

Addition of Methyl Grignard Reagents to Germasilenes and Digermenes: Unusual Ligand Exchange Reaction of the Resulting Germyl Grignard Reagents

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Abstract: Methylmagnesium iodide (or bromide) has been found to add to tetramesitylgermasilene and tetramesityldigermene. The addition to the germasilene is regioselective, with the methyl group adding to the silicon end of the silicon–germanium double bond to produce a germylmagnesium iodide (or bromide) species. The germyl Grignard reagents give the corresponding germanes upon hydrolysis. At 110 °C in the presence of excess methylmagnesium halide, the mesityl substituents on the germyl Grignard reagent germanium atom were exchanged for methyl groups. A mechanism involving the α -elimination of MesMgX followed by the addition of MeMgX to the intermediate germylene has been proposed to explain the observed ligand exchange. Evidence for the presence of intermediate germylenes has been obtained in trapping experiments with 2,3-dimethylbutadiene.

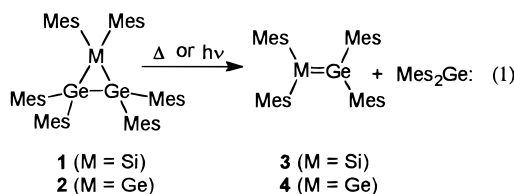
Introduction

Much has been learned about the chemistry of relatively stable or stable disilenes, germasilenes, and digermenes since the discovery of these compounds about 15 years ago.¹ Surprisingly, however, the reactivity of these compounds toward Grignard reagents is completely unknown. The only reports, to our knowledge, on the reaction between Grignard reagents and doubly bonded silicon or germanium compounds involve the reaction with a stable silene² or a stable germaphosphene.³ With such a paucity of information available, we decided to investigate the reaction between Grignard reagents and tetramesitylgermasilene. In particular, we were interested in the regiochemistry of the reaction, if, indeed, the Grignard reagent added. Furthermore, considering the recent interest in the generation and chemistry of both germyl⁴ and silyl⁵ Grignard

reagents, the addition of Grignard reagents to germasilenes appeared to be a potentially novel way of generating these compounds. Thus, the reaction between tetramesitylgermasilene and -digermene (for comparison purposes) and methyl Grignard reagents was examined under different conditions.

Results and Discussion

The thermolysis⁶ or photolysis⁷ of hexamesitylsiladigermirane (**1**) has been shown to give tetramesitylgermasilene and dimesitylgermylene regioselectively. Hexamesitylsiladigermirane is unreactive toward methylmagnesium bromide in the dark. Similarly, the thermolysis⁸ or photolysis⁹ of hexamesitylcyclo-trigermene¹⁰ (**2**) yields tetramesityldigermene and dimesitylgermylene (eq 1).



Hexamesitylsiladigermirane (**1**) was photolyzed at -78 °C in toluene in the presence of excess tris(trimethylsilyl)silane.¹¹ Methylmagnesium bromide was then added to the yellow solution in the cold. The color of the solution did not fade,

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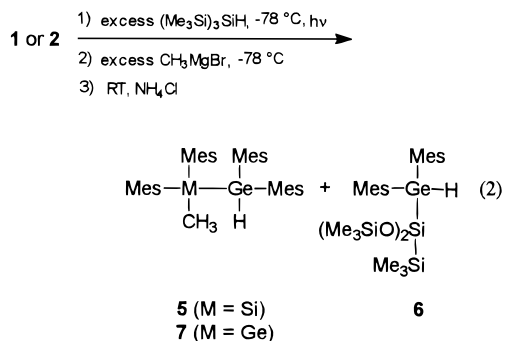
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(11) Our initial attempts to separate the products from the photolysis of **1** at -78 °C in toluene in the presence of Et₃SiH as a trapping reagent for Mes₂Ge: were unsuccessful, and thus (Me₃Si)₃SiH was chosen as an alternative trapping reagent: Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075–1077.

and thus the reaction mixture was warmed slowly to room temperature. The reaction mixture was hydrolyzed using aqueous NH_4Cl . Two major products, **5** and **6**, were observed by ^1H NMR spectroscopy in approximately a 1:1 ratio (eq 2).



