ge(II) building block for the double Si–Cl activation of SiCl<sub>4</sub> to yield >Ge(Cl)–SiCl<sub>2</sub>–Ge(Cl)< species, because the rigid cyclic skeleton should overcome the entropy-disadvantage, and the rigidity of the cyclic skeleton should suppress the α-Si–Cl elimination. Finally, it was found that the stable 1,2-digermacyclobutadiene **1** (1,2-Tbb<sub>2</sub>-3,4-Ph<sub>2</sub>-digermacyclobutadiene, Tbb = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-*t*-Bu-C<sub>6</sub>H<sub>2</sub>, Scheme 2) [24] with SiCl<sub>4</sub> afforded the corresponding 1,3-digermene-2-sila-cyclopent-4-ene derivative, the cyclic >Ge(Cl)–SiCl<sub>2</sub>–Ge(Cl)< compound. 1,2-Digermacyclobut-1-ene derivative was reacted with SiCl<sub>4</sub> to give the double-Si–Cl-insertion product, and the following reduction reaction gave the corresponding >Ge = Si = Ge< species [11]. Although **1** could undergo facile double Si–Cl activation toward SiCl<sub>4</sub>, neither double Ge–Cl nor C–Cl activation could occur in the reaction of **1** with GeCl<sub>4</sub>/CCl<sub>4</sub>.



**Scheme 1.** Depictions for Si–Cl activations of Ge(II) species and Si–Cl  $\alpha$ -elimination from a chlorosilylgermane.

## 2. Results and Discussions

When the stable digermene **2** bearing bulky aryl substituents, Tbb groups (2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-*t*-Bu-C<sub>6</sub>H<sub>2</sub>), was treated with PhC≡CPh (tolan) at room temperature, 1,2-digermacyclobutadiene **1** was isolated as a stable crystalline compound [23–26] via formal [2+2] cycloaddition (Scheme 2). As one can see from the structure of **1**, it is a cyclic 4 $\pi$ -electron conjugated, anti-aromatic compound incorporating Ge(II) moieties. On the basis of theoretical calculations, **1** has considerable –Ge=Ge=C=C– character rather than =Ge–Ge=C=C– [24]. Accordingly, as expected, **1** could work as a building block of the bis-Ge(II) moiety. Reaction of **1** with SiCl<sub>4</sub> afforded digermadichlorosilane **3** quantitatively, which could be formed via double Si–Cl insertion reactions of the Ge(II) moieties of the 1,2-digermacyclobutadiene skeleton in **1**. This reaction has been performed under the neat condition at 55 °C because the addition of small amount of SiCl<sub>4</sub> or reaction at r.t. afforded very slow conversion of **3**. The obtained dichlorosilane **3** has the >Ge(Cl)–SiCl<sub>2</sub>–Ge(Cl)< moiety in its 1,3-digerma-2-sila-cyclopent-4-ene skeleton, i.e., **2** should be one of a unique class of compounds of oligohalo-oligometallanes. Thus, **1** was found to work as a bis-germylene building block (>Ge: + :Ge<) towards a double Si–Cl activation.

