Reaction between (Chlorodimesityisilyi)diaryigermanes 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 = SiMe₃; 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 semiconductors¹ 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 dichlorodimesitylsilane⁵ 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.

$$\begin{array}{rcl} \operatorname{Ar_2GeH_2} + t\operatorname{BuLi} & \longrightarrow & \operatorname{Ar_2GeHLi} + & \operatorname{Me_2SO_4} & \longrightarrow & \operatorname{Ar_2GeHMe} & (1) \\ & & \operatorname{Ar} = & \operatorname{Mes}^6 \\ & & \operatorname{Ar} = & 2,4,6-\text{triisopropylphenyl} \\ & & \operatorname{Ar_2GeHLi} + & \operatorname{Mes_2SiCl_2} & \xrightarrow{\mathsf{THF}} & \operatorname{Ar_2Ge-SiMes_2} & (2) \\ & & & | & | \\ & & \operatorname{H} & \operatorname{Cl} \\ & & 1: & \operatorname{Ar} = & \operatorname{Mes} \\ & & 2: & \operatorname{Ar} = & 2,4,6-\text{triisopropylphenyl} \end{array}$$

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 ²⁹Si 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

(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-workers7 when $(Me_2XSi)(Me_3Si)_2CBr$ (X = F, SPh) was treated with t-BuLi. They attributed the formation of (Me₂XSi)- $(Me_3Si)_2CH$ (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- $Bu_2FGe)PHAr$ (Ar = 2,4,6-tri-tert-butylphenyl) with t-BuLi in diethyl ether/pentane gave (t-Bu₂HGe)PHAr.⁸ Formation of the hydridogermane was believed to be a consequence of the diradical nature of t-Bu₂Ge=PAr. Similarly, treatment of Bis₂GeF-CHR₂⁹ or Bis₂SnCl- CHR_2^{10} (Bis = bisyl = $CH(SiMe_3)_2$ and CR_2 = fluorenylidene) with t-BuLi in Et₂O 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.

$$Bis_{2}M - CR_{2}$$
$$|$$
Li
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 ²⁹Si

$$\begin{array}{c} \text{Ar}_2\text{Ge}-\text{SiMes}_2 \\ | & | \\ \text{H} & \text{Cl} \end{array}$$
1: Ar = Mes
2: Ar = 2,4,6-triisopropylphenyl
$$\begin{array}{c} \text{(i) } 2r\text{-Bull, THF} \\ \text{(ii) } MeOH-d_4 \end{array}$$

$$\begin{array}{c} \text{Ar}_2\text{Ge}-\text{SiMes}_2 \\ | & | \\ \text{D} & \text{H} \end{array}$$
3a: Ar = Mes
4a: Ar = 2,4,6-triisopropylphenyl

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

$$\begin{array}{cccc} \operatorname{Mes}_2 \operatorname{Ge} & -\operatorname{SiMes}_2 & \xrightarrow{(i) & 27 \operatorname{BuLi}, \ THF} & \operatorname{Mes}_2 \operatorname{Ge} & -\operatorname{SiMes}_2 & (5) \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\$$

(dimesitylsilyl)dimesityl(trimethylsilyl)germane (6), and use of benzyl bromide led to the formation of (dimesi-



Figure 1. (a) ¹H NMR spectrum of 2 in C_6D_6 at 20 °C. (b) ¹H NMR spectrum of 2 in $\overline{C_7}D_8$ at 130 °C.

Scheme I



mechanism B



tylsilyl)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.

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(trimethyls]y])-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.



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 ¹H and ²H 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 omethyls 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



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

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 germasilenetype intermediate generated by initial dehydrochlorination of 2.

