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# Reaction of [Tris(trimethylsilyl)methyl]tribromogermane with Magnesium: Generation of a Bromogermylene

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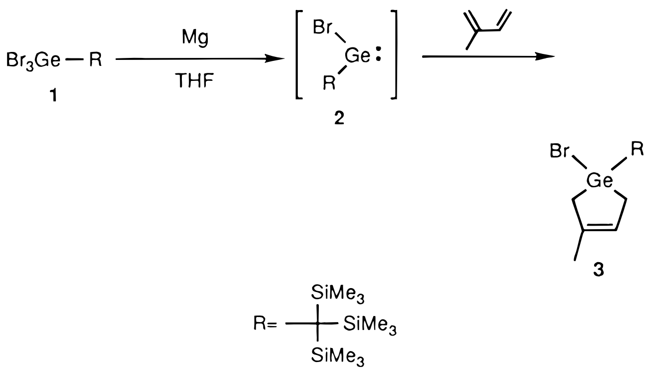
*Summary: The reaction of [tris(trimethylsilyl)methyl]-tribromogermane with magnesium in the presence of olefins and acetylenes has been investigated. 1,4-Digermabicyclo[2.2.0]hexanes and bromogermacyclopent-3-ene are obtained in the reactions of [tris(trimethylsilyl)-methyl]bromogermylene with olefins and 1,3-butadiene, respectively. In the presence of diphenylacetylene a 1,2-dihydro-1,2-digermacyclobutene was formed, which can be explained in terms of an electron-transfer reaction of the bromogermylene intermediate.*

Despite extensive studies of reactions of trihalogermanes that contain a bulky substituent with alkali metals,[1] no attempt has been made to find the reactive intermediate involved in such reactions. On the other hand, the chemistry of germylenes has been studied over the last two decades, and several organohalogermylenes (R−Ge−X) were identified as synthetic intermediates;[2] a few stable ones (Cp*−Ge−Cl, Mes*−Ge−Cl) even could be isolated.[3] Very recently, we reported a stable chlorogermylene which reacts with ethylene to form a 1,2-dichloro-1,2-digermacyclobutane and a 1,4-digermabicyclo[2.2.0]hexane.[4] In this communication we report that the halogermylene and, possibly, its radical anion are important intermediates in the reaction of (trisyl)trihalogermanes (trisyl = tris(trimethylsilyl)methyl) with magnesium.

Treatment of (trisyl)tribromogermane[5] (**1**; 200 mg, 0.38 mmol) with Mg[6] (48 mg, 2.0 mmol) in THF (5 mL) containning 2-methyl-1,3-butadiene (780 mg, 11 mmol) at room temperature for 10 h produced a [1 + 4] cycloadduct, the bromogermacyclopent-3-ene compound **3** in 45% yield[7] (77 mg) (Scheme 1). Moreover, **1** was reduced by Mg in the absence of a germylene trapping reagent over 10 h. After removal of unreacted magnesium, addition of 2-methyl-1,3-butadiene to the remaining solution resulted in formation of **3** in 40% yield. This result shows that (trisyl)bromogermylene (**2**) formed in the **1**/Mg reaction is a stable species in THF and that it has the characteristic reactivity of a germylene. Reactions of **1** with magnesium in the presence of olefins gave 1,4-digermabicyclo[2.2.0]hexanes. Thus, the **1** (200 mg, 0.38 mmol)/Mg reaction in the presence of gaseous ethylene gave **4a** (5 mg, 8% yield),[8a] while **4b** (21 mg, 28% yield) was produced in the presence of an excess of styrene[8b] (Scheme 2).

**Scheme 1**



Although (trisyl)trichlorogermane was not reduced by magnesium alone, (trisyl)chlorogermylene could be generated by the action of the magnesium/magnesium dibromide system on this germane. Thus, reaction of (trisyl)trichlorogermane (200 mg, 0.49 mmol) with magnesium (60 mg) and magnesium dibromide (120 mg) in the presence of 2-methyl-1,3-butadiene (170 mg, 2.5 mmol) yielded the [1 + 4] cycloadduct chlorogermacy-

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(1) (a) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55. (b) Sekiguchi, A.; Yatabe, T.; Kamatani, H.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6260.