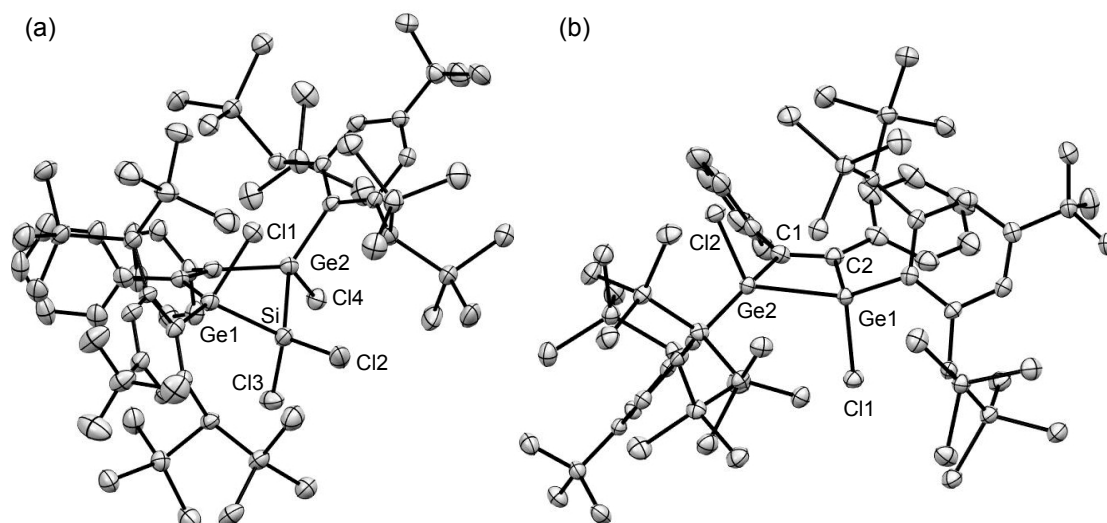


**Scheme 2.** Preparation of 1,2-digermacyclobutadiene **1**, and its reaction with ECl<sub>4</sub> giving digermadichlorosilane **3** (E = Si) and dichlorodigermacyclobutene **5** (E = C, Ge), respectively.

The molecular structure of digermadichlorosilane **3** was definitively determined by X-ray crystallographic analysis (Figure 1). The two Tbb/Cl groups are oriented in (*E*)-geometry probably due to steric reasons. The five-membered ring skeleton in **3** exhibits the envelope geometry with a deviation of the Si atom from the Ge–C=C–Ge plane by *ca.* 1.27 Å. While the two Ge–Cl bond lengths are almost the same (Ge1–Cl1: 2.2094(14) Å, Ge2–Cl4: 2.2011(15) Å) within a range of standard deviations, the orientation of the two Cl atoms are slightly different to each other. That is, one of the Cl atom (Cl4) is oriented to outside of the five-membered ring skeleton, but another one (Cl1) is approaching to the central Si atom with the Cl1...Si distance of 3.25 Å, which is far from the other one (Cl4...Si = 3.66 Å) [27]. In addition, the two Cl–Ge–Si angles are considerably different from each

other, ( $\text{Cl1-Ge1-Si} = 90.20(8)$ ,  $\text{Cl4-Ge2-Si} = 105.40(8)$ ). These asymmetrical structural features indicate weak  $n(\text{Cl1})\cdots\sigma^*(\text{Si-Cl3})$  interaction. These structural features were reasonably reproduced by the theoretical structural optimization at B3PW91/6-311G(2d) [28]. The theoretically-optimized structure of the less hindered model **3'**, which has Me groups instead of Tbb groups, exhibits a completely planar five-membered skeleton with  $C_2$  symmetry. Thus, these structural features observed in **3** could be due to the steric congestion.

In the expectation of obtaining the Ge analogue of **3**, digermadichlorogermane **4**, the reaction of **1** with  $\text{GeCl}_4$  was attempted. As a result, the expected product, **4**, was not obtained, but the 1,2-dichloro-1,2-digermacyclobut-3-ene **5** was obtained as a predominant product even under the conditions of using only a small amount of  $\text{GeCl}_4$  in the dark [29]. In addition, the reaction of **1** with  $\text{CCl}_4$  also furnished the formation of **5** without any formation of the  $\text{CCl}_2$ -insertion product **6**. 1,2-Dichloro-1,2-digermacyclobutene **5** showed considerable stability in the air, and it can object to further purification by silica gel column chromatography. Although the reaction mechanism for the formation of **5** by the reaction of **1** with  $\text{GeCl}_4$  or  $\text{CCl}_4$  was not clear at present, the formation of **5** is most likely interpreted in terms of the double-chlorination of **1** with the elimination of  $\text{ECl}_2$  ( $\text{E} = \text{Ge}$  or  $\text{C}$ ) moiety.