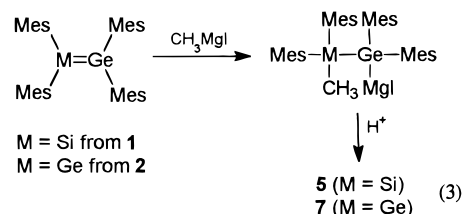
Compound **5** was readily identified by NMR and IR spectroscopy and mass spectrometry. The ^1H NMR spectrum of **5** exhibited resonances for two different mesityl groups as well as singlets consistent with an M–H moiety (5.73 ppm) and an M–Me group (1.24 ppm). The IR spectrum showed an absorbance at 2026 cm^{-1} , which supports the assignment of the M–H resonance in the ^1H NMR spectrum as Ge–H. The resonance observed at -17.83 ppm in the ^{29}Si NMR spectrum of **5** is not in the correct chemical shift range for a diaryl Si–H moiety. The ^{29}Si NMR chemical shift for the isomeric $\text{Mes}_2\text{MeGeSiHMes}_2$ was observed at -48.41 ppm ($^1J_{\text{Si}-\text{H}} = 189\text{ Hz}$),¹² confirming the assigned regiochemistry of **5**.

Compound **6** was also identified by IR and NMR spectroscopy and mass spectrometry. The ^1H NMR spectrum of **6** revealed one type of mesityl group, one M–H resonance at 5.32 ppm, and two different trimethylsilyl groups in a ratio of 2:1. The highest mass ion was found at m/z 592. Exact mass determination of the parent ion corresponded to a molecular formula of $\text{C}_{27}\text{H}_{50}\text{GeO}_2\text{Si}_4$. The IR absorption at 1995 cm^{-1} as well as the absence of any large coupling in the ^1H -coupled ^{29}Si NMR spectrum led to the assignment of the Ge–H moiety. The chemical shifts of 8.71 and -20.58 ppm in the ^{29}Si NMR spectrum are consistent with a trimethylsiloxy- and a silyl-substituted trimethylsilyl group, respectively.¹³ All these data led to the structural assignment of **6**. The structure $(\text{Me}_3\text{Si})_2(\text{Me}_3\text{SiO})\text{SiOGeMes}_2\text{H}$ was eliminated on the basis of the chemical shift of the germane hydrogen (5.32 ppm). Silyl-substituted dimesitylgermanes have a chemical shift of approximately 5–6 ppm (for example: $\text{MeMes}_2\text{SiGeMes}_2\text{H}$, GeH at 5.73 ppm; $\text{MeOMes}_2\text{SiGeMes}_2\text{H}$, GeH at 5.57 ppm⁶), whereas the chemical shifts of alkoxy- or chloro-substituted dimesitylgermanes are typically about 1 ppm downfield (for example: $(\text{MeO})\text{Mes}_2\text{GeH}$, GeH at 6.67 ppm;⁶ ClMes_2GeH , GeH at 6.7 ppm¹⁴). The formation of **6** is, indeed, surprising. It is known that the addition of the Grignard reagent to tetramesityldigermene (and, presumably, also the germsilene) is not related to the formation of **6**: photolysis of hexamesitylcyclo-trigermene (**2**) at -70°C in toluene in the presence of $\text{HSi}(\text{SiMe}_3)_3$ followed by quenching with methanol gave a 1:1 ratio of **6** and $\text{Mes}_2\text{Ge}(\text{OMe})\text{GeHMes}_2$.⁶ It is possible that dimesitylgermylene inserts preferentially into the product of autoxi-

dation of $\text{HSi}(\text{SiMe}_3)_3$, $\text{HSi}(\text{SiMe}_3)(\text{OSiMe}_3)_2$, which may have been present in small amounts.¹⁵ We are continuing to investigate this possibility.

To compare the observed reactivity of tetramesitylgermasilene and methylmagnesium bromide with tetramesityldigermene, hexamesitylcyclo-trigermene (**2**) was photolyzed at -78°C in the presence of excess $\text{HSi}(\text{SiMe}_3)_3$ (eq 2). Addition of Grignard reagent to a cold solution of the digermene resulted in the immediate discharge of the yellow-green color associated with the digermene. Following quenching of the reaction mixture with aqueous NH_4Cl , two products, **6** and **7**,^{4b} were formed in a 1:1 ratio as determined by ^1H NMR spectroscopy.

