# **ORGANOMETALLICS**

# 1,2-Bis(ferrocenyl)digermene: A $d-\pi$ Electron System Containing a Ge=Ge Unit

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**Supporting Information** 

**ABSTRACT:** The synthesis and structural analysis of the 1,2bis(ferrocenyl)digermene (*E*)-Tip(Fc)Ge=Ge(Fc)Tip (Tip = 2,4,6-triisopropylphenyl, Fc = ferrocenyl), a stable crystalline compound, is reported. In this digermene, two ferrocenyl d electron systems are bridged by a Ge=Ge  $\pi$  spacer. As is evident from X-ray crystallographic, spectroscopic, and electrochemical analysis, this 1,2-bis(ferrocenyl)digermene shows effective d- $\pi$  interaction and the Ge=Ge  $\pi$  bond is stable in the solid state. The Ge=Ge double bond is cleaved at elevated temperatures in the presence of butadiene, with concomitant loss of the  $\pi$  conjugation in the molecule.

The systematic investigation of intramolecular electronic communication between transition-metal centers (d electron systems) via organic  $\pi$ -conjugated spacers is important for the understanding of the fundamental electrochemical processes in multistep redox systems.<sup>1</sup> These  $d-\pi$  electron systems also represent a good model for compounds with mixed-valence oxidation states. Multinuclear ferrocenyl systems with organic  $\pi$ -conjugated spacers such as FcC=CFc,<sup>2</sup>  $Ph(Fc)C=C(Fc)Ph^3$  and  $FcN=NFc^{1b,4}$  (Fc = ferrocenyl) have already attracted considerable interest, due to the extraordinary stability and the characteristic electrochemical properties of the ferrocene redox system. Previously, we have reported the successful synthesis of the stable 1,2-bis-(ferrocenyl)disilene (E)-Tip(Fc)Si=Si(Fc)Tip(1; Tip = 2,4,6-triisopropylphenyl), which is a heavier element analogue of olefins, bridging two ferrocenyl units with a Si=Si  $\pi$  bond.<sup>5</sup> As opposed to olefins, disilenes  $(R_2Si=SiR_2)$  are usually highly reactive and difficult to isolate.<sup>6</sup> By the attachment of bulky substituents such as Tip (kinetic stabilization) and/or by  $\pi$ electron conjugation (thermodynamic stabilization), the reactive Si=Si moiety in 1 can be stabilized sufficiently in order to allow handling under ambient conditions. The electrochemical analysis of 1 showed a stable four-step-fiveelectron redox system with high HOMO and low LUMO levels. The observed HOMO-LUMO gap for the Si=Si  $\pi$ bond was smaller compared to that observed for C=C  $\pi$ bonds,<sup>7</sup> facilitating effective interaction between the two delectron units.<sup>1</sup>

Digermenes (R<sub>2</sub>Ge=GeR<sub>2</sub>), the heavier analogues of olefins and disilenes, are known to exhibit even smaller HOMO– LUMO gaps<sup>8</sup> and should therefore be even better candidates for use as  $\pi$  spacers in d- $\pi$  electron systems. The ability of digermenes to readily undergo controlled retrodimerizations in



solution,<sup>9–11</sup> as well as the ability of the Ge=Ge moiety to respond to external thermal, chemical, and photoinduced stimuli, should moreover result in highly interesting reactivity patterns. In the following, we present the synthesis, structure, and spectroscopic properties of the 1,2-bis(ferrocenyl)-digermene (*E*)-Tip(Fc)Ge=Ge(Fc)Tip (2).

# RESULTS AND DISCUSSION

Ferrocenylgermane **3** was prepared from the reaction of TipGeH<sub>2</sub>Cl with ferrocenyllithium. Bromination of **3** with CBr<sub>4</sub> in C<sub>6</sub>H<sub>6</sub> resulted in the formation of dibromogermane **4**, which was subsequently reduced with KC<sub>8</sub> in THF to give the 1,2-bis(ferrocenyl)digermene **2** as a stable, orange crystalline solid (overall yield 21%, see Scheme 1). Digermene **2** is stable in the solid state (mp 159.4 °C dec), but slow decomposition was observed in solution ( $t_{1/2}$  = ca. 0.5 h at 60 °C in C<sub>6</sub>D<sub>6</sub>), resulting in a complex mixture of products. Interestingly, disilene **1** exhibited much higher thermal stability in toluene- $d_8$  and no decomposition was apparent, even when **1** was heated to 90 °C for 10 days.<sup>5</sup> The high reactivity of the Ge=Ge  $\pi$  bond in digermene **2** is also reflected in its sensitivity toward atmospheric oxygen, resulting in the facile formation of the corresponding 1,3,2,4-dioxadigermetane **5**.<sup>12</sup>

The molecular structure of **2** was obtained from single-crystal X-ray diffraction analysis,<sup>13</sup> showing a center of symmetry in the middle of the Ge=Ge bond (see Figure 1). The Ge=Ge bond length of 2.3320(5) Å is slightly longer than that of Tip<sub>2</sub>Ge=GeTip<sub>2</sub> (6; 2.2130(9) Å).<sup>14</sup> Digermene **2** exhibits a significantly larger trans-bent angle ( $\theta = 43.7^{\circ}$ ) in comparison to those of previously reported tetraaryldigermenes (e.g.,  $\theta =$ 

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Scheme 1. Synthesis of Ferrocenylgermanes 3 and 4 and 1,2-Bis(ferrocenyl)digermene 2



Figure 1. Molecular structure of 1,2-bis(ferrocenyl)digermene 2 (left) and a schematic representation of the Ge=Ge core (right) with experimental and calculated<sup>17</sup> (in parentheses) structural parameters. Thermal displacement ellipsoids are drawn at the 50% probability level, all hydrogen atoms have been omitted for clarity, and selected atoms have been labeled. Selected bond lengths (Å) and angles (deg): Ge1-Ge1', 2.3320(5); Ge1-C1(Fc), 1.935(3); Ge2-C2(Tip), 1.981(2); C1(Fc)-Ge1-Ge1', 114.56(8); C2(Tip)-Ge1-Ge1', 116.49(7); C1(Fc)-Ge1-C2(Tip), 106.78(11).