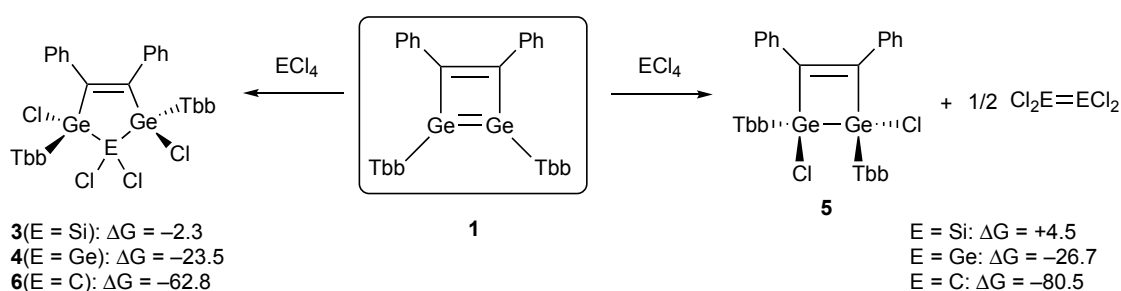


**Figure 1.** Molecular structures of (a) digermadichlorosilane **3** and (b) dichlorodigermacyclobutene **5** with atomic displacement parameters set at 50% probability. All hydrogen atoms and solvent molecules (THF and benzene) were omitted for clarity and only selected atoms are labeled. Selected bond lengths (Å) and angles (deg.): (a) **3**:  $\text{Ge1-Si}$ , 2.3734(16);  $\text{Ge2-Si}$ , 2.3938(15);  $\text{Ge1-Cl1}$ , 2.2094(14);  $\text{Ge2-Cl4}$ : 2.2011(15);  $\text{Si-Cl2}$ , 2.052(2);  $\text{Si-Cl3}$ , 2.053(2);  $\text{Ge1-Si-Ge2}$ , 91.15(5);  $\text{Cl1-Ge1-Si}$ , 90.29(5);  $\text{Cl4-Ge2-Si}$ , 105.40(6);  $\text{Cl2-Si-Cl3}$ , 106.04(9); (b) **5**:  $\text{Ge1-Ge2}$ , 2.4694(6);  $\text{Ge1-Cl1}$ , 2.2098(11);  $\text{Ge2-Cl2}$ , 2.2049(11);  $\text{Ge1-C2}$ , 1.984(4);  $\text{Ge2-C1}$ , 1.996(4);  $\text{C2-Ge1-Ge2}$ , 74.24(13);  $\text{Ge1-Ge2-C1}$ , 73.02(12);  $\text{Ge2-C1-C2}$ , 106.8(3);  $\text{C1-C2-Ge1}$ , 105.6(3).

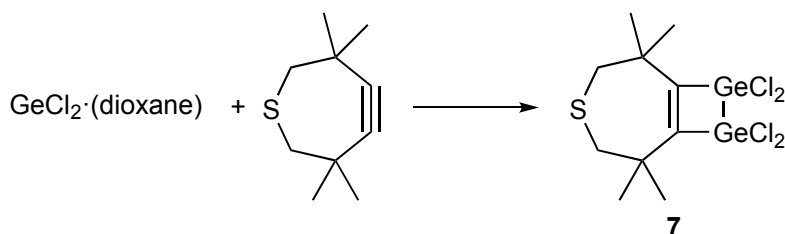
The difference of the products in the reaction of **1** with  $\text{ECl}_4$  ( $\text{E} = \text{Si}$ ,  $\text{Ge}$ , and  $\text{C}$ ) between  $\text{E} = \text{Si}$  and  $\text{E} = \text{Ge}$ ,  $\text{C}$  cases should be of great interest. Although we could not draw a definitive conclusion, we performed the thermodynamic energy calculations (free energies) on the reaction of **1** with  $\text{ECl}_4$  ( $\text{E} = \text{Si}$ ,  $\text{Ge}$ ,  $\text{C}$ ) to give the insertion products, **3**, **4**, and **6**, or the chlorination products, **5** and  $\text{Cl}_2\text{E}$ : (calculated as  $1/2 \text{Cl}_2\text{E} = \text{ECl}_2$ ) at the B3PW91/6-311G(2d) level of theory (Scheme 3) [28]. In the case of  $\text{E} = \text{Si}$ , the formation of **3** should be exothermic by 2.3 kcal/mol, and that of **5** with  $\text{Cl}_2\text{Si} = \text{SiCl}_2$  was estimated as an endothermic reaction by 4.5 kcal/mol. However, in the case of  $\text{E} = \text{Ge}$  or  $\text{C}$ , the formation of **5** with  $\text{Cl}_2\text{E} = \text{ECl}_2$  was thermodynamically favorable ( $\text{E} = \text{Ge}$ :  $\Delta G = -27$  kcal/mol,  $\text{E} = \text{C}$ :  $\Delta G = -81$  kcal/mol) relative to the formation of **4** or **6** ( $\text{E} = \text{Ge}$  (**4**):  $\Delta G = -24$  kcal/mol,  $\text{E} = \text{C}$

(6):  $\Delta G = -63$  kcal/mol). Thus, thermodynamic energy difference between cases of E = Si, Ge, and C could give us some hints on the difference of the reaction products, though the reasonable reaction mechanisms are not clear at present.