Cophotolysis of either hexamesitylsiladigermirane or -cyclo-trigermene in the presence of methylmagnesium iodide at approximately -70°C also results in the formation of **5** and **7**, respectively, in addition to MeMes_2GeH (**8**), apparently from addition of the Grignard reagent to dimesitylgermylene. Thus, at low temperature, it appears that the Grignard reagent will add across the double bond of the dimetallene (generated by the photolysis of **1** or **2**), producing a germyl Grignard intermediate, which can be protonated by hydrolysis to give the observed products (eq 3). With tetramesitylgermasilene,



the anionic portion of the Grignard reagent adds to the silicon end of the Si–Ge double bond regioselectively. The high regioselectivity is, most probably, the result of the greater electronegativity of germanium in comparison to that of silicon,¹⁷ although the greater strength of the Si–C versus the Ge–C bond may contribute.¹⁸ The regioselectivity of the cleavage of the π bond of the germsilene is the same as that observed in the anionic cleavage of Si–Ge σ bonds.¹⁹

The initial results suggest that addition of methylmagnesium halides to the $\text{M}_1\text{--M}_2$ double bonds of germsilenes and digermenes is straightforward. However, when tetramesitylgermasilene or -digermene was generated thermally from **1** or **2**, respectively, in the presence of an excess of methylmagnesium bromide or iodide, some very unexpected chemistry was observed. Thermolysis of **1** in the presence of methylmagnesium bromide followed by quenching with aqueous NH_4Cl yielded a single product, **9**, in very high yield (eq 4). Compound **9** was identified by NMR and IR spectroscopy and mass spectrometry. The ^1H NMR spectrum showed one distinct mesityl group along with a septet, a singlet, and a doublet

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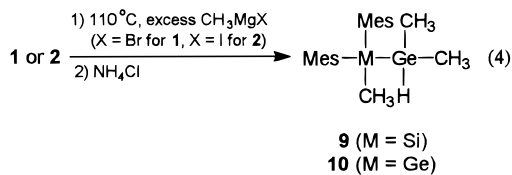
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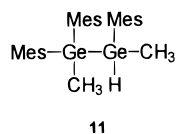
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consistent with the Ge–H, the Si–CH₃, and the Ge(CH₃)₂ moieties found in **9**, respectively. The IR spectrum exhibited an absorbance at 2100 cm⁻¹, which is consistent with a Ge–H stretching vibration. The ²⁹Si NMR resonance at –20.20 ppm, again, suggests the absence of a diaryl Si–H moiety.

Similarly, thermolysis of **2** in the presence of an excess of methylmagnesium iodide followed by quenching with aqueous NH₄Cl yielded a single product, **10** (eq 4). The spectral data of **10** were very similar to those of **9**.

The isolation of **9** and **10** as the sole reaction products from the above experiments was interesting for a number of reasons. First, there appears to have been an exchange of mesityl groups for methyl groups at the germanium atom. Second, there were no compounds observed that were obviously derived from reaction between dimesitylgermylene and the Grignard reagent. The products of the cyclotriggermane thermolyses in the presence of the Grignard reagent vary with time. For example, if the thermolysis of **2** is quenched after 4 h, products **8** and **11** are isolated; however, after 18 h, products **10** and **11** are obtained. The ratio of the products also appears to be dependent on the reaction conditions. Compound **10** is the only product formed when the amount of ether (the Grignard reagent solvent) is kept to a minimum. The isolation of **11** suggests that the mesityl–methyl exchange was occurring in a stepwise manner.

