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Reaction between (Chlorodimesitylsilyl)diarylgermanes and *tert*-Butyllithium in THF: Formation of New Germyllithium Compounds

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Treatment of (chlorodimesitylsilyl)diarylgermanes (1, Ar = 2,4,6-trimethylphenyl = mesityl = Mes; 2, Ar = 2,4,6-triisopropylphenyl) with excess *tert*-butyllithium in THF followed by quenching the reaction mixture with methanol gave (dimesitylsilyl)diarylgermanes (3, Ar = Mes; Ar = 2,4,6-triisopropylphenyl). Surprisingly, when either reaction mixture was quenched with methanol-d_4, the corresponding (dimesitylsilyl)diaryldeuteriogermanes (3a, Ar = Mes; 4a, Ar = 2,4,6-triisopropylphenyl) were formed. The germyllithium compound $Ar_2GeLiSiHMes_2$ has been proposed as an intermediate. The germyllithium (Ar = Mes) was also trapped with other electrophiles, e.g. methyl iodide, chlorotrimethylsilane, and benzyl bromide, to give $Mes_2GeESiHMes_2$ (5, E = Me; 6, E = $SiMe_3$; 7, E = Br). Possible mechanisms for the formation of these compounds are also discussed.

Introduction

An understanding of the nature of compounds containing a silicon–germanium bond is becoming more important with the development of Si–Ge systems in the area of semiconductors[1] and polymers.[2] Although there are many examples in the literature of compounds containing a silicon–germanium bond, reports on the chemistry of these compounds are sporadic.[3] We have initiated a study on the chemistry of mixed silicon–germanium compounds;[4] in particular, we are interested in potential precursors of germasilenes, compounds containing a silicon–germanium double bond. We now report on the synthesis of (chlorodimesitylsilyl)diarylgermanes (1, Ar = 2,4,6-trimethylphenyl = mesityl = Mes; 2, Ar = 2,4,6-triisopropylphenyl) and on our investigations of the reactions between 1 or 2 and alkyllithium reagents in hydrocarbon or ethereal solvents. Although compounds 1 and 2 did not yield a germasilene by a β-elimination reaction; the chemistry described herein is an important and interesting report on the reactivity of compounds containing a silicon–germanium bond.

Results and Discussion

The (chlorodimesitylsilyl)diarylgermanes can readily be prepared by the treatment of dichlorodimesitylsilane[5] with 1 equiv of the appropriate diarylgermyllithium reagent in tetrahydrofuran (THF) in good to excellent yield. (Bis(2,4,6-triisopropylphenyl)germyl)lithium is prepared in the same manner as the known (dimesitylgermyl)lithium:[6] by treatment of the diarylgermane with *tert*-butyllithium (*t*-BuLi) in THF. Treatment of the so formed reagent with dimethyl sulfate gave a good yield of methylbis(2,4,6-triisopropylphenyl)germane.

$$Ar_2GeH_2 + t\text{-BuLi} \longrightarrow Ar_2GeHLi + Me_2SO_4 \longrightarrow Ar_2GeHMe \qquad (1)$$

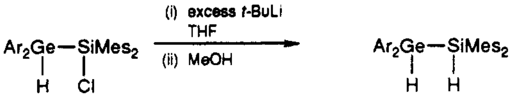
Ar = Mes[6]
Ar = 2,4,6-triisopropylphenyl

$$Ar_2GeHLi + Mes_2SiCl_2 \xrightarrow{THF} Ar_2\underset{H}{Ge}-\underset{Cl}{Si}Mes_2 \qquad (2)$$

1: Ar = Mes
2: Ar = 2,4,6-triisopropylphenyl

The ^1H NMR spectrum of 1 indicates restricted rotation about one of the M–mesityl bonds (M = Ge or Si), most probably the Si–Mes bond. The ^1H NMR spectrum of 2 is also temperature dependent, indicating hindered rotation about both the Ge–aryl and the Si–Mes bonds. When the temperature of the sample is raised to 130 °C, the signals of the spectrum sharpen considerably (see Figure 1). In accordance with the assigned structures of compounds 1 and 2, the ^{29}Si NMR spectrum of 1 and of 2 shows one doublet in the range 4–7 ppm with a coupling constant of approximately 19 Hz. This is consistent with a chlorosilane with a two-bond coupling to hydrogen, but clearly not with a compound with a direct Si–H linkage.

When 1 or 2, in cyclohexane at room temperature, was treated with *t*-BuLi, or potassium hydride, no reaction took place: the starting material was recovered in good yield. Likewise, treatment of 2, in pentanes at room temperature, with methyllithium, butyllithium, phenyllithium, or *t*-BuLi, also gave no observable reaction. However, addition of *t*-BuLi to 1 or 2 in THF in the cold followed by warming to room temperature yields a red-brown solution, which upon treatment with methanol immediately decolorizes (to pale yellow). After workup, the products were purified by chromatography to give (dimesitylsilyl)dimesitylgermane



$$Ar_2\underset{H}{Ge}-\underset{Cl}{Si}Mes_2 \xrightarrow[\text{(ii) MeOH}]{\text{(i) excess } t\text{-BuLi, THF}} Ar_2\underset{H}{Ge}-\underset{H}{Si}Mes_2 \qquad (3)$$

3: Ar = Mes
4: Ar = 2,4,6-triisopropylphenyl

(3) or (dimesitylsilyl)bis(2,4,6-triisopropylphenyl)germane (4) in moderate isolated yields. In the reaction of 2, minor amounts of 1,3,5-triisopropylbenzene and bis(2,4,6-triisopropylphenyl)germane are also formed, indicating some