 $12.3^{\circ}$  in 6).<sup>14</sup> These metric parameters indicate a relatively weak Ge=Ge double bond in 2 and suggest the possibility of thermally controlled dissociation of 2 in solution, to give 2 equiv of the corresponding germylene Tip(Fc)Ge: (7). In the solid-state Raman spectrum of 2, one strong absorption line at 340 cm<sup>-1</sup> was observed for the  $\nu_{GeGe}$  vibration. This value is in good agreement with those for previously reported digermenes (ca.  $300-400 \text{ cm}^{-1}$ ; e.g.  $300 \text{ cm}^{-1}$  for  $Dis_2Ge=GeDis_2$ ),<sup>15</sup> indicating a comparable degree of double-bond character for the Ge=Ge bond in 2. The combined results of the solid-state Raman spectrum (comparable magnitude of the  $\nu_{GeGe}$ vibration) and the X-ray crystallographic analysis (Ge=Ge bond length and trans-bent angle) suggest a weak, but nevertheless distinct, Ge=Ge double bond in 2 in the solid state. The <sup>1</sup>H NMR spectrum of 2 in  $C_6D_6$  was indicative of a symmetric structure. Only one singlet signal for the meta aryl protons of the Tip groups, one septet signal for the ortho benzyl protons of the Tip groups, one singlet for the free Cp groups, and two sets of pseudotriplets for the  $\alpha$  and  $\beta$  protons of the Ge-substituted Cp groups were observed. The presence of two independent doublet signals for the methyl protons of the o-isopropyl groups would support a trans-bent structure for 2, but the assumed trans-bent structure would in turn be inconsistent with equivalent resonances for the  $\alpha$  and  $\beta$  protons of the Ge-substituted Cp groups. This assignment is based on the assumption that facile vertex inversion of the Ge moiety and/or Ge=Ge bond dissociation and subsequent recombination processes (i.e. the equilibrium between digermene 2 and germylenes 7) occur more quickly on the NMR time scale than the rotation of the Tip–Ge bond.<sup>16</sup> The UV–vis spectrum of 2 in hexane showed a strong and broadened absorption between 380 and 500 nm ( $\lambda_{max} = 430$  nm ( $\varepsilon = 17000$  M<sup>-1</sup> cm<sup>-1</sup>), 500 nm (sh)). TD-DFT calculations for 2 suggested a combination of several MLCT modes to be responsible for the observed absorption.<sup>17</sup> The calculation results furthermore suggested effective interaction for the d electrons of the ferrocenyl units with the  $\pi$  electrons of the Ge=Ge moiety in the form of the HOMO-LUMO transition (d- $\pi^*$  transition). The HOMO orbital contains predominantly contributions from Fe d orbitals and minor contributions from the Cp  $\pi$  orbital, whereas the LUMO orbital contains predominantly contributions from the Ge=Ge  $\pi^*$  orbital and the Cp  $\pi$  orbital. The <sup>1</sup>H NMR and UV-vis spectra of **2** at slightly elevated temperatures ( $T \le 70$ °C) were almost identical with those measured at ambient temperature. A concentration increase of germylene 7, as a result of the thermally induced dissociation of the Ge=Ge double bond in 2, can accordingly be neglected.



Figure 2. Cyclic voltammograms of 1,2-bis(ferrocenyl)digermene 2: (a) oxidation region (2 mM, 0.1 M  $[(n-Bu)_4N][PF_6]$  in THF); (b) reduction region (2 mM, 0.1 M  $[(n-Bu)_4N][B(C_6F_5)_4]$  in o-dichlorobenzene).

The cyclic voltammogram of 2 exhibited one reversible redox couple in the reduction region at  $E_{1/2} = -2.27$  V (1e). The silicon analogue 1 showed, in contrast, two reversible redox couples at  $E_{1/2} = -2.64$  (2e) and -3.09 V (1e) V ( $E_{1/2}$  vs FcH/  $FcH^+$  in THF with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) (see Figure 2). The significantly lower reduction potential of 2 relative to 1 suggests a lower LUMO level of the Ge=Ge  $\pi$  bond with respect to the LUMO level of the corresponding Si=Si  $\pi$  bond.<sup>18</sup> In the oxidation region, a two-step reversible redox couple at  $E_{1/2}$  = -0.41 (1e) and +0.03 V (1e) ( $E_{1/2}$  vs FcH/FcH<sup>+</sup> in odichlorobenzene and 0.1 M  $Bu_4NB(C_6F_5)_4$ ) was observed for 2, suggesting a desirable coupling of the two ferrocenyl moieties through the Ge=Ge  $\pi$  bond. Interestingly, the first oxidation potential was much lower than that of ferrocene or disilene 1, which also showed two redox couples in the oxidation region at  $E_{1/2}$  = +0.05 (1e) and +0.24 V (1e).<sup>5</sup> The separation of the half-wave oxidation potentials  $\Delta E_{1/2}$  is thereby indicative of the magnitude of the electronic interaction between two redox centers.  $\Delta E_{1/2}$  is significantly larger in 2 ( $\Delta E_{1/2} = 0.44$  V) compared to those in disilene 1 ( $\Delta E_{1/2} = 0.19$  V)<sup>5</sup> and (*E*)-Ph(Fc)C=C(Fc)Ph ( $\Delta E_{1/2} = 0.31$  V),<sup>3c</sup> respectively, reflecting again an increased degree of  $d-\pi$  electron conjugation in 2. In conclusion, the electrochemical analysis indicated that 2 is a very effective  $d-\pi$  electron system with stable, multistep redox behavior. Moreover, a consolidated analysis of the photophysical and electrochemical properties suggested an effective overlapping of d and  $\pi^*$  orbitals in 2.

We turned our attention then to the chemical reactivity of the Ge=Ge  $\pi$  bond in **2**, which represents a heavier element homologue of olefins. Since digermenes are known to react easily with elemental chalcogens with formation of the corresponding heterocycles,<sup>19,9g</sup> we were interested in the reactions of **2** with O<sub>2</sub>, S<sub>8</sub>, and Se (see Scheme 2 and Figure 3).