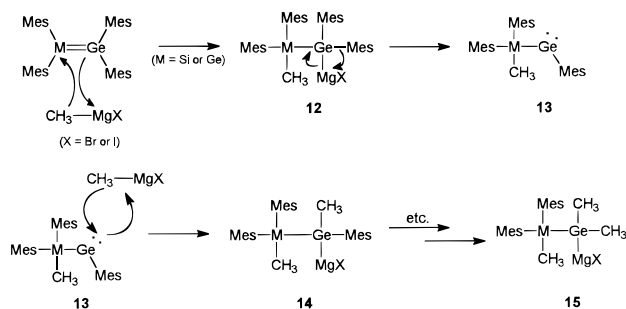


To explain the mesityl–methyl exchange, one may invoke an α-elimination of MesMgBr from the initially formed germyl Grignard species **12** to generate the metallylgermylene **13** (Scheme 1). A second equivalent of methylmagnesium bromide may then add to the metallylgermylene intermediate to give the germyl Grignard species **14**. A similar series of α-eliminations and additions would result in the formation of the germyl Grignard species **15**. Hydrolysis of **15** (M = Si) would yield **9**, whereas hydrolysis of both intermediates **14** and **15** (M = Ge) would give **11** and **10**, respectively.

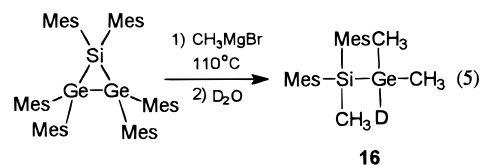
There are accounts in the literature that offer precedents for the proposed mechanism. For example, Glockling and Hooton have reported that Bu₃SnLi apparently dissociates, by α-elimination, to Bu₂Sn: and BuLi.²⁰ A similar α-elimination has been reported by Castel and co-workers to occur from Ph₂GeHLi to give LiH and the corresponding germylene species, which reacts further to yield polygermanes, following hydrolysis.¹⁶ Furthermore, Seyferth²¹ and others²² have postulated that diorganogermynes, R₂Ge:, may react with Grignard reagents, RMgX, to form germyl Grignard species of the type R₃GeMgX.

Confirmation of the presence of a germyl Grignard reagent, as proposed in the above mechanism, was obtained by trapping experiments with deuterium oxide. Thermolysis of hexamesitylsiladigermirane in the presence of an excess of methylmag-

Scheme 1

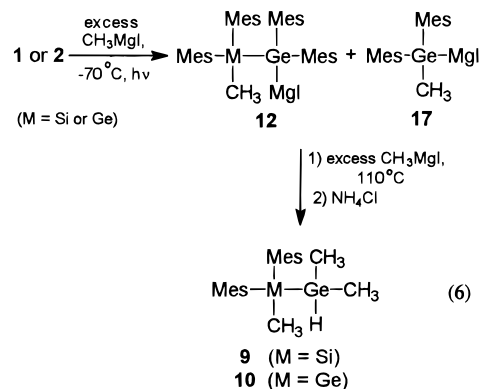


nesium bromide yielded **16** upon quenching of the reaction mixture with D₂O (eq 5). This result supports the presumption



that the final product in each of the thermolysis experiments is basic in nature and that the compound is, presumably, **15**.

Central to this mechanism is the assumption that the first-formed intermediate in these thermolyses reactions is the germyl Grignard reagent **12**. When a solution of **12**²³ and **17**, generated by photolysis of **1** or **2** at –70 °C in the presence of an excess of methylmagnesium iodide, is heated to 110 °C followed by hydrolysis with aqueous NH₄Cl, **9** (M = Si) and **10** (M = Ge) are isolated as the sole products of reaction, respectively (eq 6). The formation of **9** and **10** from solutions containing



intermediates **12** and **17** supports the idea that intermediates **12** (M = Si or Ge) and **17** are formed first upon the thermolysis of hexamesitylsiladigermirane or -cyclotriggermane in the presence of methylmagnesium halide, and that thermolysis of **12** (M = Si or Ge) and **17** ultimately leads to **9** and **10**, respectively. Consistent with the earlier thermolyses, there were no products isolated from either experiment that could be identified as being derived from reaction of intermediate **17**, which is the expected product of reaction from dimesitylgermylene and methylmagnesium bromide or iodide.