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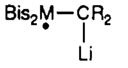
cleavage of the silicon–germanium bond and the germanium–aryl bond under these conditions. A similar reaction was observed by Wiberg and co-workers[7] when $(Me_2XSi)(Me_3Si)_2CBr$ (X = F, SPh) was treated with *t*-BuLi. They attributed the formation of $(Me_2XSi)(Me_3Si)_2CH$ (X = F, SPh) to initial Li/Br exchange, followed by abstraction of a proton, at least in part, from *tert*-butyl bromide. Satgé and co-workers have obtained similar products on several occasions. Treatment of $(t\text{-}Bu_2FGe)PHAr$ (Ar = 2,4,6-tri-*tert*-butylphenyl) with *t*-BuLi in diethyl ether/pentane gave $(t\text{-}Bu_2HGe)PHAr$.[8] Formation of the hydridogermane was believed to be a consequence of the diradical nature of $t\text{-}Bu_2Ge{=}PAr$. Similarly, treatment of $Bis_2GeF{-}CHR_2$[9] or $Bis_2SnCl{-}CHR_2$[10] (Bis = bisyl = $CH(SiMe_3)_2$ and CR_2 = fluorenylidene) with *t*-BuLi in Et_2O also gave the hydridogermane and the hydridostannane as well as recovered starting material. In each case, the formation of the hydrides was attributed to initial dehydrochlorination followed by a single-electron-transfer reaction with a second equivalent of *t*-BuLi to give an intermediate radical anion.

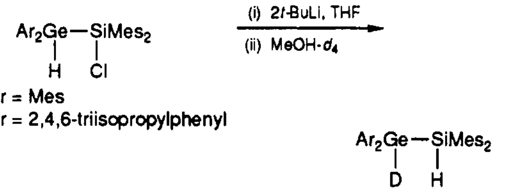


$$Bis_2\dot{M}{-}\underset{\displaystyle Li}{CR_2}$$

M = Ge, Sn

The radical anion is believed to abstract a hydrogen atom from the solvent. The resulting carbanion is then quenched with methanol to give the observed products.

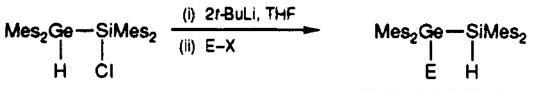
In order to probe the mechanism for the formation of the dihydrides **3** and **4** and the nature of the intermediate(s), the reaction between **1** and *t*-BuLi was carried out in THF-d_8. Deuterium incorporation at the Si-H or Ge-H position was not observed by ^2H NMR spectroscopy. On the other hand, when the reaction mixture was quenched with methanol-d_4, a deuterium atom was incorporated into the product, but surprisingly, it was *attached to the germanium atom (**3a** and **4a**)*, as shown by ^1H, ^2H, and ^{29}Si NMR spectroscopy. Similar results were obtained with compound **2**. In the same manner, quenching the reaction mixture derived from **1** and *t*-BuLi with methyl iodide led to the formation of (dimesitylsilyl)dimesitylmethylgermane (**5**), use of chlorotrimethylsilane led to the formation of (dimesitylsilyl)dimesityl(trimethylsilyl)germane (**6**), and use of benzyl bromide led to the formation of (dimesitylsilyl)bromodimesitylgermane (**7**).[11] Minor amounts of **3** were formed in each case. The use of excess *t*-BuLi decreased the reaction time required; however, increasing amounts of cleavage products [i.e. Mes_2GeHE (E = Me, $SiMe_3$, CH_2Ph)] were observed.



$$\underset{\displaystyle H}{Ar_2Ge}{-}\underset{\displaystyle Cl}{SiMes_2} \xrightarrow[\text{(ii) MeOH-}d_4]{\text{(i) 2}t\text{-BuLi, THF}} \underset{\displaystyle D}{Ar_2Ge}{-}\underset{\displaystyle H}{SiMes_2} \quad (4)$$

1: Ar = Mes
2: Ar = 2,4,6-triisopropylphenyl

3a: Ar = Mes
4a: Ar = 2,4,6-triisopropylphenyl



$$\underset{\displaystyle H}{Mes_2Ge}{-}\underset{\displaystyle Cl}{SiMes_2} \xrightarrow[\text{(ii) E–X}]{\text{(i) 2}t\text{-BuLi, THF}} \underset{\displaystyle E}{Mes_2Ge}{-}\underset{\displaystyle H}{SiMes_2} \quad (5)$$

5: E–X = MeI, E = Me
6: E–X = $ClSiMe_3$, E = $SiMe_3$
7: E–X = $BrCH_2Ph$, E = Br

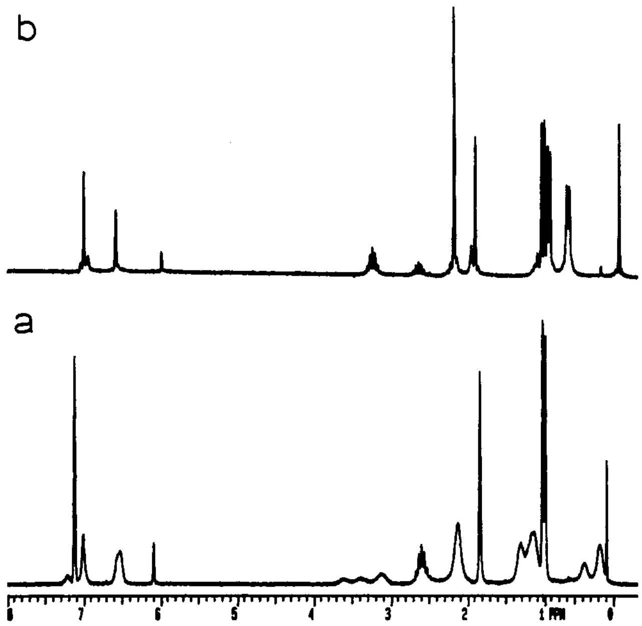
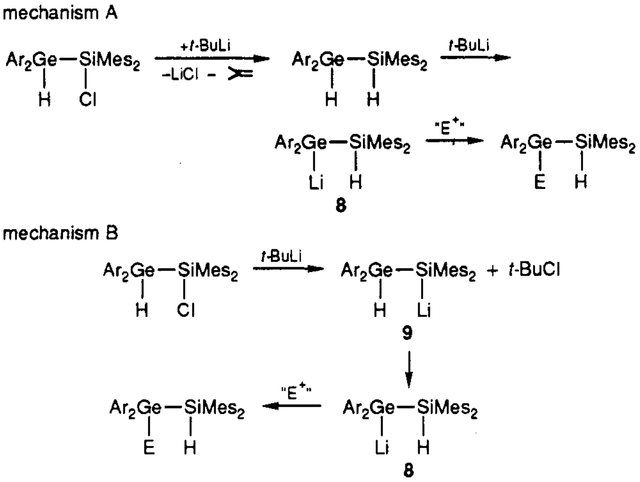


Figure 1. (a) ^1H NMR spectrum of **2** in C_6D_6 at 20 °C. (b) ^1H NMR spectrum of **2** in C_7D_8 at 130 °C.