Scheme 2. Chalcogenation Reactions of 2 with Formation of 8-10



Figure 3. Molecular structures of 1,3,2,4-dioxadigermetane 5 (a), selenadigermirane 8 (b), thiadigermirane 9 (c), and 1,2,3,4-dithiadigermirane 10 (d). Thermal displacement ellipsoids are set at the 50% probability level, all hydrogen atoms have been omitted for clarity, and selected atoms have been labeled. Selected bond lengths (Å) and angles (deg) are as follows. 5: Ge–O, 1.8169(11), 1.8153(11); Ge–O–Ge, 92.82(5); O–Ge–O, 87.18(5). 8: Ge–Se, 2.3961(4), 2.4017(4); Ge–Ge, 2.3701(4); Ge–Se–Ge, 59.207(12); Se–Ge–Ge, 60.513(12), 60.280(12). 9: Ge–S, 2.2740(6), 2.2752(6); Ge–Ge, 2.3588(3); Ge–S–Ge, 62.463(17); S–Ge–Ge, 58.743(16), 58.794(16). 10: Ge–S, 2.2856(5), 2.2871(5); Ge–Ge, 2.4730(3); S–S, 2.0995(7); Ge–S–S, 90.75(2), 91.10(2); Ge–Ge–S, 82.292(15), 81.923(15).

Exposure of a benzene solution of 2 to atmospheric oxygen resulted in the formation of 1,3,2,4-dioxadigermetane 5, probably via the intermediary 1,2,3,4-dioxadigermetane and subsequent isomerization.<sup>9c,f</sup> The corresponding reaction of 2 with elemental selenium was found to proceed readily and afforded selenadigermirane 8 in high yield (94%). The analogous sulfurization of 2 with S<sub>8</sub> resulted in the formation of both thiadigermirane 9 and 1,2,3,4-dithiadigermetane 10, whereas no evidence for the formation of 1,3,2,4-dithiadiger

metane 11 could be observed. This result is in sharp contrast to previously reported sulfurization reactions of digermenes with  $S_{s_1}$  which typically result in the formation of the corresponding thiadigermirane and/or 1,3,2,4-dithiadigermetane.<sup>19</sup> In these cases, the 1,3,2,4-dithiadigermetane is most likely formed via a head-to-tail dimerization of the intermediary germanethione  $(R_2Ge=S)$ . We carried out theoretical calculations,<sup>17</sup> which suggested both thiadigermirane 9 and 1,2,3,4-dithiadigermetane 10 to be the kinetic rather than the thermodynamic products. The sulfurization reaction of 2 to give 11 was found to be highly exothermic (76.4 kcal/mol), relative to those resulting in the formation of 9 and 10 (39.9 and 39.4 kcal/mol. respectively). All attempts to induce thermal interconversion between 9 and 10 (i.e., sulfurization of 9 and/or desulfurization of 10), as well as the thermal isomerization of 10 to obtain 11. were unsuccessful, supporting the direct reaction of digermene 2 (not germylene 7) with  $S_8$  to give 9 and 10. We wish to point out that the activation energy barrier for the isomerization of 10 into the thermally stable isomer 11 is, as a result of the steric demand of the ferrocenyl substituents, probably very high. The formation of 8-10 strongly suggests the interpretation of 2 in solution and at room temperature in terms of a digermene, not a germylene.

Heating a benzene solution of **2** to reflux for 1 h in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene resulted in the formation of germolene  $12^{9f,19-21}$  and germylgermolene  $13^{11,21}$  in 55% and 36% yields, respectively (see Scheme 3 and Figure 4). The [2 + 4] cycloaddition

Scheme 3. [1 + 4] Cycloaddition Reactions of 2, 7, and 15 with 2,3-Dimethyl-1,3-butadiene Compounds



Figure 4. Molecular structures of germolene 12 (a) and germylgermolene 13 (b). Only one of the two independent molecules of 13 per unit cell is shown here. Thermal displacement ellipsoids are set at the 50% probability level, all hydrogen atoms have been omitted for clarity, and selected atoms have been labeled. Selected bond lengths (Å) for 12: Ge–C1, 1.968(2); C1–C2, 1.517(3); C2–C3, 1.335(3); C3–C4, 1.514(3); C4–Ge, 1.9716(19). Selected bond lengths (Å) for 13: Ge1–Ge2, 2.4665(15), 2.4605(13); Ge1–C1, 1.958(8), 1.974(9); C1–C2, 1.503(12), 1.527(11); C2–C3, 1.319(12), 1.344(12); C3–C4, 1.540(12), 1.494(12); C4–Ge1, 1.967(9), 1.970(9).

product digermacyclohexene 14 could not be observed.<sup>22</sup> The generation of 12 and 13 is tentatively explained here by an initial nucleophilic attack of one C=C double bond of butadiene toward the low-lying LUMO orbital of the Ge=Ge moiety. The weakening of the Ge=Ge double bond subsequently leads to either expulsion of 1 equiv of 7 with formation of 12 or a thermally induced 1,2-migration of one of the Tip groups (leading to 1 equiv of 13).<sup>23</sup> Heating  $C_6 D_6$ solutions of germolene 12 or germylgermolene 13 to 80 °C in the presence of an excess amount of isoprene did not initiate any further reactions. The regeneration of germylene 7 from 12 or 13 via a potential retro-[1 + 4] cvcloaddition was not observed. Exposing a  $C_6D_6$  solution of 2 in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene to photoirradiation did not induce any reaction, demonstrating the extraordinary stability of 2 toward UV light. In conclusion, 2,3-dimethyl-1,3-butadiene can be used as an effective thermal trigger to scissor the  $d-\pi$  electron system in 2. In contrast, reactions of 1,2-bis(ferrocenyl)disilene 1 with excess 2,3dimethyl-1,3-butadiene afforded under similar reaction conditions complex mixtures from which we were unable to identify any distinct products. The cleavage of digermene 2, induced by the addition of 2,3-dimethyl-1,3-butadiene, can therefore be directly associated with the intrinsic nature of the Ge=Ge  $\pi$  bond.