It is believed that intermediate **17** also undergoes a series of α-eliminations (of MesMgX) and additions of CH₃MgX, the end result of which is the production of trimethylgermylmagnesium halide. Upon hydrolysis, however, trimethylgermyl-

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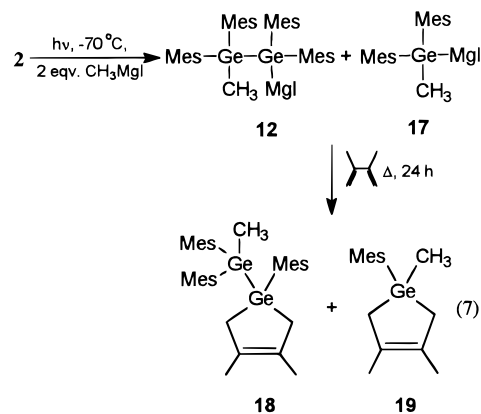
(23) The presence of **12** (M = Si or M = Ge) and **17** was confirmed prior to heating by analysis of an aliquot of the reaction mixture. Following hydrolysis of the aliquot, the only products observable by ¹H NMR spectroscopy were **5** (M = Si) or **7** (M = Ge) and **8**.

magnesium halide will yield trimethylgermane, which is a relatively volatile compound (bp = 26 °C) and, thus, difficult to isolate. To support, or exclude, the formation of Me₃GeH when intermediate **17** is heated in the presence of an excess of methylmagnesium iodide, hexamethylcyclotrigermane was heated to 110 °C for 12 h in the presence of excess methylmagnesium iodide. Following hydrolysis with NH₄Cl, analysis of the headspace gas revealed the presence of two additional compounds in the GC–MS trace, as compared to the GC–MS trace of the headspace gas of the reaction mixture prior to hydrolysis. One of the compounds was readily identified as mesitylene (1,3,5-trimethylbenzene) by comparison of the experimental mass spectrum with the known mass spectrum for mesitylene. The mass spectrum of the other compound was found to be consistent with Me₃GeH. There was a fragment cluster at *m/z* 118.²⁴ A comparison of the calculated theoretical cluster for C₃H₁₀Ge to the experimental fragment cluster found at *m/z* 118 showed a very good correlation between the observed and calculated isotopic ratios. Thus, Me₃GeH appears to be a product in the thermolysis of hexamethylcyclotrigermane in the presence of excess methylmagnesium iodide.

Intercepting a reactive intermediate proposed to be participating in a reaction has long been taken as evidence for the existence of that intermediate and, thus, taken as support for a proposed mechanism. Therefore, support for the α -elimination mechanism may be obtained by intercepting any of the proposed germylene intermediates thought to be produced by the α -elimination of MesMgBr. Since conjugated dienes are well-known traps for germylene species,²⁵ any germylene intermediates produced during the thermolysis experiments should readily be intercepted by the diene. Isolation of any such trapped germylene species could be taken as strong evidence for the presence of these species in the reaction mixture and, furthermore, taken as evidence for the operation of the proposed α -elimination mechanism.

Photolysis of hexamethylcyclotrigermane in the presence of exactly 2 equiv of methylmagnesium iodide produced a solution of **12** (M = Ge) and **17** in a 1:1 ratio as determined by examination of a hydrolyzed aliquot by ¹H NMR spectroscopy. Addition of 2,3-dimethylbutadiene to the solution of **12** (M = Ge) and **17** followed by heating of the reaction mixture to 110 °C for several hours produced **18** and **19** (eq 7).

The identification of **18** was readily achieved by ¹H and ¹³C NMR spectroscopy and mass spectrometry. The ¹H NMR spectrum exhibited resonances for two different mesityl groups in a ratio of 2:1 as well as a singlet at 0.98 ppm, which is assigned to the Ge–CH₃ group. Moreover, a singlet at 1.69 ppm in the ¹H NMR spectrum is consistent with the vinylic methyl group of the germacyclopentene ring. There is also an AB spin system (2.05 and 2.28 ppm; *J*_{AB} = 15 Hz) in the ¹H NMR spectrum, which is compatible with the methylene hydrogen atoms of the germacyclopentene structure assigned to **18**. The DEPT and ¹H/¹³C HETCOR NMR spectra are each supportive of these assignments. For example, the DEPT NMR spectrum identifies the signal found at 30.76 ppm in the ¹³C