Scheme I



These results lead us to believe that the immediate precursor to compounds **3**–**7** is the germyllithium **8**. Several possible mechanisms for the formation of **8** can be envisaged. The possibility of initial formation of a germasilene by dehydrochlorination, followed by a single-electron transfer from a second equivalent of *t*-BuLi and, finally, abstraction of a hydrogen from the solvent, similar to the process described by Satgé,[9,10] has been eliminated since no deuterium incorporation was observed when the reaction was carried out in THF-d_8. Alternatively, *t*-BuLi may act as a hydride-transfer reagent, reducing the (chlorosilyl)germane to the dihydride **3**. A

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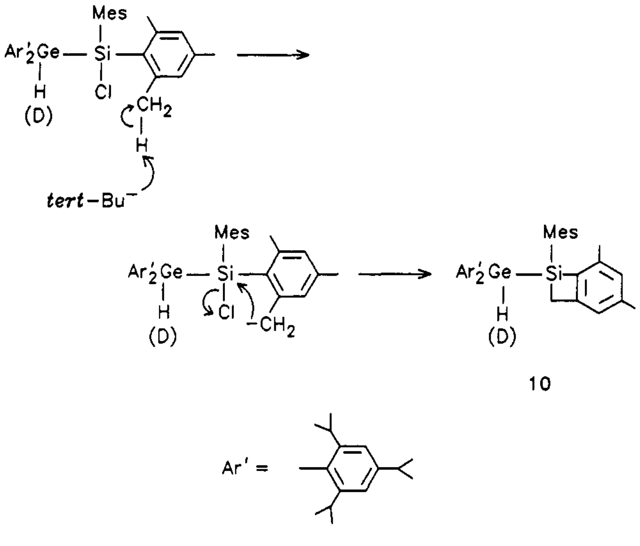
[11] The formation of compound **7** is presumably due to a lithium bromine exchange reaction between **8** (Ar = Mes) and benzyl bromide. A similar process was observed when 2,4,6-tris(bis(trimethylsilyl)methyl)phenyllithium was treated with benzyl bromide in THF in the cold.[17] The formation of the product, in this case, was presumed to be formed via an electron-transfer reaction mechanism. Such a mechanism for the formation of **7** cannot be ruled out at this point.

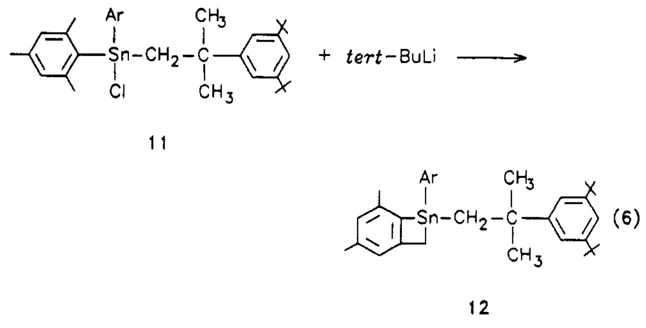
Scheme II



second equivalent of t-BuLi may then abstract a proton from the germanium atom to give the desired germyllithium compound **8** (mechanism A, Scheme I). The reduction of bulky chlorosilanes by alkyllithium reagents has been observed.[12] Another possible mechanism involves initial Li/Cl exchange between t-BuLi and the (chlorosilyl)germane to give the silyllithium **9**. Formation of the germyllithium may then take place by an intramolecular (or intermolecular) proton shift (mechanism B, Scheme I).

We have preliminary results concerning the nature of the mechanism for the formation of the germyl anion. Firstly, we have established that a minimum of 2 equiv of t-BuLi is required to complete the reaction (from **1** to **3**). This does not enable us to distinguish between mechanism A or B since in mechanism B a second equivalent of t-BuLi will most probably react with the formed t-BuCl. We have also independently synthesized the germyl anion **8** by treatment of **3** with t-BuLi in THF followed by trapping with methyl iodide to give **5**, confirming the feasibility of the second step of mechanism A. Attempts to trap the intermediate silyl anion have met with limited success. Quenching the reaction mixture between **1** and t-BuLi after short reaction times (less than 1 h) with deuterium oxide or methanol-d_4 leads to the formation of minor amounts of (deuteriodimesitylsilyl)dimesitylgermane, as observed by ^{1}H and ^{2}H NMR spectroscopy. In contrast, when (chlorodimesitylsilyl)deuteriodimesitylgermane is used as a starting material, no evidence is found for transfer of the deuterium from germanium to silicon in the product mixture.

Although the treatment of **2**, in cyclohexane at room temperature, with t-BuLi gave no detectable products, refluxing the reaction mixture led to minor quantities of the 1-siladihydrobenzocyclobutene, **10**. The formation of this product can be accounted for by the following mechanism. t-BuLi may abstract a proton of one of the o-methyls of the silyl-substituted mesityl groups to give a carbanion which could then undergo intramolecular substitution with the silyl chloride to give the observed compound (Scheme II). A similar mechanism has been proposed by Weidenbruch for the formation of the stannacyclobutene **12**, when the chlorostannane **11**, dissolved in petroleum ether, is treated with t-BuLi.[13] This mechanism is supported by deuterium-labeling studies. If we begin with (chlorodimesitylsilyl)deuteriobis(2,4,6-triisopropylphenyl)germane, after carrying out the reaction under the same conditions, it is found that the product does not contain any hydrogen attached to the germanium; the deuterium is retained throughout the reaction. This eliminates a reaction mechanism through a germasilene-type intermediate generated by initial dehydrochlorination of **2**.