We have shown here, in conclusion, the synthesis and characterization of 1,2-bis(ferrocenyl)digermene 2, which contains a highly unusual  $d-\pi$  electron system. Digermene 2 exhibits a stable, three-step redox couple in solution, and the thermal reaction with 2,3-dimethyl-1,3-butadiene leads to the corresponding [1 + 4] cycloaddition products with cleavage of the Ge=Ge  $\pi$ -bond.

# EXPERIMENTAL SECTION

General Procedures and Instrumentation. Unless otherwise stated, all experiments were performed under a dry argon atmosphere free of oxygen. All solvents were purified by standard methods and/or the use of "The Ultimate Solvent System" (Glass Contour Co.).<sup>24</sup> <sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75 MHz) and <sup>77</sup>Se NMR (76 MHz) spectra were measured in  $C_6D_6$  with a JEOL JNM AL-300 spectrometer, referenced to residual protic impurities of the NMR solvent (C<sub>6</sub>D<sub>5</sub>H 7.15 ppm for <sup>1</sup>H NMR spectra) or the NMR solvent itself ( $C_6D_6$  128 ppm for <sup>13</sup>C NMR spectra). The signal of Ph<sub>2</sub>Se<sub>2</sub> (460 ppm) was used as an external standard for the measurements of <sup>77</sup>Se NMR spectra. The multiplicity of signals in the <sup>13</sup>C NMR spectra was determined by DEPT techniques. High-resolution mass spectrometry data were obtained on a JEOL JMS-700 spectrometer (FAB) or on a Bruker microTOF (APPI-TOF). UV/vis spectra were measured on a JASCO Ubest V-570 instrument. GPLC (gel permeation liquid chromatography) purifications were performed on an LC-908 or LC-918 instrument (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent toluene). Electrochemical experiments were carried out with an ALS 600A potentiostat/galvanostat using a glassy-carbon-disk working electrode, a Pt-wire counter electrode, and an Ag/0.01 M AgNO3 reference electrode. Measurements were carried out with scan rates of 10 mV s<sup>-1</sup>, at ambient temperature in an argon-filled glovebox using odichlorobenzene or THF solutions, containing 0.1 M  $[(n-Bu)_4N][B (C_6F_5)_4$ ] or  $[(n-Bu)_4N][PF_6]$  as the supporting electrolyte. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Theoretical calculations were conducted using electronic structure programs of the Gaussian 03 series.<sup>25</sup> Geometries were optimized with density functional theory at the B3PW91 level using the basis sets of 6-31+G(2d) (for Ge), 6-31G(d) (for C, H), and

DZVP (for Fe).<sup>26</sup> Frequency calculations confirmed minimum energies for the optimized structures. Computation time was provided from the Supercomputer Laboratory at the Institute for Chemical Research, Kyoto University. 2,4,6-Triisopropylphenylchlorogermane (TipGeH<sub>2</sub>Cl) was prepared according to literature procedures.<sup>27</sup>

Synthesis of Ferrocenyl-2,4,6-triisopropylphenylgermane (3). A solution of ferrocene (3.07 g, 16.5 mmol) and potassium tertbutoxide (0.17 g, 1.5 mmol) in THF (120 mL) was cooled to -78 °C, before t-BuLi (1.57 M pentane solution, 21 mL, 33 mmol) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h, warmed to room temperature, where stirring was continued for 1 h before the solution was cooled to -78 °C again. This solution containing the resulting lithioferrocene was transferred via cannula to a solution of 2,4,6-triisopropylphenylchlorogermane (4.70 g, 15.0 mmol)^{26} in  $\text{Et}_2\text{O}$ (60 mL) at -78 °C. After it was stirred at -78 °C for 1 h, the solution was warmed to room temperature, stirred for 10 h, and then quenched by the addition of saturated aqueous  $\mathrm{NH}_4\mathrm{Cl}$  solution. The aqueous phase was extracted with Et<sub>2</sub>O, and the combined organic phases were dried over MgSO4, filtered, and evaporated in vacuo. The obtained residue was purified by column chromatography (hexane/Et<sub>2</sub>O) to give TipFcGeH<sub>2</sub> (3; 4.88 g, 10.5 mmol, 70%). 3: orange solid; mp 56.8–58.7 °C. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6D_6$ ):  $\delta$  1.22 (d, 6H, p-i-Pr-Me,  ${}^{3}J(H-H) = 6.9$  Hz), 1.29 (d, 12H, o-i-Pr-Me,  ${}^{3}J(H-H) = 6.8 \text{ Hz}), 2.79 \text{ (sept, 1H, } p-i-Pr-CH, {}^{3}J(H-H) = 6.9 \text{ Hz}),$ 3.54 (sept, 2H, *o-i*-Pr-CH  ${}^{3}J(H-H) = 6.8$  Hz), 4.05 (s, 5H, Cp), 4.12 (pseudo-t, 2H, Cp), 4.17 (pseudo-t, 2H, Cp), 5.33 (s, 2H, GeH), 7.15 (s, 2H, Ar-H). <sup>13</sup>C NMR (75 MHz, room temperature,  $C_6D_6$ ):  $\delta$  24.20 (q), 24.70 (q), 34.81 (d), 34.90 (d), 68.25 (s), 69.13 (d), 70.77 (d), 74.28 (d), 121.26 (d), 130.28 (s), 150.49 (s), 154.64 (s), HRMS (FAB): m/z calcd for  $C_{25}H_{34}{}^{56}Fe^{74}Ge$  464.1228 ([M]<sup>+</sup>), found 464.1221 ([M]<sup>+</sup>). Anal. Calcd for C<sub>25</sub>H<sub>34</sub>FeGe: C, 64.85; H, 7.40. Found: C, 65.08; H, 7.53.