NMR spectrum as CH₂, and the HETCOR NMR spectrum demonstrated that this signal correlates with the resonances at 2.05 and 2.28 ppm in the ¹H dimension. Furthermore, resonances found at 18.92 and 4.69 ppm were shown to be CH₃ by the DEPT NMR spectrum, and these signals correlated with resonances at 1.69 and 0.98 ppm in the ¹H NMR spectrum, which are assigned to the =C–CH₃ and Ge–CH₃ moieties, respectively. The IR and mass spectra also agree with the assignment for **18**. Compound **19** was readily identified by ¹H and ¹³C NMR spectroscopy. Resonances for a single mesityl group and two singlets, which may be assigned to the C=C–CH₃ (1.75 ppm) and Ge–CH₃ (0.41 ppm) methyl groups in structure **19**, were observed in the ¹H NMR spectrum. Signals consistent with an AB spin system (1.68 and 2.02 ppm; *J*_{AB} = 15 Hz) were also clearly observable in the ¹H NMR spectrum, which is again entirely compatible with the assigned germacyclopentene structure of **19**. The ¹³C NMR spectrum exhibited the correct number of resonances, which are in the correct chemical shift range for the carbon atoms found in the above structure. Again, the IR and mass spectra also agree with the assignment for **19**.

Structures **18** and **19** are consistent with the trapping of mesityl(dimethylmethylgermyl)germylene (**13**, M = Ge, Scheme 1) and mesitylmethylgermylene (produced by α -elimination of MesMgI from **17**) by 2,3-dimethylbutadiene. The formation of these germylene intermediates is consistent with the α -elimination mechanism proposed for the mesityl–methyl substitution observed in the thermolysis experiments. Thus, isolation of **18** and **19** is taken as support for the operation of this mechanistic pathway.

Summary

In summary, the work detailed in this paper represents the first investigations into dimetalene reactivity toward Grignard reagents. It has been found that, under mild conditions, methylmagnesium halide will add, with apparently high regioselectivity, to tetramesitylgermasilene. The methyl group of the Grignard reagent adds to the silicon atom of the Si–Ge double bond, producing an intermediate germyl Grignard species. The germyl Grignard species so produced can then be protonated upon hydrolysis to yield the corresponding germane.

Likewise, tetramesityldigermene will add methylmagnesium halide under mild conditions to yield a germyl Grignard reagent that gives the corresponding germane upon hydrolysis. Qualitatively, MeMgX adds more readily to the digermene (rapid reaction at –78 °C), compared to the germasilene (reaction at approximately –10 °C) presumably because of the greater polarizability of the Ge–Ge double bond. The nature of the addition is unknown at this point.

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The reactivity of tetramesitylgermasilene toward methylmagnesium iodide (or bromide) under thermal conditions revealed some interesting and unexpected chemistry. It was found that, at elevated temperatures, the germyl Grignard intermediate generated by reaction of the methyl Grignard reagent with the germasilene underwent an unprecedented mesityl–methyl ligand exchange. The exchange was also observed upon addition of MeMgX to tetramesityldigermene at elevated temperatures. The formation of the products can be explained by α -elimination of MesMgI (or Br) from the germyl Grignard intermediate to give a germylene which subsequently reacts with the excess MeMgX . The intermediate germylene was trapped with 2,3-dimethylbutadiene, providing excellent support for the proposed mechanism.

We believe this is the first evidence for the facile elimination of (aryl) Grignard reagents from germyl Grignard reagents. Our findings are important for two reasons. Germylenes are important intermediates in organogermanium chemistry.²⁵ Our results provide a new and unique source of germylenes. Furthermore, considering the recent interest in germyl Grignard reagents,⁴ this new aspect of the reactivity of these compounds should play a critical role in understanding the chemical reactions involving these compounds. We are continuing our investigations into the generality of the addition of Grignard reagents and other organometallic reagents to stable dimetallenes as well as the chemistry of the resulting adducts.