Ar = 2,4,6-tri-*tert*-butylphenyl

In conclusion, the treatment of **1** or **2** with t-BuLi in THF yields the novel silyl-substituted germyllithium **8**. The germyllithium reagent can be trapped with electrophiles to give a variety of substituted silylgermanes. Additional synthetic uses of this novel germyllithium reagent are being investigated. Although the mechanism for the formation of the germyllithium is still under consideration, we currently favor mechanism A shown in Scheme I. The bulky chlorosilane is first reduced by t-BuLi to give the dihydride. The germyl hydrogen is then abstracted by a second equivalent of t-BuLi, and the resulting germyllithium compound can then be trapped by electrophiles. In refluxing cyclohexane, the reaction between **2** and t-BuLi takes another course. The evidence suggests that abstraction of the o-benzylic proton of a silyl-substituted mesityl group followed by an intramolecular substitution gives the 1-siladihydrobenzocyclobutene. We are continuing our investigations of the chemistry of (halosilyl)germanes.

Experimental Section

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. THF and Et_2O were distilled from the sodium ketyl of benzophenone, pentanes and cyclohexane were distilled from $LiAlH_4$, and MeOH was distilled from magnesium methoxide prior to use. MeLi, BuLi, PhLi, and t-BuLi were obtained from the Aldrich Chemical Co., and their concentrations were periodically checked using the Gilman double-titration method.[14] $GeCl_4$ was used as received from the Toronto Research Co. 1,3,5-Triisopropylbenzene was used as received from the Aldrich Chemical Co. 1-Bromo-2,4,6-triisopropylbenzene was prepared according to a literature procedure.[15] Chromatography was carried out on silica gel plates using a Chromatotron (Harrison Research) or conventional preparative plates.

NMR spectra were recorded on a Gemini 200, Varian XL-200 (200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C), or an XL-300 (299.9 MHz for ^{1}H, 75.4 MHz for ^{13}C, and 59.6 MHz for ^{29}Si) spectrometer using deuterated benzene as a solvent unless otherwise noted. The standards used were as follows: residual C_6D_5H, 7.15 ppm for ^{1}H NMR spectra; C_6D_6 central transition, 128.00 ppm for ^{13}C NMR spectra; Me_4Si as an external standard, 0.00 ppm for ^{29}Si NMR spectra. The ^{13}C NMR signal assignments were made by using the DEPT[16] pulse sequence or by recording the

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(13) Weidenbruch, M.; Schäfers, K.; Schlaefke, J.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1991**, *415*, 343.

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(15) Whitesides, G. M.; Eisenhut, M.; Bunting, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5398.

proton-coupled spectra. IR spectra were recorded on a Bruker FT infrared spectrometer controlled by an IBM System 9000 computer; a Finnegan MAT Model 8230 system was used with an ionizing voltage of 70 eV to obtain electron impact mass spectra (reported in mass-to-charge units, *m*/*z*, with intensities of peaks relative to the base peak and ion identity in parentheses). Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Bis(2,4,6-triisopropylphenyl)germane. (2,4,6-Triisopropylphenyl)magnesium bromide was prepared by the addition of a solution of 1-bromo-2,4,6-triisopropylbenzene[15] (25.6 g, 90 mmol) dissolved in THF (70 mL) into a flask containing Mg (4.4 g, 181 mmol) in THF (32 mL), over 30 min. The mixture in the flask was stirred well during the addition and for 1 h afterward at room temperature and then for 2 h at 40 °C. The concentration of the Grignard reagent solution was determined by back-titration. To a vigorously stirred solution of $GeCl_4$ (4 mL, 34.4 mmol) dissolved in benzene (40 mL) was added the Grignard reagent (103.5 mL, 0.7 M, 72.5 mmol) over 50 min. The mixture was then *gently* refluxed for 10.5 h, hydrolyzed using 6 M HCl, and extracted with Et_2O, and the combined extracts were dried over $MgSO_4$. All the solvents were removed to yield a cream-colored solid mass. Ethanol was added (10 mL) and the mixture filtered to yield 14.3 g of bis(2,4,6-triisopropylphenyl)dihalogermane as a white powder.

To a well-stirred suspension of $LiAlH_4$ (1.6 g, 42 mmol) in Et_2O was added a solution of the above dihalogermane (14.3 g) in Et_2O (25 mL) over 40 min. The mixture was then *gently* refluxed for 11 h. Excess $LiAlH_4$ was destroyed by the slow addition of 6 M HCl. The reaction mixture was extracted with Et_2O. The combined organic layers were washed with brine (80 mL) and then dried over $MgSO_4$ and filtered. All the solvents were removed to yield bis(2,4,6-triisopropylphenyl)germane as a colorless liquid, in 71% yield (11.8 g). IR (neat, cm^{-1}): 2056 (s, Ge–H). ^1H NMR (ppm): 7.12 (s, 4 H, Ar′–H), 5.57 (s, 2 H, Ge–H), 3.52 (sept, 4 H, J = 6.8 Hz, *o*-C*H*(Me)$_2$), 2.77 (sept, 2 H, J = 6.9 Hz, *p*-C*H*(Me)$_2$), 1.20 (d, 12 H, J = 6.9 Hz, *p*-CH(*Me*)$_2$), 1.19 (d, 24 H, J = 6.8 Hz, *o*-CH(*Me*)$_2$). ^{13}C NMR (ppm): 154.45, 150.16, 131.81, (Ar′–C), 121.55 (Ar′–CH), 34.84 (*o*-*C*H(Me)$_2$), 34.7 (*p*-*C*H(Me)$_2$, 24.6 (*o*-CH(*Me*)$_2$), 24.19 (*p*-CH(*Me*)$_2$). MS [*m*/*z* (%)]: 482 (6, M^+), 278 (92, $M^+ - C_{15}H_{24}$), 235 (15), 203 (100, $C_{15}H_{23}^+$), 189 (22).