(2) (a) Wiberg, N.; Hochmuth, W.; Nöth, H.; Appel, A.; Schmidt-Amelunxen, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1333. (b) Jutzi, P.; Hampel, B.; Hursthouse, M. B.; Howes, A. J. *Organometallics* **1986**, *5*, 1994. (c) Jutzi, P.; Becker, A.; Stammer, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 1647. (d) Jutzi, P.; Becker, A.; Leue, C.; Stammer, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 3838. (e) Kobayashi, S.; Cao, S. *Chem. Lett.* **1994**, 941. (f) Braunschweig, H.; Hitchcock, P. B.; Lappert, M.; Pierssens, L. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1156. (g) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R. *J. Am. Chem. Soc.* **1991**, *113*, 7047. (h) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

(3) (a) Jutzi, P.; Leue, C. *Organometallics* **1994**, *13*, 2898. (b) Lange, L.; Meyer, B.; du Mont, W. W. *J. Organomet. Chem.* **1987**, *329*, C17. (c) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 31. (d) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1.

(4) Ohtaki, T.; Ando, W. *Organometallics* **1996**, *15*, 3103.

(5) **1** was prepared by bromination of (trisyl)trihydrogermane in 74% yield: white solid; decomp >300 °C; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 0.46 (s, 27H, $SiCH_3$); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 5.4 ($SiCH_3$), 30.5 (GeCSi); MS (EI) $m/z$ 529 ($M^+ - Me$). Anal. Calcd for $C_{10}H_{27}Br_3Si_3Ge$: C, 22.08; H, 5.00. Found C, 22.30; H, 4.90.

(6) These reductions require 99.98% pure magnesium (Aldrich).

(7) **3**: colorless crystals; decomp. >300 °C; $^1$H NMR ($C_6D_6$, 300 MHz) $\delta$ 0.33 (s, 27H, $SiCH_3$), 1.72 (s, 3H, $CCH_3$), 2.07−2.23 (m, 4H, $GeCH_2C$), 5.63 (m, 1H, $CH_2CH$); $^{13}$C NMR ($C_6D_6$, 75 MHz) $\delta$ 4.5 ($SiCH_3$), 8.0 (GeCSi), 22.6 ($CCH_3$), 31.0 ($GeCH_2C$), 33.6 ($GeCH_2CH$), 123.8 ($GeCH_2CH$), 138.3 ($GeCH_2C$); MS (EI) $m/z$ 437 ($M^+ - Me$). Anal. Calcd for $C_{15}H_{35}BrSi_3Ge$: C, 39.84; H, 7.80. Found: C, 39.94; H, 7.23.

(8) (a) Reaction of (trisyl)tribromogermane (**1**; 200 mg, 0.38 mmol) with Mg (48 mg, 2.0 mmol) in the presence of gaseous ethylene at room temperature gave the 1,4-digermabicyclo[2.2.0]hexane **4a** in 8% yield (5 mg). **4a**: colorless crystals; decomp 202 °C; $^1$H NMR ($C_6D_6$, 300 MHz) $\delta$ 0.50 (s, 54H, $SiCH_3$), 2.43 (m, 4H, $GeCH_2$); $^{13}$C NMR ($C_6D_6$, 75 MHz) $\delta$ 5.7 ($SiCH_3$), 26.8 (GeCSi), 34.8 ($GeCH_2$).[4] (b) Reaction of **1** (200 mg, 0.38 mmol) with Mg (48 mg, 2.0 mmol) in the presence of an excess of styrene (100 mg, 0.96 mmol) gave the 1,4-digerma-2,5-diphenylbicyclo-[2.2.0]-hexane **4b** in 28% yield (21 mg). **4b**: colorless waxy solid; $^1$H NMR ($C_6D_6$, 300 MHz) $\delta$ 0.20 (br, 27H, $SiCH_3$), 0.40 (s, 27H, $SiCH_3$), 2.72 (dd, $J$ = 7.7, 14.5 Hz, 1H, $GeCH_2$), 2.96 (dd, $J$ = 11.2, 13.2 Hz, 1H, $GeCH_2$), 3.06 (dd, $J$ = 7.7, 13.2 Hz, 1H, $GeCH_2$), 3.11 (dd, $J$ = 11.2, 14.5 Hz, 1H, $GeCH_2$), 4.10 (dd, $J$ = 7.7, 11.2 Hz, 1H, $GeCHC_6H_5$), 4.85 (dd, $J$ = 7.7, 11.2 Hz, 1H, $GeCHC_6H_5$), 6.85−7.66 (m, 10H, $C_6H_5$); $^{13}$C NMR ($C_6D_6$, 75 MHz) $\delta$ 5.2 ($SiCH_3$), 5.5 ($SiCH_3$), 12.2 (GeCSi), 20.8 (GeCSi), 38.4 ($GeCH_2$), 41.7 ($GeCH_2$), 48.1 (GeCH), 53.0 (GeCH), 125.1 ($C_6H_5$), 124.5 ($C_6H_5$), 128.1 ($C_6H_5$), 128.4 ($C_6H_5$), 129.2 ($C_6H_5$), 129.4 ($C_6H_5$), 146.8 ($CHC_6H_5$), 147.3 ($CHC_6H_5$); MS (EI) $m/z$ 710 ($M^+ - C_6H_5CHCH_2$), 606 ($M^+ - (C_6H_5CHCH_2)_2$).