The structure of 1,2-dichloro-1,2-digermacyclobut-3-ene **5** was revealed by the X-ray crystallographic analysis. The two Tbb/Cl moieties are oriented in (*E*)-geometries, in the digermacyclobutene skeleton in **5**. The Ge–Ge bond length is 2.4694(6) Å, which is within a range of singly-bonded Ge–Ge distances. The lengths of the two Ge–Cl bonds are almost identical as Ge1–Cl1 = 2.2098(11) Å and Ge2–Cl2 = 2.2049(11) Å, which are similar to those of **3**. The Ge1–C2 and Ge2–C1 (1.984(4), 1.996(4) Å) bond lengths in the digermacyclobutene skeleton of **5** are slightly longer, and shorter relative to those of the only example of the previously reported chlorinated 1,2-digerma-3-cyclobutadiene derivative **7** (Ge–Cl: 2.145(2)–2.150(2), Ge–C: 1.998(6), 2.002(6) Å) (Scheme 4) [30]. Interestingly, reduction of the isolated **5** with lithium naphthalenide was found to reproduce 1,2-digermacyclobutadiene **1** quantitatively, as evidenced by the  $^1\text{H}$  NMR spectra.



**Scheme 3.** Theoretical calculations on  $\Delta G$  values (in kcal/mol) in the reactions of **1** with  $\text{ECl}_4$  (E = Si, Ge, C) to give insertion products (**3**, **4**, **6**) or chlorinated product **5**.



**Scheme 4.** Reported reaction of  $\text{GeCl}_2 \cdot (\text{dioxane})$  with the highly strained alkyne to give the first example of chlorinated 1,2-digerma-3-cyclobutadiene derivative **7** [30].

### 3. Materials and Methods

#### 3.1. General Information

All manipulations were carried out under an argon atmosphere using either a Schlenk line techniques or glove boxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company (Laguna Beach, CA, USA) [31].  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were measured on a JEOL AL-300 spectrometer ( $^1\text{H}$ : 300 MHz,  $^{13}\text{C}$ : 75 MHz,  $^{29}\text{Si}$ : 59 MHz). Signals arising from residual  $\text{C}_6\text{D}_5\text{H}$  (7.15 ppm) in the  $\text{C}_6\text{D}_6$  were used as an internal standard for the  $^1\text{H}$  NMR spectra, and that of  $\text{C}_6\text{D}_6$  (128.0 ppm) for the  $^{13}\text{C}$  NMR spectra, and external  $\text{SiMe}_4$  0.0 ppm for the  $^{29}\text{Si}$  NMR spectra. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF focus-Kci mass spectrometer (on ESI-positive mode). All melting points were determined on a Büchi Melting Point Apparatus M-565 and are uncorrected. 1,2-digermacyclobutadiene **1** was prepared according to literature procedure [24].

### 3.2. Experimental Details

#### 3.2.1. Reaction of 1,2-Tbb<sub>2</sub>-1,2-Digermacyclobutadiene **1** with an Excess of SiCl<sub>4</sub>

A solution of 1,2-Tbb<sub>2</sub>-1,2-digermacyclobutadiene **1** (56.0 mg, 0.046 mmol) in SiCl<sub>4</sub> (1.0 mL, 8.8 mmol, excess) was treated at 55 °C for 48 h, and the color of the dark red solution disappeared. After removal of residual SiCl<sub>4</sub> under the reduced pressure, the residue was recrystallized from THF at room temperature to give compound **3** as colorless crystals in quantitative yield (64.2 mg, 0.046 mmol).