Experimental Section

All experiments were carried out in flame-dried glassware under an atmosphere of argon. Toluene and Et_2O were freshly distilled from sodium/benzophenone. Methylmagnesium iodide and bromide were used in the following experiments. Methylmagnesium bromide was obtained from the Aldrich Chemical Co., whereas methylmagnesium iodide was prepared in the laboratory with magnesium purchased from Lancaster Chemical Co. and methyl iodide purchased from BDH. The choice of halide did not appear to influence the outcome of the reactions. Selection of which reagent was to be used was based solely on availability. Chromatography was carried out using a Chromatotron (Harrison Research) or on conventional silica gel preparative plates. Photolyses were carried out at 350 nm using a Rayonet photochemical reactor.

NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for ^1H , 50.3 MHz for ^{13}C), an XL-300, or a Varian Gemini 300 (299.9 MHz for ^1H , 75.4 MHz for ^{13}C , 59.6 MHz for ^{29}Si) using benzene- d_6 as a solvent, unless otherwise noted. The standards were as follows: residual $\text{C}_6\text{D}_5\text{H}$ 7.15 ppm for ^1H spectra; C_6D_6 or CDCl_3 central transition for ^{13}C NMR spectra; and Me_4Si as an external standard, 0 ppm for ^{29}Si . IR spectra were recorded (cm^{-1}) as thin films on a Perkin-Elmer System 2000 FT IR spectrometer. A Finnegan MAT model 8230 instrument, with an ionizing voltage of 70 eV, was used to obtain electron impact mass spectra (reported in mass-to-charge units, m/z , with ion identity and peak intensities relative to the base peak in parentheses).

Photolysis of Hexamesitylsiladigermirane in the Presence of $(\text{Me}_3\text{Si})_3\text{SiH}$ Followed by Addition of Methylmagnesium Bromide. A solution of $\text{SiGe}_2\text{Mes}_6$ (40 mg, 0.046 mmol; contaminated with some Ge_3Mes_6) and excess $(\text{Me}_3\text{Si})_3\text{SiH}$ in toluene (4 mL) was photolyzed at -78°C for 8 h. The reaction mixture was quenched with excess $(100\times)\text{CH}_3\text{MgBr}$ dissolved in diethyl ether. The reaction mixture was kept cold overnight and then allowed to warm gradually over 8 h. The reaction mixture was then hydrolyzed with saturated NH_4Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with an Et_2O /toluene mixture. The combined organic extracts were dried over MgSO_4 and then filtered to remove the MgSO_4 , followed by evaporation of the solvent. The residue was separated by preparative chromatography using the Chromatotron (1:9 CH_2Cl_2 /hexanes) to give $(\text{Me}_3\text{SiO})_2(\text{Me}_3\text{Si})\text{SiGeMes}_2\text{H}$ (**6**) (13 mg, 0.022 mmol, 48%) and a mixture of (dimesitylmethylsilyl)dimesitylgermane (**5**) and

(dimesitylmethylgermyl)dimesitylgermane (**7**) (17 mg) in a ratio of 10:1 as determined by ^1H NMR spectroscopy.

(Dimesitylmethylsilyl)dimesitylgermane (5): IR (thin film, cm^{-1}) 2921 (s), 2025 (m, Ge-H), 1603 (s), 1551 (w), 1451 (s), 1027 (m), 847 (s), 803 (m), 739 (m), 703 (w), 684 (w); ^1H NMR (ppm) 6.73 (s, 4 H, Mes H), 6.67 (s, 4 H, Mes H), 5.73 (s, 1 H, GeH), 2.28 (s), 2.25 (s, 24 H total, Mes oCH_3), 2.11 (s), 2.08 (s, 12 H total, Mes pCH_3), 1.24 (s, 3 H, SiCH_3); ^{13}C NMR (ppm) 144.54, 143.86, 138.58, 137.67, 136.65, 134.37 (Mes C), 129.87, 129.02 (Mes CH), 24.82, 24.78, 20.99, 20.90 (Mes CH_3), 6.34 (Si-CH_3); ^{29}Si NMR (ppm) -17.83 ; MS (m/z) 594 (M^+ , 0.86), 431 (Mes₃Ge, 2.1), 312 (Mes₂Ge, 35), 281 (Mes₂SiCH₃, 100), 192 (MesGe – H, 14); high-resolution MS, calcd for $\text{C}_{37}\text{H}_{48}\text{SiGe}$ 594.2737, found 594.2521.