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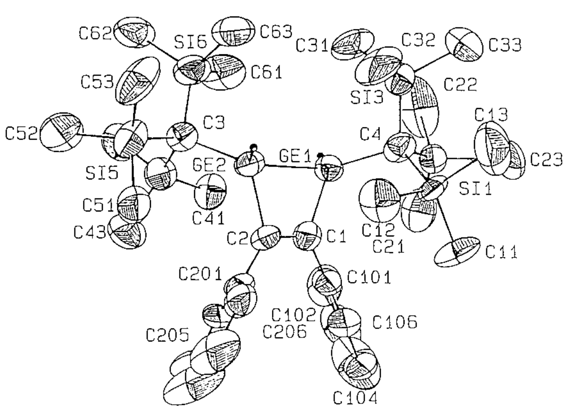
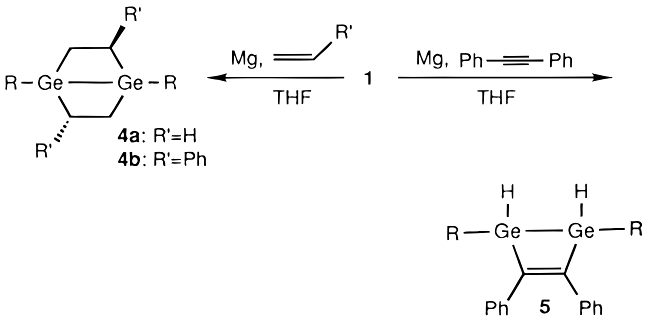


**Figure 1.** Ortep drawing of **5**. Selected bond lengths (Å) and angles (deg): Ge(1)–Ge(2), 2.514(2); Ge(1)–C(1), 1.95(1); Ge(2)–C(2), 2.00(1); C(1)–C(2), 1.33(2); C(1)–C(101), 1.52(2); C(2)–C(201), 1.50(2); Ge(2)–Ge(1)–C(1), 72.7(4); Ge(1)–Ge(2)–C(2), 72.5(4); Ge(1)–C(1)–C(2), 109.6(9); Ge(2)–C(2)–C(1), 105.3(9); Ge(1)–C(1)–C(101), 130(1); C(2)–C(1)–C(101), 120(1); Ge(2)–C(2)–C(201), 129.1(9); C(1)–C(2)–C(201), 125(1).

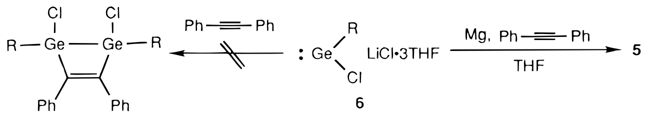
**Scheme 2**



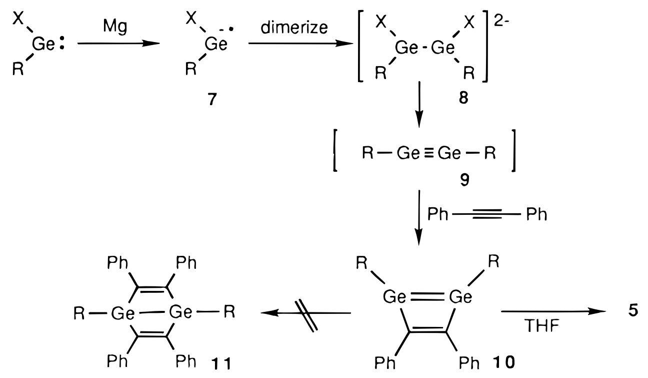
clopent-3-ene (32 mg) in 20% yield and the halogen-exchange product **3** in 40% yield (64 mg).[9]