Synthesis of Ferrocenyl-2,4,6-triisopropylphenyldibromogermane (4). A solution of ferrocenylgermane 3 (2.32 g, 5.00 mmol) and CBr<sub>4</sub> (4.97 g, 15.0 mmol) in benzene (50 mL) was heated to reflux for 1 h. After the mixture was cooled to ambient temperature, all volatiles were removed under reduced pressure. The reaction mixture was extracted with hexane and filtered through a pad of Celite, and the filtrate was evaporated in vacuo. The obtained residue was purified by GPLC (toluene) to give TipFcGeBr<sub>2</sub> (4; 2.13 g, 3.43 mmol, 59%). 4: yellow crystals; mp 146.9-148.3 °C. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6D_6$ ):  $\delta$  1.12 (d, 6H, *p-i*-Pr-Me, <sup>3</sup>J(H–H) = 6.9 Hz), 1.22 (d, 12H, *o-i*-Pr-Me,  ${}^{3}J(H-H) = 6.7$  Hz), 2.66 (sept, 1H, p-*i*-Pr-CH,  ${}^{3}J(H-H) = 6.9$  Hz), 3.93 (sept, 2H, *o*-*i*-Pr-CH,  ${}^{3}J(H-H) =$ 6.7 Hz), 4.15 (pseudo-t, 2H, Cp), 4.31 (s, 5H, Cp), 4.44 (pseudo-t, 2H, Cp), 7.08 (s, 2H, Ar-H). <sup>13</sup>C NMR (75 MHz, room temperature,  $C_6 D_6$ :  $\delta$  23.83 (q), 25.00 (q), 33.22 (d), 34.56 (d), 70.86 (d), 71.06 (d), 73.11 (d), 84.87 (s), 123.01 (d), 133.94 (s), 152.73 (s), 154.39 (s). HRMS (EI): m/z calcd for  $C_{25}H_{32}Br_2^{56}Fe^{74}Ge$  619.9430 ([M]<sup>+</sup>), found 619.9435 ([M]<sup>+</sup>). Anal. Calcd for C<sub>25</sub>H<sub>32</sub>Br<sub>2</sub>FeGe: C, 48.37; H, 5.20. Found: C, 48.60; H, 5.30.

Synthesis of (E)-1,2-Bis(ferrocenyl)-1,2-bis(2,4,6triisopropylphenyl)digermene (2).  $KC_8$  (222 mg, 1.64 mmol) was added to a solution of 4 (500 mg, 0.805 mmol) in THF (20 mL) at -78 °C. After the suspension was stirred at -78 °C for 1 h, the reaction mixture was warmed to -50 °C and stirred for 30 min at this temperature. After all volatiles were removed under reduced pressure at room temperature, the residue was taken up in hexane and filtered through a pad of Celite. All volatiles were removed from the filtrate in vacuo, and the resulting residue was purified by recrystallization from hexane to give Tip(Fc)Ge=Ge(Fc)Tip (2; 189 mg, 0.205 mmol, 51%). 2: orange crystals; mp 159.4 °C dec. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6D_6$ ):  $\delta$  1.28 (d, 12H, *p-i*-Pr-Me,  ${}^{3}J(H-H) = 6.9$  Hz), 1.47 (d, 12H, *o-i*-Pr-Me,  ${}^{3}J(H-H) = 6.8$  Hz), 1.51 (d, 12H, *o-i*-Pr-Me,  ${}^{3}J(H-H) = 6.8 \text{ Hz}$ , 2.89 (sept, 2H, *p-i*-Pr-CH,  ${}^{3}J(H-H) = 6.9 \text{ Hz}$ ), 3.93 (pseudo-t, 4H, Cp), 3.95 (s, 10H, Cp), 3.99 (sept, 4H, o-i-Pr-CH), 4.00 (pseudo-t, 4H, Cp), 7.36 (s, 4H, Ar-H); <sup>13</sup>C NMR (75 MHz, room temperature, C<sub>6</sub>D<sub>6</sub>): 24.26 (q), 24.29 (q), 26.26 (q), 34.80 (d), 38.32 (d), 68.74 (d), 71.28 (d), 73.85 (d), 78.38 (s), 121.50 (d), 140.08 (s), 150.77 (s), 154.91 (s); HRMS (ESI TOF): *m/z* calcd

#### Organometallics

for  $C_{50}H_{65}{}^{56}Fe_2{}^{74}Ge_2$  923.2235 ([M + H]+), found: 923.2208 ([M + H]+).

Reaction of (E)-1,2-Bis(ferrocenyl)-1,2-bis(2,4,6triisopropylphenyl)digermene (2) with Atmospheric Oxygen. At room temperature, a solution of 2 (20.4 mg, 22.1  $\mu$ mol) in benzene (5 mL) was exposed to air through a tube filled with CaCl\_2. An instant color change of the solution to yellow was observed. After removal of all volatiles, the crude mixture was recrystallized from hexane to give 1,3,2,4-dioxadigermetane 5 (8.4 mg, 8.8  $\mu$ mol, 40%). 5: yellow crystals; mp 150.1–151.3 °C. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6D_6$ ):  $\delta$  1.20 (d, 12H, *p-i*-Pr-Me, <sup>3</sup>*J*(H–H) = 7.0 Hz), 1.34 (d, 12H, *o-i*-Pr-Me,  ${}^{3}J(H-H) = 6.8$  Hz), 1.64 (d, 12H, *o-i*-Pr-Me,  ${}^{3}J(H-H) = 6.8$  Hz), 2.79 (sept, 2H, *p-i*-Pr-CH,  ${}^{3}J(H-H) = 7.0$  Hz), 4.03 (sept, 4H, *o-i*-Pr-CH,  ${}^{3}I(H-H) = 6.8$  Hz), 4.04 (pseudo-t, 4H), 4.19 (s, 10H, Cp), 4.23 (pseudo-t, 4H), 7.30 (s, 4H, Ar-H). <sup>13</sup>C NMR (75 MHz, room temperature, C<sub>6</sub>D<sub>6</sub>): 24.08 (q), 25.56 (q), 25.65 (q), 34.77 (d), 34.89 (d), 69.08 (d), 71.21 (d), 72.99 (d), 74.18 (s), 121.85 (d), 133.11 (s), 151.85 (s), 155.16 (s). HRMS (EI): m/z calcd for C<sub>50</sub>H<sub>64</sub><sup>56</sup>Fe<sub>2</sub><sup>74</sup>Ge<sub>2</sub>O<sub>2</sub> 956.2054 ([M]<sup>+</sup>), found 956.2003 ([M]<sup>+</sup>).