Data for **3**: colorless crystals, m.p. = 68.7–69.7 °C (dec.); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, r.t.): δ 0.11 (s, 36H, SiMe<sub>3</sub>), 0.32 (s, 36 H, SiMe<sub>3</sub>), 1.24 (s, 18H, *t*-Bu), 2.51 (bs, 4H, CH), 6.70–6.76 (m, 2H, ArH), 6.84–6.90 (m, 8H, ArH), 7.22 (d, 4H, *J* = 7.2 Hz, ArH); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 1.80 (SiMe<sub>3</sub>), 2.17 (SiMe<sub>3</sub>), 30.96 (CMe<sub>3</sub>), 30.99 (CH), 34.32 (CMe<sub>3</sub>), 124.20 (ArH), 126.87 (ArH), 127.81 (ArH), 130.97 (ArH), 132.28 (Ar), 140.70 (Ar), 150.13 (Ar), 151.14 (Ar), 162.66 (CAr); <sup>29</sup>Si NMR (59 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 3.61 (SiMe<sub>3</sub>), 3.84 (SiMe<sub>3</sub>), 28.83 (GeSiGe); MS (DART-TOF, positive mode): *m/z* calcd. for C<sub>62</sub>H<sub>109</sub><sup>35</sup>Cl<sub>4</sub><sup>74</sup>Ge<sub>2</sub>Si<sub>9</sub> 1393.3630 ([M + H]<sup>+</sup>), found 1393.3681 ([M + H]<sup>+</sup>).

#### 3.2.2. Reaction of 1,2-Tbb<sub>2</sub>-1,2-Digermacyclobutadiene **1** with an Excess of GeCl<sub>4</sub>

A C<sub>6</sub>D<sub>6</sub> solution of 1,2-Tbb<sub>2</sub>-1,2-digermacyclobutadiene **1** (38.3 mg, 0.0313 mmol) was treated with an excess amount of GeCl<sub>4</sub> (0.3 mL, 2.6 mmol) at room temperature. After stirring of the reaction mixture for 10 min, the solvent and GeCl<sub>4</sub> were removed under reduced pressure. The residue was recrystallized from benzene at room temperature to give compound **5** as main product in 61% yield (24.6 mg, 0.0190 mmol).

Data for **5**: colorless crystals, m.p. 90.4–91.4 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, r.t.): δ 0.13 (s, 36H, SiMe<sub>3</sub>), 0.27 (s, 36 H, SiMe<sub>3</sub>), 1.26 (s, 18H, *t*-Bu), 2.58 (s, 4H, CH), 6.88–6.93 (m, 6H, ArH), 7.00 (t, 4H, *J* = 7.2 Hz, ArH), 7.39 (d, 4H, *J* = 7.2 Hz, ArH); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 1.83 (SiMe<sub>3</sub>), 1.86 (SiMe<sub>3</sub>), 30.26 (CMe<sub>3</sub>), 31.03 (CH), 34.39 (CMe<sub>3</sub>), 124.16 (ArH), 128.00 (ArH), 128.67 (ArH), 129.79 (ArH), 133.71 (Ar), 139.21 (Ar), 150.45 (Ar), 151.29 (Ar), 167.29 (CAr); MS (DART-TOF, positive mode): *m/z* calcd. for C<sub>62</sub>H<sub>109</sub><sup>35</sup>Cl<sub>2</sub><sup>74</sup>Ge<sub>2</sub>Si<sub>8</sub> 1295.4484 ([M + H]<sup>+</sup>), found 1295.4492 ([M + H]<sup>+</sup>).

#### 3.2.3. Reaction of 1,2-Tbb<sub>2</sub>-1,2-Digermacyclobutadiene **1** with an Excess of CCl<sub>4</sub>

A C<sub>6</sub>D<sub>6</sub> solution of 1,2-Tbb<sub>2</sub>-1,2-digermacyclobutadiene **1** (32.9 mg, 0.0269 mmol) was treated with an excess amount of CCl<sub>4</sub> (0.2 mL, 2.1 mmol) at room temperature. After stirring of the reaction mixture for 10 min, the solvent and CCl<sub>4</sub> were removed under reduced pressure. The residue was recrystallized from benzene at room temperature to give compound **3** as main product in 55% yield (22.8 mg, 0.0175 mmol).

### 3.3. Computational Methods

The level of theory and the basis sets used for the structural optimization are contained within the main text. Frequency calculations confirmed minimum energies for all optimized structures. All calculations were carried out using the *Gaussian 09* program package [28]. Computational time was generously provided by the Supercomputer Laboratory in the Institute for Chemical Research of Kyoto University.