The reduction of **1** (100 mg, 0.19 mmol) with Mg in the presence of an excess of diphenylacetylene (320 mg, 1.8 mmol) gave the unexpected 1,2-dihydro-1,2-digermacyclobutene **5** in 36% yield (27 mg).[10,11] The structure of **5**, determined by single-crystal X-ray diffraction, is shown in Figure 1.[12] The $Ge_2C_2$ trapezoidal core has planarity (torsional angle 1.08°). The bulky substituents inhibit free rotation of the two phenyl groups and spread the angle Ge(1)–C(1)–C(101) to 130(1)° and Ge(2)–C(2)–C(201) to 129.1(9)°; also, the C(1)–C(101) and C(2)–C(201) bond lengths are 1.52(2) and 1.50(2) Å, which are near the length of a carbon–carbon single bond. Interestingly, although an isolated (trisyl)chlorogermylene–LiCl complex (**6**; 120 mg, 0.2 mmol)[4] did not react with diphenylacetylene,[13] **5** was formed in the presence of magnesium (35 mg) in 16% yield (13 mg)[14] (Scheme 3). These results would suggest that in the present case a reactive intermediate is generated by single-electron transfer from magnesium to the halogermylene. Electron-transfer reactions of a stable germylene have been reported[15] to produce germylene anion radicals. Such electron transfer from magnesium to the halogermylene might be expected to result in dimerization of anion radical **7** to form the 1,2-dihalo digerma 1,2-dianion (Scheme 4). The latter then could

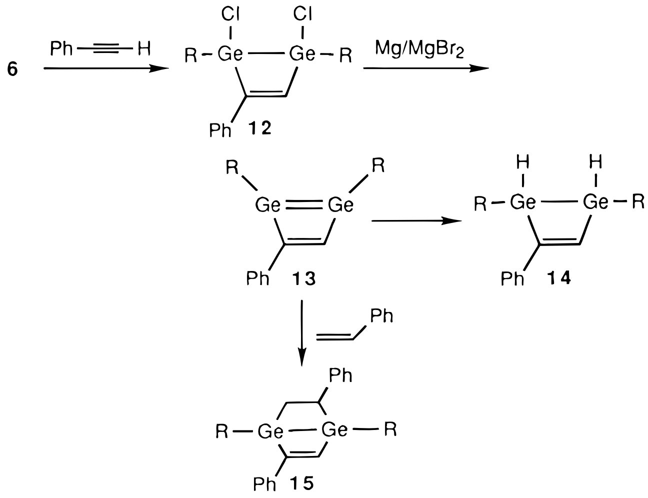
**Scheme 3**



**Scheme 4**



**Scheme 5**



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[9] Chlorogermacyclopent-3-ene: colorless crystals; decomp >300 °C; $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$ 0.32 (s, 27H, $SiCH_3$), 1.72 (s, 3H, $CCH_3$), 2.07–2.23 (m, 4H, $GeCH_2$), 5.63 (m, 1H, $CH_2CH$); $^{13}C$ NMR ($C_6D_6$, 75 MHz) $\delta$ 4.5 ($SiCH_3$), 8.0 (GeCSi), 22.6 ($CCH_3$), 31.0 ($GeCH_2C$), 33.6 ($GeCH_2CH$), 123.8 ($GeCH_2CH$), 138.3 ($GeCH_2C$); MS (EI) $m/z$ 393 ($M^+$ – Me).

[10] **5**: colorless crystals: decomp >300 °C; $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$ 0.33 (s, 54H, $SiCH_3$), 6.03 (s, 2H, GeH), 6.90–7.10 (m, 10H, $C_6H_5$); $^{13}C$ NMR ($C_6D_6$, 75 MHz) $\delta$ 5.1 ($SiCH_3$), 30.1 (GeCSi), 127.5 ($C_6H_5$), 127.8 ($C_6H_5$), 129.4 ($C_6H_5$), 141.7 ($CC_6H_5$), 166.6 ($GeCC_6H_5$); MS (EI) $m/z$ 788 ($M^+$). Anal. Calcd for $C_{34}H_{66}Si_6Ge$: C, 51.78; H, 8.44. Found: C, 51.04; H, 7.73.