Reaction of (E)-1,2-Bis(ferrocenyl)-1,2-bis(2,4,6triisopropylphenyl)digermene (2) with Elemental Selenium. At room temperature, elemental selenium (17.7 mg, 22.4  $\mu$ mol) was added to a solution of 2 (20.6 mg, 22.3  $\mu$ mol) in benzene (5 mL) and the reaction mixture was stirred for 1 h. After removal of all volatiles, the crude mixture was purified by GPLC (toluene) to give the corresponding selenadigermirane 8 (20.9 mg, 20.9  $\mu$ mol, 94%). 8: orange crystals; mp 112.5 °C dec. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6 D_6$ ):  $\delta$  1.18 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0$  Hz), 1.21  $(d, 6H, i-Pr-Me, {}^{3}J(H-H) = 6.9 Hz), 1.22 (d, 6H, i-Pr-Me, {}^{3}J(H-H))$ = 7.0 Hz), 1.23 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H)$  = 7.0 Hz), 1.57 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0$  Hz), 1.81 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H) = 6.9$  Hz), 2.81 (sept, 2H, *i*-Pr-CH, <sup>3</sup>J(H-H) = 7.0 Hz), 3.65 (sept, 2H, *i*-Pr-CH,  ${}^{3}J(H-H) = 7.0 \text{ Hz}$ , 3.83–3.85 (m, 2H, Cp), 3.87–3.89 (m, 2H, Cp), 3.90-3.93 (m, 2H, Cp), 4.03-4.05 (m, 2H, Cp), 4.20 (s, 10H, Cp), 4.67 (sept, 2H, *i*-Pr-CH,  ${}^{3}J(H-H) = 7.0$  Hz), 7.16 (d, 2H, Ar-H,  ${}^{4}J(H-H) = 1.5 \text{ Hz}$ , 7.31 (d, 2H, Ar-H,  ${}^{4}J(H-H) = 1.5 \text{ Hz}$ ).  ${}^{13}C$ NMR (75 MHz, room temperature, C<sub>6</sub>D<sub>6</sub>): δ 24.07 (q), 24.10 (q), 24.17 (q), 25.37 (q), 26.26 (q), 26.36 (q), 34.64 (d), 36.81 (d), 37.72 (d), 69.20 (d), 69.94 (d), 70.65 (d), 72.23 (d), 74.75 (d), 75.10 (s), 121.24 (d), 122.94 (d), 131.61 (s), 151.26 (s), 154.04 (s), 156.13 (s).  $^{77}\text{Se}$  NMR (76 MHz, room temperature, C\_6D\_6):  $\delta$  –331.0. HRMS (EI): m/z calcd for  $C_{50}H_{64}^{56}Fe_2^{74}Ge_2^{80}Se$  1004.1326 ([M]<sup>+</sup>), found 1004.1354 ([M]<sup>+</sup>). Anal. Calcd for C<sub>53</sub>H<sub>71</sub>Fe<sub>2</sub>Ge<sub>2</sub>Se: C, 60.97; H, 6.85. Found: C, 60.67; H, 6.89.

Reaction of (E)-1,2-Bis(ferrocenyl)-1,2-bis(2,4,6triisopropylphenyl)digermene (2) with Elemental Sulfur (S<sub>8</sub>). At room temperature, elemental sulfur (5.9 mg, 23  $\mu$ mol) was added to a solution of digermene 2 (20.3 mg, 22.0  $\mu$ mol) in benzene (5 mL) and the reaction mixture was stirred for 30 min. After removal of all volatiles, the crude mixture was purified by GPLC (toluene) to give a mixture of thiadigermirane 9 (54%, as evident from the <sup>1</sup>H NMR spectrum) and 1,2,3,4-dithiadigermetane 10 (40%, as evident from the <sup>1</sup>H NMR spectrum). Product separation and purification was achieved by GPLC and subsequent recrystallization from hexane to give small amounts of compounds 9 and 10 in the form of single crystals. 9: orange crystals; mp 118.8-120.1 °C. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6D_6$ ):  $\delta$  1.22 (d, 18H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0$  Hz), 1.23 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0$  Hz), 1.58 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0 \text{ Hz}$ , 1.83 (d, 6H, *i*-Pr-Me,  ${}^{3}J(H-H) = 6.8 \text{ Hz}$ ), 2.81 (sept, 2H, i-Pr-CH, <sup>3</sup>J(H-H) = 7.0 Hz), 3.67 (sept, 2H, i-Pr-CH,  ${}^{3}J(H-H) = 7.0 \text{ Hz}$ , 3.81-3.84 (m, 2H, Cp), 3.85-3.88 (m, 2H, Cp), 3.89-3.92 (m, 2H, Cp), 4.00-4.03 (m, 2H, Cp), 4.24 (s, 10H, Cp), 4.59 (sept, 2H, *i*-Pr-CH  ${}^{3}J(H-H) = 6.8$  Hz), 7.17 (d, 2H, Ar-H,  ${}^{4}J(H-H) = 1.7$  Hz), 7.32 (d, 2H, Ar-H,  ${}^{4}J(H-H) = 1.7$  Hz).  ${}^{13}C$ NMR (75 MHz, room temperature, C<sub>6</sub>D<sub>6</sub>): δ 24.10 (q), 24.11 (q), 24.34 (q), 25.21 (q), 25.75 (q), 26.52 (q), 34.66 (d), 36.51 (d), 37.43 (d), 69.06 (d), 69.99 (d), 70.86 (d), 72.15 (d), 74.55 (d), 75.99 (s), 121.35 (d), 122.76 (d), 132.49 (s), 151.32 (s), 154.23 (s), 155.94 (s). HRMS (EI<sup>+</sup>): m/z calcd for  $C_{50}H_{64}^{-56}Fe_2^{-74}Ge_2^{-32}S$  956.1851 ([M]<sup>+</sup>),