Methylbis(2,4,6-triisopropylphenyl)germane. To a solution of bis(2,4,6-triisopropylphenyl)germane (0.48 g, 1 mmol) dissolved in THF (4 mL) at −23 °C was added, all at once, a solution of *t*-BuLi (0.8 mL, 1.4 mmol, 1.7 M in pentanes), and the mixture was stirred at −23 °C (dry ice–CCl_4) for 1 h. The bright yellow solution was then added dropwise to a solution of dimethyl sulfate (0.2 mL, 1.7 mmol) dissolved in THF (0.5 mL) at room temperature. The yellow color disappeared after 1.5 h of stirring. The mixture was stirred for another 2.5 h, hydrolyzed using 6 M HCl, and extracted with Et_2O. The combined organic phase was then dried over $MgSO_4$ and filtered, and the solvents were removed to yield methylbis(2,4,6-triisopropylphenyl)germane which was purified by chromatography to give 0.35 g (69%). IR (neat, cm^{-1}): 2033 (s, Ge–H). ^1H NMR (ppm 70 °C): 7.08 (s, 4 H, Ar′–H), 5.78 (q, 1 H, J = 4.1 Hz, Ge–H), 3.47 (sept, 4 H, J = 6.9 Hz, *o*-C*H*(Me)$_2$), 2.78 (sept, 2 H, J = 6.9 Hz, *p*-C*H*(Me)$_2$), 1.20 (J = 6.9 Hz), 1.16 (J = 6.8 Hz), 1.15 (J = 6.8 Hz) (each d, total 36 H, CH(*Me*)$_2$), 1.0 (d, 3 H, J = 4.1 Hz, Ge–Me). ^{13}C NMR (ppm): 154.1, 149.77, 134.95 (Ar′–C), 121.64 (Ar′–CH), 34.64 (*p*-*C*H(Me)$_2$), 34.13 (*o*-*C*H(Me)$_2$), 24.85, 24.18 and 24.64 (CH(*Me*)$_2$), 3.34 (Ge–Me). MS [*m*/*z* (%)]: 496 (38, M^+), 495 (100, $M^+ - H$), 479 (34), 289 (50), 275 (62), 231 (14), 189 (24), 91 (45).

(Chlorodimesitylsilyl)dimesitylgermane (1). A solution of Mes_2GeHLi (from *t*-BuLi, 7.75 mmol, and Mes_2GeH_2, 1.50 g, 4.79 mmol, in anhydrous THF)[6] was added to Mes_2SiCl_2 (1.62 g, 4.82 mmol) in THF (10 mL) at −23 °C (dry ice–CCl_4). The solution was allowed to warm to 20 °C and stirred for 21 h before workup under acidic conditions (1 M HCl). The crude product was triturated with methanol, yielding a white solid (2.79 g, 94%). Mp 200 °C dec. IR (KBr pellet, cm^{-1}): 2046 (s, Ge–H). ^1H NMR (ppm): 6.72, 6.63 (each s, 4 H, Mes–H), 5.86 (s, 1 H, Ge–H), 2.37 (bs, 12 H, *o*-Me), 2.36 (s, 12 H, *o*-Me), 2.09, 2.03 (each s, 6 H, *p*-Me). ^{13}C NMR (ppm, 60 °C): 144.62, 144.28, 139.88, 138.30, 135.20, 132.62 (Mes–C), 130.23, 129.17 (Mes–CH), 24.85, 24.57, 20.93, 20.86 (Me); ^{29}Si NMR ($CDCl_3$, ppm): 4.58 (d, J = 19 Hz). MS [*m*/*z* (%)]: 613 (6, $M^+ - 1$), 579 (32), 495 (16), 312 (100), 301 (64), 265 (16), 192 (24), 119 (10). High-resolution MS for $C_{36}H_{45}{}^{35}Cl^{74}Ge^{28}Si$ (*m*/*z*): calcd 614.2191; found 614.2196. Anal. Calcd for $C_{36}H_{45}ClGeSi$: C, 70.44; H, 7.39. Found: C, 69.28; H, 7.15.

(Chlorodimesitylsilyl)deuteriodimesitylgermane (1a). Mes_2GeD_2 was prepared by reduction of Mes_2GeX_2 with $LiAlD_4$. Mes_2GeD_2 was then substituted for Mes_2GeH_2 in the preparation of **1** to give **1a**. IR (thin film, cm^{-1}): no Ge–H. ^2H NMR (C_6H_6, ppm): 5.89 (Ge–D).