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 LiAlH₄, 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 GeCl₄ 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 ¹H and 50.3 MHz for ¹³C), or an XL-300 (299.9 MHz for ¹H, 75.4 MHz for ¹³C, and 59.6 MHz for ²⁹Si) spectrometer using deuterated benzene as a solvent unless otherwise noted. The standards used were as follows: residual C_6D_6H , 7.15 ppm for ¹H NMR spectra; C_6D_6 central transition, 128.00 ppm for ¹³C NMR spectra; Me_4Si as an external standard, 0.00 ppm for ²⁹Si NMR spectra. The ¹³C NMR signal assignments were made by using the DEPT¹⁶ pulse sequence or by recording the

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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-triisopropylbenzene¹⁵ (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 GeCl₄ (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 Et₂O, and the combined extracts were dried over MgSO₄. 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 LiAlH₄ (1.6 g, 42 mmol) in Et₂O was added a solution of the above dihalogermane (14.3 g) in Et₂O (25 mL) over 40 min. The mixture was then gently refluxed for 11 h. Excess LiAlH₄ was destroyed by the slow addition of 6 M HCl. The reaction mixture was extracted with Et₂O. The combined organic layers were washed with brine (80 mL) and then dried over MgSO₄ 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-CH(Me)₂), 2.77 (sept, 2 H, J = 6.9 Hz, p-CH(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). ¹³C NMR (ppm): 154.45, 150.16, 131.81, (Ar'-C), 121.55 (Ar'-CH), 34.84 (o-CH(Me)₂), 34.7 (p-CH(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-CCl₄) 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 Et₂O. The combined organic phase was then dried over MgSO4 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 = 6.9Hz, o-CH(Me)₂), 2.78 (sept, 2 H, J = 6.9 Hz, p-CH(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). ¹³C NMR (ppm): 154.1, 149.77, 134.95 (Ar'-C), 121.64 (Ar'-CH), 34.64 (p-CH(Me)₂), 34.13 (o-CH(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-CCl₄). 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). ¹³C 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); ²⁹Si NMR (CDCl₃, 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 C₃₆H₄₅³⁵Cl⁷⁴Ge³²Si (m/z): calcd 614.2191; found 614.2196. Anal. Calcd for C₃₆H₄₅ClGeSi: C, 70.44; H, 7.39. Found: C, 69.28; H, 7.15.

(Chlorodimesitylsilyl)deuteriodimesitylgermane (1a). Mes₂GeD₂ was prepared by reduction of Mes₂GeX₂ with LiAlD₄. Mes₂GeD₂ was then substituted for Mes₂GeH₂ in the preparation of 1 to give 1a. IR (thin film, cm⁻¹): no Ge–H. ²H NMR (C₆H₆, 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-CCl₄) 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 Mes₂SiCl₂ (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 Et₂O. The combined organic layers were dried over MgSO₄ 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 (CCl₄ solution, cm⁻¹): 2014 (s, Ge–H). ¹H NMR (C₇D₈, 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-CHMe₂), 2.78 (sept, 2 H, J = 6.8 Hz, p-CHMe₂), 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, CHMe₂). ¹³C NMR (C₇D₈, 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 (CHMe₂), 34.49 (CHMe₂), 24.77, 24.61, 24.42, 23.86, 20.63 (all Me). ²⁹Si 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⁺ - SiClMes₂), 480 (100, M⁺ - H - SiClMes₂), 301 (16, M⁺ -(C₁₅H₂₃)₂GeH), 277 (38), 235 (10), 203 (2, C₁₅H₂₃). 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 C48H69ClGeSi: 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 (CHCl₃, 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-CCl₄) 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, 10.15 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 ²⁹Si⁻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 (CDCl₃, ppm) 6.68 (b s), 5.60 (d), 5.33 (d), 2.20 (s), 2.19 (s), 2.15 (s), 2.09 (s); ¹³C 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); ²⁹Si 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 C₃₆H₄₅⁷⁴Ge²⁸Si $(M^+ - 1) (m/z)$ calcd 579.2508, found 579.2493. Anal. Calcd for C₃₆H₄₆GeSi: 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 (CHCl₃, ppm) 5.27 (b s); ²H NMR (C₆H₆, ppm) 5.75 (b s); ²⁹Si NMR (CDCl₃, 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-CCl₄)