### 3.4. X-ray Crystallographic Analysis

Single crystals of [3·(thf)] and [5·2(benzene)] were obtained from recrystallization from THF and benzene, respectively. Intensity data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo Optics using Mo Kα radiation (λ = 0.71075 Å). The structures were solved by a direct method (SIR2004 [32]) and refined by a full-matrix least square method on *F*<sup>2</sup> for all reflections (SHELXL-97 [33]). All hydrogen atoms were placed using AFIX instructions, while all

other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC; under reference numbers: CCDC-1578241 and 1578242 for [3·(thf)] and [5·2(benzene)], respectively) and can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. X-ray crystallographic data for [3·(thf)] and [5·2(benzene)]. Data for [3·(thf)] ( $C_{66}H_{116}Cl_4Ge_2OSi_9$ ):  $M = 1465.37$ , triclinic,  $P\bar{1}$  (no.2),  $a = 12.6367(7)$  Å,  $b = 16.9170(6)$  Å,  $c = 20.4887(10)$  Å,  $\alpha = 91.3815(14)^\circ$ ,  $\beta = 105.252(2)^\circ$ ,  $\gamma = 109.642(3)^\circ$ ,  $V = 3949.2(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc.} = 1.232$  g·cm<sup>−3</sup>,  $\mu = 1.070$  mm<sup>−1</sup>,  $2\theta_{max} = 51.0^\circ$ , measd./unique refls. = 83580/14641 ( $R_{int.} = 0.1095$ ), param = 767,  $GOF = 1.117$ ,  $R_1 = 0.0683/0.1122$  [ $I > 2\sigma(I)$ /all data],  $wR_2 = 0.1188/0.1359$  [ $I > 2\sigma(I)$ /all data], largest diff. peak and hole 1.681 and  $-0.592$  e·Å<sup>−3</sup> (CCDC-1578241). Data for [5·2(benzene)] ( $C_{74}H_{120}Cl_2Ge_2Si_8$ ):  $M = 1450.49$ , triclinic,  $P\bar{1}$  (no.2),  $a = 11.6792(2)$  Å,  $b = 15.7581(3)$  Å,  $c = 24.7906(5)$  Å,  $\alpha = 76.2640(10)^\circ$ ,  $\beta = 88.0800(10)^\circ$ ,  $\gamma = 70.2510(10)^\circ$ ,  $V = 4165.89(14)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc.} = 1.156$  g·cm<sup>−3</sup>,  $\mu = 0.937$  mm<sup>−1</sup>,  $2\theta_{max} = 50.0^\circ$ , measd./unique refls. = 64887/14555 ( $R_{int.} = 0.0810$ ), param = 805,  $GOF = 1.289$ ,  $R_1 = 0.0637/0.0804$  [ $I > 2\sigma(I)$ /all data],  $wR_2 = 0.1247/0.1311$  [ $I > 2\sigma(I)$ /all data], largest diff. peak and hole 0.983 and  $-0.689$  e·Å<sup>−3</sup> (CCDC-1578242).

#### 4. Conclusions

It was demonstrated that 1,2-digermacyclobutadiene **1** could work as a bis-germylene building block ( $>Ge: + :Ge<$ ) towards double Si–Cl activation in the reaction of **1** with SiCl<sub>4</sub> to give the halogenated oligometallane, bis(chlorogermyl)dichlorosilane **3**. Conversely, GeCl<sub>4</sub> and CCl<sub>4</sub> were found to work as double-chlorinating reagents towards **1** giving dichlorodigermacyclobutene **5**. Thus, **1** would be an interesting building block for oligohalo-oligometallanes.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2304-6740/5/4/79/s1](http://www.mdpi.com/2304-6740/5/4/79/s1). Cif and cif-checked files. Figures S1–S5.

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**Author Contributions:** Takahiro Sasamori and Norihiro Tokitoh conceived and designed the experiments; Tomohiro Sugahara performed the experiments; Takahiro Sasamori and Tomohiro Sugahara performed the XRD analysis and wrote the paper; and Takahiro Sasamori performed theoretical calculations.

**Conflicts of Interest:** The authors declare no conflict of interest.

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