(Chlorodimesitylsilyl)bis(2,4,6-triisopropylphenyl)germane (2). To a solution of bis(2,4,6-triisopropylphenyl)germane (1.44 g, 3.00 mmol) dissolved in THF (12 mL) at −23 °C (dry ice–CCl_4) was added *t*-BuLi (2.5 mL, 4.2 mmol, 1.7 M in pentanes) in one shot. The reaction mixture was stirred well for 1 h at −23 °C. The yellow germyllithium solution was then added dropwise to a solution of Mes_2SiCl_2 (1.01 g, 3.00 mmol) dissolved in THF (6 mL) at −23 °C. The resulting solution was warmed to room temperature and stirred overnight. The reaction mixture was then hydrolyzed using 3 M HCl and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvents were removed. The crude product was purified by chromatography to yield **2** (1.63 g, 70%) as a white powder. Mp 186–188 °C. IR (KBr, cm^{-1}): 2002, 2014 (s, Ge–H). IR (CCl_4 solution, cm^{-1}): 2014 (s, Ge–H). ^1H NMR (C_7D_8, ppm, 130 °C): 7.03 (s, 4 H, Ar–H), 6.63 (s, 4 H, Ar–H), 6.05 (s, 1 H, Ge–H), 3.36 (sept, 4 H, J = 6.6 Hz, *o*-C*H*Me$_2$), 2.78 (sept, 2 H, J = 6.8 Hz, *p*-C*H*Me$_2$), 2.32 (s, 12 H, *o*-Me), 2.06 (s, 6 H, *p*-Me), 1.20 (J = 6.9 Hz), 1.13 (J = 6.6 Hz), 0.88 (J = 6.7 Hz) (each d, total 36 H, CH*Me*$_2$). ^{13}C NMR (C_7D_8, ppm, 120 °C): 154.99, 150.07, 145.06, 139.76, 136.07, 133.61 (Ar–C), 130.18, 122.58 (Ar–CH), 35.82 (*C*HMe$_2$), 34.49 (*C*HMe$_2$), 24.77, 24.61, 24.42, 23.86, 20.63 (all Me). ^{29}Si NMR (C_7D_8, ppm): 7.27 (d, J = 19.8 Hz). MS [*m*/*z* (%)]: 782 (0.6, M^+), 781 (0.9, $M^+ - H$), 746 (0.3, $M^+ - HCl$), 481 (65, $M^+ - SiClMes_2$), 480 (100, $M^+ - H - SiClMes_2$), 301 (16, $M^+ - (C_{15}H_{23})_2GeH$), 277 (38), 235 (10), 203 (2, $C_{15}H_{23}$). High-resolution MS for $C_{48}H_{68}{}^{35}Cl^{74}Ge^{28}Si$ ($M^+ - H$) (*m*/*z*): calcd 781.3991; found 781.4074. Anal. Calcd for $C_{48}H_{69}ClGeSi$: C, 73.71; H, 8.89. Found: C, 73.65; H, 8.68.

(Chlorodimesitylsilyl)deuteriobis(2,4,6-triisopropylphenyl)germane (2a). Prepared in the same manner as **1a**. ^2H NMR ($CHCl_3$, ppm): 5.63 (b s).

(Dimesitylsilyl)dimesitylgermane (3). Addition of *t*-BuLi (3.2 mL, 5.0 mmol, 1.55 M in pentane) to **1** (0.50 g, 0.82 mmol) in anhydrous THF (15 mL) at −23 °C (dry ice–CCl_4) followed by warming to 20 °C and stirring for 6 h yielded a red-brown solution. Addition of methanol to the reaction mixture resulted in immediate decolorization (to pale yellow). After aqueous workup, the product was purified by chromatography to give **3** (0.15 g, 33%) and dimesitylgermane (0.02 g, 8%). Characterization for **3**: mp 183 °C dec; IR (KBr pellet, cm^{-1}) 2133, 2023 (SiH/GeH); Raman (solid, cm^{-1}) 578, 563, 553, 528, 434, 149; ^1H NMR (ppm) 6.69, 6.65 (each s, 4 H, Mes–H), 6.01 (d, 1 H, J = 11 Hz, Si–H; assigned by ^{29}Si–^1H correlation spectroscopy), 5.75 (d, 1 H, J = 11 Hz, Ge–H), 2.37, 2.34 (each s, 12 H, *o*-Me), 2.08, 2.05 (each s, 6 H, *p*-Me); ^1H NMR ($CDCl_3$, ppm) 6.68 (b s), 5.60 (d), 5.33 (d), 2.20 (s), 2.19 (s), 2.15 (s), 2.09 (s); ^{13}C NMR (ppm) 145.17, 144.05, 139.11, 135.96, 135.07, 130.05 (Mes–C), 129.22, 128.96 (Mes–CH), 24.30, 23.91, 21.05, 21.00 (Me); ^{29}Si NMR (ppm) −47.96 (d of m, J = 194 Hz); MS [*m*/*z* (%)] 579 (4, $M^+ - 1$), 312 (50), 267 (40), 207 (100), 192 (46), 119 (32); high-resolution MS for $C_{36}H_{45}{}^{74}Ge^{28}Si$ ($M^+ - 1$) (*m*/*z*) calcd 579.2508, found 579.2493. Anal. Calcd for $C_{36}H_{46}GeSi$: C, 74.62; H, 8.00. Found: C, 74.06; H, 7.72.

(Dimesitylsilyl)deuteriodimesitylgermane (3a). Characterization for **3a** containing approximately 40% of **3**: ^1H NMR (ppm) 6.01 (b s, Si–H); ^2H NMR ($CHCl_3$, ppm) 5.27 (b s); ^2H NMR (C_6H_6, ppm) 5.75 (b s); ^{29}Si NMR ($CDCl_3$, ppm) −48.71 (m, J = 191 Hz).

(Dimesitylsilyl)bis(2,4,6-triisopropylphenyl)germane (4). Addition of *t*-BuLi (0.8 mL, 1.2 mmol, 1.5 M in pentane) to **2** (0.10 g, 0.13 mmol) in anhydrous THF (5 mL) at −23 °C (dry ice–CCl_4)