found 956.1815 ([M]<sup>+</sup>). Anal. Calcd. for  $C_{50}H_{64}Fe_2Ge_2S$ : C, 62.94; H, 6.76. Found: C, 62.68; H, 6.96. **10**: orange crystals, mp 96.2–97.1 °C. <sup>1</sup>H NMR (300 MHz, 70 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.26 (d, 6H, *p*-*i*-Pr-Me, <sup>3</sup>*J*(H–H) = 7.0 Hz), 1.27 (d, 6H, *p*-*i*-Pr-Me, <sup>3</sup>*J*(H–H) = 7.0 Hz), 1.27 (d, 6H, *p*-*i*-Pr-Me, <sup>3</sup>*J*(H–H) = 7.0 Hz), 1.12–1.59 (br, 24H, *i*-Pr-Me), 2.86 (pseudosept, *p*-*i*-Pr-CH, 2H), 3.97–4.02 (m, Cp, 6H), 4.19 (s, Cp, 10H), 4.33–4.36 (m, Cp, 2H), 7.25 (s, Ar-H, 4H), Signals for *o*-*i*-Pr-CH (4H) were not observed probably due to extensive broadening. <sup>13</sup>C NMR (75 MHz, 70 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  24.00 (q), 24.02 (q), 25.25 (q), 27.06 (q), 34.56 (d), 35.42 (d), 69.14 (d), 69.80 (d), 71.12 (d), 73.48 (d), 75.62 (d), 80.71 (s), 122.49 (d), 132.65 (s), 151.07 (s), 155.60 (s). HRMS (FAB<sup>+</sup>): *m/z* calcd for C<sub>50</sub>H<sub>64</sub><sup>56</sup>Fe<sub>2</sub><sup>74</sup>Ge<sub>2</sub><sup>32</sup>S<sub>2</sub> 988.1594 ([M]<sup>+</sup>), found 988.1625 ([M]<sup>+</sup>). Anal. Calcd for C<sub>50</sub>H<sub>64</sub>Fe<sub>2</sub>Ge<sub>2</sub>S<sub>2</sub>: C, 60.90; H, 6.54. Found: C, 60.90; H, 6.76.

Reaction of (E)-1,2-Bis(ferrocenyl)-1,2-bis(2,4,6triisopropylphenyl)digermene (2) with 2,3-Dimethyl-1,3-butadiene. 2,3-Dimethyl-1,3-butadiene (0.27 mL, 2.2 mmol) was added to a solution of 2 (20.3 mg, 22.0  $\mu$ mol) in benzene (5 mL). The reaction mixture was heated to 80 °C for 1 h. After removal of all volatiles, the crude mixture was extracted with hexane and filtered through a pad of Celite and all volatiles were evaporated from the filtrate in vacuo. The residue was purified by GPLC (toluene) to give 1-ferrocenyl-1-(2,4,6triisopropylphenyl)-3,4-dimethyl-3-germolene (12; 13.2 mg, 24.3  $\mu$ mol, 55%) and 1-ferrocenyl-1-{bis(2,4,6-triisopropylphenyl)ferrocenyl}germyl-3,4-dimethyl-3-germolene (13; 7.9 mg, 7.9 µmol, 36%). 12: orange crystals; mp 107.0 °C dec. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6 D_6$ ):  $\delta$  1.25 (d, 6H, *p-i*-Pr-Me,  ${}^{3}J(H-H) = 7.0$ Hz), 1.28 (d, 12H, *o-i*-Pr-Me,  ${}^{3}J(H-H) = 6.8$  Hz), 1.84 (s, 6H, CCH<sub>3</sub>), 2.21 (dd, 4H, CCH<sub>2</sub>,  ${}^{2}J(H-H) = 15.7$  Hz, 33.0 Hz), 2.82 (sept, 1H, p-i-Pr-CH, <sup>3</sup>J(H-H) = 7.0 Hz), 3.28 (sept, 2H, o-i-Pr-CH,  ${}^{3}J(H-H) = 6.8$  Hz), 4.10 (s, 5H, Cp), 4.12 (pseudo-t, 2H), 4.16 (pseudo-t, 2H), 7.14 (s, 2H, Ar-H). <sup>13</sup>C NMR (75 MHz, room temperature,  $C_6D_6$ ):  $\delta$  19.31 (q), 24.23 (q), 25.49 (q), 30.92 (t), 34.71 (d), 35.35 (d), 68.45 (d), 70.17 (d), 72.84 (d), 76.13 (s), 121.67 (d), 131.05 (s), 134.24 (s), 149.96 (s), 154.67. HRMS (FAB): m/z calcd for C<sub>31</sub>H<sub>42</sub><sup>56</sup>Fe<sup>74</sup>Ge 544.1856 ([M]<sup>+</sup>), found 544.1850 ([M]<sup>+</sup>). Anal. Calcd for C<sub>31</sub>H<sub>42</sub>FeGe: C, 68.55; H, 7.79. Found: C, 68.81; H, 8.03. 13: orange crystals; mp 142.0 °C dec. <sup>1</sup>H NMR (300 MHz, room temperature,  $C_6 D_6$ ):  $\delta$  0.46 (d, 3H, *i*-Pr-Me, <sup>3</sup>*J*(H–H) = 6.4 Hz), 0.54 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 6.4$  Hz), 0.74 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H)$ = 6.8 Hz), 1.17 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H)$  = 7.0 Hz), 1.18 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0 \text{ Hz}$ , 1.22 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0 \text{ Hz}$ ), 1.23 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0$  Hz), 1.25 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 7.0 \text{ Hz}$ , 1.38 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 6.6 \text{ Hz}$ ), 1.44 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H) = 6.7$  Hz), 1.46 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H)$ = 6.3 Hz), 1.47 (d, 3H, *i*-Pr-Me,  ${}^{3}J(H-H)$  = 6.9 Hz), 1.87 (s, 3H, CCH<sub>3</sub>), 1.90 (s, 6H, CCH<sub>3</sub>), 2.26 (m, 2H, CCH<sub>2</sub>), 2.42 (dd, 2H,  $CCH_2$ ,  ${}^2J(H-H) = 17.0$  Hz, 61.3 Hz), 2.72 (sept, 1H, *i*-Pr-CH,  ${}^3J(H-H)$ H) = 6.8 Hz), 2.80 (sept, 1H, *i*-Pr-CH,  ${}^{3}J(H-H) = 7.0$  Hz), 3.20-3.41 (m, 3H, *i*-Pr-CH), 3.53 (sept, 1H, *i*-Pr-CH,  ${}^{3}J(H-H) = 6.6$  Hz), 3.56 (m, 1H, Cp), 3.92 (m, 1H, Cp), 3.977 (s, 5H, Cp), 3.984 (s, 5H, Cp), 4.13 (m, 1H, Cp), 4.23 (m, 1H, Cp), 4.25 (m, 1H, Cp), 4.33 (m, 1H, Cp), 4.38 (m, 1H, Cp), 4.51 (m, 1H, Cp), 6.97 (d, 1H, Ar-H, <sup>4</sup>J(H-H) = 1.7 Hz), 7.00 (d, 1H, Ar-H,  ${}^{4}J(H-H) = 1.7$  Hz), 7.10 (d, 1H, Ar-H,  ${}^{4}J(H-H) = 1.7$  Hz), 7.22 (d, 1H, Ar-H,  ${}^{4}J(H-H) = 1.7$  Hz).  ${}^{13}C$ NMR (75 MHz, room temperature, C<sub>6</sub>D<sub>6</sub>): δ 19.63 (q), 19.69 (q), 23.65 (q), 24.01 (q), 24.14 (q), 24.18 (q), 24.21 (q), 24.25 (q), 25.58 (q), 25.86 (q), 26.29 (q), 26.39 (q), 26.68 (q), 27.25 (q), 29.53 (t), 30.88 (t), 32.67 (d), 34.39 (d), 34.52 (d), 35.10 (d), 35.82 (d), 36.65 (d), 68.63 (d), 69.04 (d), 69.27 (d), 69.79 (d), 70.24 (d), 70.68 (d), 73.31 (d), 73.69 (d), 74.51 (d), 76.33 (d), 77.52 (s), 83.28 (s), 122.02 (d), 122.26 (d), 122.51 (d), 122.89 (d), 132.30 (s), 133.03 (s), 137.59 (s), 140.07 (s), 148.91 (s), 149.53 (s), 152.50 (s), 153.35 (s), 154.40 (s), 154.75 (s). HRMS (FAB): m/z calcd for  $C_{56}H_{74}^{56}Fe_2^{74}Ge_2$ 1006.2942 ([M]<sup>+</sup>), found 1006.2940 ([M]<sup>+</sup>). Anal. Calcd for C56H74Fe2Ge2: C, 66.98; H, 7.43. Found: C, 66.95; H, 7.65.