[11] When **1** was reacted with magnesium/magnesium dibromide in the absence of diphenylacetylene, *tetrahedro*-tetragermane[2a] was not formed. Only an oligogermane and tris(trimethylsilyl)methane were obtained.

[12] Crystal data for **5**: fw 788.60, triclinic, with $a = 13.668(5)$ Å, $b = 16.182(10)$ Å, $c = 20.095(17)$ Å, $\alpha = 90.11(7)°$, $\beta = 79.70(6)°$, $\gamma = 90.09(4)°$, $V = 4372.9$ Å$^3$, space group $P2_1/a$, $Z = 4$, $\mu$(Mo K$\alpha$) 15.4 cm$^{-1}$, $\rho$(calcd) 1.20 g/cm$^3$. A total of 2695 independent reflections ($2\theta \leq 50°$; $|F_o|^2 \geq 3\sigma|F_o|^2$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo K$\alpha$ irradiation and $\omega$–$2\theta$ scan. An empirical absorption correction based on a series of $\psi$ scans were applied to the data 0.86/1.00. The structure was solved by direct methods, and hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. All non-hydrogen atoms were refined anisotropically to $R = 0.049$ ($R_w = 0.056$).

[13] An isolated (trisyl)chlorogermylene–LiCl complex (**6**; 120 mg, 0.2 mmol) was stirred in THF containing an excess of diphenylacetylene (250 mg, 1.5 mmol) for 24 h, and then 2-methyl-1,3-butadiene was added to the reaction mixture; only the [1 + 4] adduct chlorogermacyclopent-3-ene was obtained in 45% yield (36 mg). No diphenylacetylene adduct was obtained.

[14] Reaction of **6** (120 mg, 0.2 mmol) with Mg (35 mg) in the presence of an excess of diphenylacetylene (320 mg, 1.8 mmol) gave **5** (13 mg) in 16% yield.

[15] Egorov, M. P.; Nefedov, O. M.; Lin, T.; Gaspar, P. P. *Organometallics* **1995**, *14*, 1539.

undergo the elimination of halogen to form the digermaacetylene (digermyne) **9**, the [2 + 2] cycloaddition of which with diphenylacetylene then would form 1,2-digermacyclobutadiene **10**, which would need to abstract two hydrogen atoms from the solvent to give the isolated product **5**. Due to the steric hindrance of the bulky trisyl groups, the 1,4-digerma Dewar benzene species **11** could not be formed by addition of 2 mol of diphenylacetylene. That **5** might be formed from 1,2-digermacyclobutadiene **10** is suggested by the formation of the 1,2-dihydro-1,2-digermacyclobutene compound **14** (89% yield) in the reaction of 1,2-dichloro-1,2-digermacyclobutene **12** with magnesium/ magnesium dibromide[16] and also the formation of 1,4-digermabicyclo-[2.2.0]hexene **15** (64% yield) in the presence of an excess of styrene[17] (Scheme 5). A disilyne intermediate, the silicon analog of a digermyne, has been suggested to be involved in the formation of 1,2-dihydro-1,2-disilacyclobutene in the reduction of a tetrabromodisilane, $RBr_2SiSiBr_2R$ (R = tri-*tert*-butylsilyl).[18] However, we point out that there is no firm evidence for such a reduction-course. While the intermediacy of digermyne is an intriguing possibility, the reaction course above is, admittedly, speculative.

**Acknowledgment.** We are grateful to Asai Germanium Institute and Shin-Etsu Co. Ltd. for their gifts of trichlorogermane and chlorosilanes. This work was supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists and a Grant-in-Aid for Scientific Research on Priority Area (Grant No. 09239101) from the Ministry of Education, Science and Culture of Japan.

**Supporting Information Available:** Text giving details of the X-ray crystal structure study and tables of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **5** and text giving details of experimental procedures (23 pages). Ordering information is given on any current masthead page.