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followed by warming to 20 °C and stirring for 5.5 h yielded a red-brown solution. Addition of methanol to the reaction mixture resulted in immediate decolorization (to pale yellow). After aqueous workup, the product was purified by chromatography to give **4** (30 mg, 31%) and bis(2,4,6-triisopropylphenyl)germane (6 mg, 9%). Mp 188–191 °C. IR (KBr, cm^{-1}): 2137, 2020 (Si–H and Ge–H). ^{1}H NMR (ppm, 20 °C): 7.05 (s, 4 H, Ar–H), 6.63 (s, 4 H, Ar–H), 6.01 and 5.98 (AB system, SiH, GeH, 2 H, J = 10.9 Hz), 3.38 (b s, 4 H, *o*-C*H*Me$_2$), 2.74 (sept, 2 H, *p*-C*H*Me$_2$), 2.42 (b s, 12 H, *o*-Me), 2.03 (s, 6 H, *p*-Me), 1.184, 1.175 (b d, 36 H, CHMe$_2$). ^{1}H NMR (ppm, 70 °C): 7.04 (s, 4 H, Ar–H), 6.65 (s, 4 H, Ar–H), 5.97 (s, 2 H, Si–H and Ge–H), 3.37 (sept, 4 H, J = 6.6 Hz, *o*-C*H*Me$_2$), 2.76 (sept, 2 H, J = 6.9 Hz, *p*-C*H*Me$_2$), 2.41 (s, 12 H, *o*-Me), 2.04 (s, 6 H, *p*-Me), 1.181, (J = 6.9 Hz), 1.177 (J = 6.9 Hz) (each d, total 12 H, *p*-CH*Me*$_2$), 1.12 (b d, 12 H, J = 6.7 Hz, *o*-CH*Me*$_2$), 0.93 (b d, 12 H, J = 6.4 Hz, *o*-CHMe$_2$). ^{13}C NMR (ppm, 70 °C); 154.8, 149.74, 145.39, 139.08, 135.9, 130.48 (Ar–C), 129.33, 122.16 (Ar–CH), 35.73, 34.54 (–*C*HMe$_2$), 24.57, 24.43, 24.07, 24.04, 20.93 (all Me). ^{29}Si NMR (ppm): −49.08 (d of d, ^1J = 191 Hz, ^2J = 8.8 Hz). MS [m/z (%)]: 747 (16, M$^+$ − H), 629 (12, M$^+$ − Mes), 545 (24, M$^+$ − $C_{15}H_{23}$), 480 (100, M$^+$ − H − SiHMes$_2$), 351 (20, SiHMes($C_{15}H_{23}$)), 277 (34, Ge($C_{15}H_{23}$)), 267 (46, M$^+$ − GeH($C_{15}H_{23}$)$_2$), 203 (14, $C_{15}H_{23}$). High-resolution MS for $C_{48}H_{69}{}^{74}Ge^{28}Si$ (M$^+$ − H) (m/z): calcd 747.4380; found 747.4389. Anal. Calcd for $C_{48}H_{70}GeSi$: C, 77.10; H, 9.44. Found: C, 76.42; H, 9.40.

(Dimesitylsilyl)deuteriobis(2,4,6-triisopropylphenyl)germane (4a). Characterization for **4a** containing a significant amount of **4**: ^{1}H NMR (ppm) 5.99 (b s, Si–H); ^{2}H NMR (CHCl$_3$, ppm) 5.52 (b s, Ge–D).

(Dimesitylsilyl)dimesitylmethylgermane (5). To a solution of **1** (98.7 mg, 0.161 mmol) dissolved in LiAlH$_4$-dried THF (5 mL) was added *t*-BuLi (0.3 mL, 0.4 mmol, 1.55 M in pentanes) at −23 °C (dry ice–CCl$_4$). The cold bath was removed, and the reaction mixture was stirred for 4.3 h. MeI (0.5 mL) was then added. After aqueous workup, the products were separated by chromatography to give 52.5 mg of a white solid which consisted of a mixture of compounds **5** and **3** in a ratio of 83:17 respectively (by ^{1}H NMR spectroscopy). Characterization for **5** containing approximately 10% of **3**: IR (thin, film, cm^{-1}) 2141, 2029; ^{1}H NMR (ppm) 6.69, 6.68 (each s, Mes–H), 5.96 (s, Si–H), 2.29, 2.23 (each s, *o*-Me), 2.10, 2.08 (each s, *p*-Me), 1.26 (s, Ge–Me); ^{13}C NMR (ppm) 145.00, 143.83, 138.83, 137.64, 131.30 (Mes–C), 129.47, 129.25 (Mes–CH), 24.72, 24.29, 21.06, 20.91, 7.12 (all Me); ^{29}Si NMR (ppm) −48.41 (d, J = 189 Hz); MS [m/z (%)] 594 (0.6, M$^+$), 578 (0.8), 475 (2), 327 (100), 311 (10), 281 (11), 267 (24), 235 (7), 147 (4), 119 (3); high-resolution MS for $C_{37}H_{47}{}^{74}Ge^{28}Si$ (M$^+$ − 1) (m/z) calcd 593.2659, found 593.2634.

(Dimesitylsilyl)dimesityl(trimethylsilyl)germane (6). To a solution of **1** (79.4 mg, 0.13 mmol) dissolved in THF (5 mL) was added *t*-BuLi (1.5 mL, 2.3 mmol, 1.55 M in pentanes) at −23 °C (dry ice–CCl$_4$). The cold bath was removed and the reaction mixture was stirred for 3.5 h. Me$_3$SiCl (0.4 mL, distilled from CaCl$_2$ prior to use) was then added. After aqueous workup, the products were separated by chromatography to give **6** (33.1 mg) and dimesityl(trimethylsilyl)germane (9.6 mg, 19.3%). Characterization for **6** containing approximately 25% of **3**: IR (thin film, cm^{-1}) 2137, 2029; ^{1}H NMR (ppm) 6.70, 6.67 (each s, Mes–H), 6.16 (s, Si–H), 2.36, 2.23 (each s, *o*-Me), 2.10, 2.08 (each s, *p*-Me), 0.34 (s, SiMe$_3$); ^{13}C NMR (ppm) 144.85, 143.83, 139.10, 138.46, 137.04, 132.06 (Mes–C), 129.07, 128.96 (Mes–CH), 25.95, 24.99, 21.05, 20.89, 3.63 (all Me); ^{29}Si NMR (ppm) −2.93 (m, J = 6 Hz), −48.50 (d, J = 186 Hz); MS [m/z, CI, isobutane (%)] 652 (6, M$^+$), 651 (10), 637 (2), 579 (5), 460 (38), 385 (100), 312 (56), 294 (33), 267 (85), 266 (23), 221 (56), 193 (40), 147 (41), 119 (42), 73 (77); high-resolution MS for $C_{39}H_{53}{}^{74}Ge^{28}Si$ (M$^+$ − 1) (m/z) calcd 651.2898, found 651.2930. Characterization for Mes$_2$GeH(SiMe$_3$): ^{1}H NMR 6.77, 5.18 (Ge–H), 2.40, 2.12, 0.25 (SiMe$_3$); ^{13}C NMR (ppm) 143.34, 137.49, 135.17, 128.22, 24.56, 20.98, 0.33; MS [m/z, CI, isobutane (%)] 386 (18, M$^+$), 385 (40), 371 (5, M$^+$ − Me), 313 (8, M$^+$ − SiMe$_3$), 267 (28, M$^+$ − Mes), 221 (20), 193 (25, MesGe), 147 (28, MesSi), 119 (20, Mes), 73 (100, SiMe$_3$).