**Reaction of Germolene 12 with Isoprene.** Isoprene (44  $\mu$ L, 0.44 mmol) was added to a solution of 8 (2.4 mg, 4.4  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub>. The reaction mixture was heated to 80 °C for 36 h. No change was observed in the <sup>1</sup>H NMR spectrum.

**Reaction of Germylgermolene 13 with Isoprene.** Isoprene (5.0  $\mu$ L, 50  $\mu$ mol) was added to a solution of **13** (3.1 mg, 3.1  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub>. The reaction mixture was heated to 80 °C for 4 h. No change was observed in the <sup>1</sup>H NMR spectrum.

Photoirradiation of Digermene 2 in the Presence of 2,3-Dimethyl-1,3-butadiene. 2,3-Dimethyl-1,3-butadiene (15  $\mu$ L, 0.13 mmol) was added to a solution of 2 (5.5 mg, 6.0  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub>. The reaction mixture was exposed to photoirradiation from a mediumpressure Hg lamp at room temperature for 1 h. No change was observed in the <sup>1</sup>H NMR spectrum.

X-ray Diffraction Analysis of 2, 4, 5, 8.0.5C<sub>6</sub>H<sub>14</sub>, 9.0.5C<sub>6</sub>H<sub>14</sub>,  $10 \cdot C_6 H_{14}$ , 12, and  $13 \cdot 0.5 C_6 H_{14}$ . Intensity refraction data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å) for 4, 10 and 12 and on a RIGAKU Saturn70 CCD(system) with VariMax Mo Optic using Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å) for 2, 5, 9, and 13. The data set of 8 was collected on the BL38B1 beamline in Spring-8, using a diffractometer and an ADSC Quantum315 CCD detector (2011A1409). Single crystals suitable for X-ray analysis were obtained either by slow recrystallization from hexane (for 4, 5, 12, and 13) or benzene (5) at room temperature or by recrystallization from hexane at -40 °C (for 2, 8, 9, and 10). Individual crystals were mounted on a glass fiber. Structures were solved by direct methods (SIR-97,<sup>28</sup> SIR-2004,<sup>29</sup> SHELXS-97<sup>30</sup>) and refined by full-matrix least-squares procedures on  $F^2$  for all reflections (SHELXL-97).<sup>29</sup> All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Crystallographic data for the structures reported in this paper are contained in the Supporting Information and have also been deposited with the Cambridge Crystallographic Data Centre under the following reference codes: CCDC-856393 (2), CCDC-856394 (4), CCDC-856395 (5), CCDC-856396  $(8 \cdot 0.5C_6H_{14})$ , CCDC-856397  $(9 \cdot 0.5C_6H_{14})$ , CCDC-856398 (10·C<sub>6</sub>H<sub>14</sub>), CCDC-856399 (12), and CCDC-856400  $(13.0.5C_6H_{14})$ . These can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac. uk/data request/cif.

# ASSOCIATED CONTENT

## **S** Supporting Information

Tables giving X-ray crystallographic data and Cartesian coordinates of the optimized structure of **2** and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

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(12) The formation of 1,3,2,4-dioxadigermetane 5 can be explained by the facile isomerization of the corresponding 1,2,3,4-dioxadigermetane, which is generated initially from the addition of aerobic oxygen onto the Ge=Ge  $\pi$ -bond of 2.<sup>9c,f</sup>

(13) Crystallographic data of the compounds described here are shown in the Supporting Information.

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