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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). ¹H 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-CHMe₂), 2.74 (sept, 2 H, p-CHMe₂), 2.42 (b s, 12 H, o-Me), 2.03 (s, 6 H, p-Me), 1.184, 1.175 (b d, 36 H, CHMe₂). ¹H 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-CHMe₂), 2.76 (sept, 2 H, J = 6.9 Hz, p-CHMe₂), 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-CHMe₂), 1.12 (b d, 12 H, J =6.7 Hz, o-CHMe₂), 0.93 (b d, 12 H, J = 6.4 Hz, o-CHMe₂). ¹³C 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 (-CHMe₂), 24.57, 24.43, 24.07, 24.04, 20.93 (all Me). ²⁹Si NMR (ppm): -49.08 (d of d, ${}^{1}J = 191$ Hz, ${}^{2}J = 8.8$ Hz). MS [m/z (%)]: 747 (16, M⁺ – H), 629 (12, M⁺ – Mes), 545 (24, M⁺ – C₁₅H₂₃), 480 (100, M⁺ – H - SiHMes₂), 351 (20, SiHMes($C_{15}H_{23}$)), 277 (34, Ge($C_{15}H_{23}$)), 267 (46, M⁺ – GeH(C₁₅H₂₃)₂), 203 (14, C₁₈H₂₃). High-resolution MS for C₄₈H₆₉⁷⁴Ge²⁸Si (M⁺ – H) (m/z): calcd 747.4380; found 747.4389. Anal. Calcd for C₄₈H₇₀GeSi: 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: ¹H NMR (ppm) 5.99 (b s, Si-H); ²H NMR (CHCl₃, ppm) 5.52 (b s, Ge-D).

(Dimesitylsilyl)dimesitylmethylgermane (5). To a solution of 1 (98.7 mg, 0.161 mmol) dissolved in LiAlH₄-dried THF (5 mL) was added t-BuLi (0.3 mL, 0.4 mmol, 1.55 M in pentanes) at -23 °C (dry ice-CCl₄). 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 ¹H NMR spectroscopy). Characterization for 5 containing approximately 10% of 3: IR (thin, film, cm⁻¹) 2141, 2029; ¹H 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); ¹³C 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); ²⁹Si 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-CCl₄). The cold bath was removed and the reaction mixture was stirred for 3.5 h. Me₃SiCl (0.4 mL, distilled from CaCl₂ 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; ¹H 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, SiMe₃); ¹³C 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); ²⁹Si NMR (ppm) -2.93 (m, J = 6 Hz), -48.50 $(d, J = 186 \text{ Hz}); \text{MS} [m/z, \text{CI, isobutane (\%)}] 652 (6, M^+), 651$ (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 Mes₂GeH(SiMe₃): ¹H NMR 6.77, 5.18 (Ge–H), 2.40, 2.12, 0.25 (SiMe₃); ¹³C 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, SiMe₃).

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-CCl₄). The reaction mixture was then stirred at room temperature for 6 h before the addition of PhCH₂Br (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. ¹H 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). ¹³C NMR (CDCl₃, 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). ²⁹Si 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, $\begin{array}{l} {\rm Mes_2Ge),\ 267\ (98,\ Mes_2SiH),\ 192\ (70),\ 147\ (50),\ 119\ (100,\ Mes).} \\ {\rm High-resolution\ MS\ for\ C_{36}H_{45}\ ^{79}{\rm Br}^{74}{\rm Ge}^{28}{\rm Si\ }(m/z):\ {\rm calcd\ 658.1686;} \end{array}$ 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 Et₂O. The ether extracts were combined and then dried over MgSO₄ 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). ¹H 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-CH(Me)₂), 2.74 $(sept, J = 6.9 \text{ Hz}, p-CH(Me)_2), 2.73 (sept, J = 6.9 \text{ Hz}, p-CH(Me)_2),$ both sept 2 H), 2.88, 2.55 (d, 2 H, J = 16.4 Hz, CH_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). ¹³C 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-CHMe₂), 34.51 (p-CHMe₂), 24.68, 24.55, 24.46, 24.23, 24.19, 24.14, 135.84, 22.42, 21.74, 21.00 (all Me), 22.50 (CH₂). ²⁹Si^{{1}H} NMR (ppm): -5.27. MS, m/z [CI, isobutane (%)]: 746 (14, M^+), 626 (32, M^+ – MesH), 542 (99, M^+ – C₁₅H₂₄), 480 $(75, (C_{15}H_{23})_2Ge), 349 (53), 277 (100, Ge(C_{15}H_{23})), 265 (20, M^+ -$ (C₁₅H₂₃)₂GeH), 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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