Bromo(dimesitylsilyl)dimesitylgermane (7). To a solution of **1** (130 mg, 0.211 mmol) dissolved in THF (5 mL) was added *t*-BuLi (1.5 mL, 2.3 mmol, 1.55 M in pentanes) at −23 °C (dry ice–CCl$_4$). The reaction mixture was then stirred at room temperature for 6 h before the addition of PhCH$_2$Br (0.3 mL). After aqueous workup, **7** was obtained by washing the crude reaction mixture with pentanes (41.5 mg, 30%). The product can be further purified by chromatography. IR (KBr, cm^{-1}): 2151 (SiH). Raman (solid, cm^{-1}): 580, 564, 553, 530, 426, 264, 184, 176, 155. ^{1}H NMR (ppm): 6.67, 6.64 (each s, Mes–H), 6.18 (s, Si–H), 2.45, 2.38 (each s, *o*-Me), 2.06, 2.05 (each s, *p*-Me). ^{13}C NMR (CDCl$_3$, ppm): 145.26, 142.96, 139.44, 138.79 (Mes–C), 129.40, 128.80 (Mes–CH), 128.51 (Mes–C), 24.42, 21.08, 20.90 (Me). ^{29}Si NMR (ppm): −44.56 (d, J = 187 Hz). MS [m/z (%)]: 660, 658 (0.4, 0.6, M$^+$), 579 (4, M$^+$ − Br), 391 (12, MesGeBr), 385 (16), 312 (98, Mes$_2$Ge), 267 (98, Mes$_2$SiH), 192 (70), 147 (50), 119 (100, Mes). High-resolution MS for $C_{36}H_{45}{}^{79}Br^{74}Ge^{28}Si$ (m/z): calcd 658.1686; found 658.1691.

1-(Bis(2,4,6-triisopropylphenyl)germyl)-1-mesityl-4,6-dimethyl-1-siladihydrobenzocyclobutene (10). To a solution of **2** (100 mg, 0.13 mmol) dissolved in cyclohexane (1 mL) at 10 °C was added *t*-BuLi (0.75 mL, 1.55 M in pentanes) in one shot. The reaction mixture was warmed to room temperature and then refluxed for 3 h. The resulting dark orange solution was cooled, and excess MeOH was added. The color of the reaction mixture changed to lemon yellow. The reaction mixture was stirred for 1 h, hydrolyzed using 1 M HCl, and extracted with Et$_2$O. The ether extracts were combined and then dried over MgSO$_4$ and filtered, and the solvent was removed to yield a mixture of the starting material (74 mg) and the rearranged product, **10**. The products were separated using chromatographic techniques. Compound **10** was isolated in 50% yield (17 mg) based on consumed **2**. Mp 135–137 °C. IR (KBr, cm^{-1}): 1983 (s, GeH). ^{1}H NMR (ppm): 7.04 (s, 2 H, Ar–H), 7.01 (s, 2 H, Ar–H), 6.76 (s, 1 H, Ar–H), 6.73 (s, 1 H, Ar–H), 6.62 (s, 2 H, Ar–H), 6.01 (s, 1 H, Ge–H), 3.32 (pseudooctet, 4 H, J = 6.8 Hz, *o*-C*H*(Me)$_2$), 2.74 (sept, J = 6.9 Hz, *p*-C*H*(Me)$_2$), 2.73 (sept, J = 6.9 Hz, *p*-C*H*(Me)$_2$, both sept 2 H), 2.88, 2.55 (d, 2 H, J = 16.4 Hz, C*H*$_2$ geminal), 2.37 (s, 6 H, *o*-Me), 2.34 (s, 3 H, Me), 2.13 (s, 3 H, Me), 2.06 (s, 3 H, Me), 1.25 (d, J = 6.8 Hz, o-CH(*Me*)$_2$), 1.20 (d, J = 6.8 Hz, o-CH(*Me*)$_2$), 1.18 (d, J = 6.8 Hz, *o*-CH(*Me*)$_2$), 1.17 (d, J = 6.7 Hz, *o*-CH(*Me*)$_2$, all four d 24 H), 0.71 (d, 6 H, J = 6.6 Hz, *p*-CH(*Me*)$_2$), 0.62 (d, 6 H, J = 6.6 Hz, *p*-CH(Me)$_2$). ^{13}C NMR (ppm): 154.42, 154.06, 151.96, 149.65, 149.48, 144.31. 141.75, 141.20, 140.68, 139.33, 136.17, 135.84, 132.33 (Ar–C), 130.09, 128.69, 124.84, 122.11, 121.92 (Ar–CH), 36.42, 36.05 (*o*-CHMe$_2$), 34.51 (*p*-CHMe$_2$), 24.68, 24.55, 24.46, 24.23, 24.19, 24.14, 135.84, 22.42, 21.74, 21.00 (all Me), 22.50 (CH$_2$). ^{29}Si{^{1}H} NMR (ppm): −5.27. MS, m/z [CI, isobutane (%)]: 746 (14, M$^+$), 626 (32, M$^+$ − MesH), 542 (99, M$^+$ − $C_{15}H_{24}$), 480 (75, ($C_{15}H_{23}$)$_2$Ge), 349 (53), 277 (100, Ge($C_{15}H_{23}$)), 265 (20, M$^+$ − ($C_{15}H_{23}$)$_2$GeH), 235 (30), 204 (42), 189 (49), 147 (39, MesSi), 119 (20, Mes), 105 (42). High-resolution MS for $C_{48}H_{68}{}^{74}Ge^{28}Si$ (m/z): calcd 746.4302; found 746.4286.

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