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[16] The reaction of **6** with phenylacetylene gave the 1,2-dichloro-1,2-digermacyclobutene **12**.[4] Dehalogenation of **12** (70 mg, 0.090 mmol) with magnesium (35 mg)/magnesium dibromide (120 mg) gave the 1,2-dihydro-1,2-digermacyclobutene **14** in 89% yield (56 mg). **14**: white powder; decomp 203−204 °C; $^1$H NMR ($C_6D_6$, 300 MHz) $\delta$ 0.31 (s, 27H, $SiCH_3$), 0.40 (s, 27H, $SiCH_3$), 5.58 (d, $J$ = 2.1 Hz, 1H, $C_6H_5CGeHGeH$), 6.02 (dd, $J$ = 2.1, 5.8 Hz, 1H, GeHGe*H*CH), 7.02−7.08 (m, 1H, $C_6H_5$), 7.11−7.18 (m, 2H, $C_6H_5$), 7.27−7.32 (m, 2H, $C_6H_5$), 7.41 (d, $J$ = 5.8 Hz, 1H, $GeHCHC_6H_5$); $^{13}$C NMR ($C_6D_6$, 75 MHz) $\delta$ 4.4 ($SiCH_3$), 4.7 ($SiCH_3$), 13.4 (GeCSi), 14.0 (GeCSi), 127.2 ($C_6H_5$), 127.4 ($C_6H_5$), 128.1 ($C_6H_5$), 145.1 ($CC_6H_5$), 156.8 ($GeCHCC_6H_5$), 174.0 (GeCPhCH); MS (EI) *m*/*z* 712 ($M^+$). Anal. Calcd for $C_{28}H_{62}Si_6Ge_2$: C, 47.23; H, 8.78. Found: C, 46.92; H, 7.73.

[17] In the presence of an excess of styrene the reaction of **12** (60 mg, 0.077 mmol) with Mg (35 mg)/$MgBr_2$ (120 mg) gave 1,4-digerma-2,5-diphenylbicyclo[2.2.0]hex-2-ene **15** in 64% yield (40 mg) and **14** in 36% yield (14 mg). **15**: colorless crystals; decomp 185 °C; $^1$H NMR ($C_6D_6$, 300 MHz) $\delta$ 0.25 (bs, 27H, $SiCH_3$), 0.40 (s, 27H, $SiCH_3$), 2.49 (dd, $J$ = 5.2, 13.0 Hz, 1H, $GeCH_2CH(C_6H_5)Ge$), 2.98 (dd, $J$ = 11.7, 13.0 Hz, 1H, $GeCH_2{-}CH(C_6H_5)Ge$), 4.05 (dd, $J$ = 5.2, 13.0 Hz, 1H, $GeCH_2{-}CH(C_6H_5)Ge$), 7.00−7.19 (m, 6H, $C_6H_5$), 7.52 (s, 1H, $GeCH{=}C(C_6H_5)Ge$), 7.53−7.70 (m, 4H, $C_6H_5$); $^{13}$C NMR ($C_6D_6$, 75 MHz) $\delta$ 5.1 ($SiCH_3$), 5.4 ($SiCH_3$), 10.3 (GeCSi), 17.2 (GeCSi), 39.4 ($GeCH_2{-}CH(C_6H_5)Ge$), 48.3 ($GeCH_2{-}CH(C_6H_5)Ge$), 125.1 ($C_6H_5$), 126.3 ($C_6H_5$), 127.9 ($C_6H_5$), 128.1 ($C_6H_5$), 128.5 ($C_6H_5$), 129.3 ($C_6H_5$), 146.4 ($GeCH_2{-}CH(C_6H_5)Ge$), 148.4 ($GeC(C_6H_5){=}CHGe$), 153.8 ($GeC(C_6H_5){=}CHGe$), 170.2 ($GeC(C_6H_5){=}CHGe$); MS (EI) *m*/*z* 710 ($M^+ - CH_2{=}CH(C_6H_5)$). Anal. Calcd for $C_{36}H_{68}Si_6Ge_2$: C, 53.08; H, 8.41. Found: C, 52.87; H, 8.27.

[18] Wiberg, N.; Finger, C. M. M.; Auner, H.; Polborn, K. *J. Organomet. Chem.* **1996**, *521*, 377.