[Bis(trimethylsiloxy)(trimethylsilyl)silyl]dimesitylgermane (6): IR (thin film, cm^{-1}) 1995 (m, GeH); ^1H NMR (ppm) 6.78 (s, 4 H, Mes H), 5.32 (s, 1 H, GeH), 2.53 (s, 12 H, Mes oCH_3), 2.11 (s, 6 H, Mes pCH_3), 0.15 (s, 9 H, $\text{SiSi}(\text{CH}_3)_3$), 0.14 (s, 18 H, $\text{OSi}(\text{CH}_3)_3$); ^{13}C NMR (ppm) 143.69, 137.66, 135.49, 128.76 (Mes C), 25.29 (Mes oCH_3), 21.01 (Mes pCH_3), 2.25 ($\text{OSi}(\text{CH}_3)_3$), -1.56 ($\text{SiSi}(\text{CH}_3)_3$); ^{29}Si NMR (ppm) 8.71 (decet, $\text{OSi}(\text{CH}_3)_3$, $J = 6.6$ Hz), -15.99 (multiplet, central Si), -20.58 (decet, $\text{Si}(\text{CH}_3)_3$, $J = 6.6$ Hz); MS (m/z) 592 (M^+ , 3), 577 ($\text{M}^+ - \text{CH}_3$, 1), 312 (Mes₂Ge, 10), 279 ($(\text{Me}_3\text{SiO})_2\text{SiSiMe}_3$, 100), 191 (51), 117 (Me_3SiOSi , 13), 91 (Me_3SiO , 14), 73 (Me_3Si , 40); high-resolution MS calcd for $\text{C}_{27}\text{H}_{50}\text{GeO}_2\text{Si}_4$ 592.2100, found 592.2080, calcd for $\text{C}_9\text{H}_{27}\text{O}_2\text{Si}_4$ 279.1088, found 279.1095.

Photolysis of Hexamesitylcyclotrigermene in the Presence of $(\text{Me}_3\text{Si})_3\text{SiH}$ Followed by Addition of Methylmagnesium Bromide. A solution of Ge_3Mes_6 (100 mg, 0.11 mmol) and excess $(\text{Me}_3\text{Si})_3\text{SiH}$ in toluene (4 mL) was photolyzed at -78°C for 16 h. The reaction mixture was quenched with excess ($5\times$) CH_3MgBr dissolved in diethyl ether. The green-yellow color of the solution disappeared immediately upon addition of the Grignard reagent. The reaction mixture was then hydrolyzed with saturated NH_4Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with Et_2O . The combined organic extracts were dried over MgSO_4 and then filtered to remove the MgSO_4 , followed by evaporation of the solvent. The products were separated by preparative chromatography using the Chromatotron (8:92 CH_2Cl_2 /hexanes) to give $(\text{Me}_3\text{SiO})_2(\text{Me}_3\text{Si})\text{SiGeMes}_2\text{H}$ (**6**) (56 mg, 0.095 mmol, 86%) and (dimesitylmethylgermyl)dimesitylgermane^{4b} (**7**) (50 mg, 0.078 mmol, 71%).

Photolysis of **2** (50 mg) under the same conditions followed by quenching the reaction mixture with excess methanol gave a 1:1 ratio of **6** and $\text{Mes}_2(\text{OMe})\text{GeGeMes}_2\text{H}$ ⁶ as determined by ^1H NMR spectroscopy. The reaction was worked up in the usual manner and the resulting product mixture separated by preparative thin-layer chromatography (92:8 hexanes/ CH_2Cl_2) to give **6** (2.6 mg) and $\text{Mes}_2(\text{OMe})\text{GeGeMes}_2\text{H}$ (5.1 mg).

(Dimesitylmethylgermyl)dimesitylgermane (7): IR (thin film, cm^{-1}) 2965 (s), 2922 (s), 2029 (m, Ge-H), 1601 (m), 1555 (m), 1453 (s), 1288 (w), 1261 (w), 1027 (m), 848 (m), 805 (m); ^1H NMR (ppm) 6.71 (s, 4 H, Mes H), 6.69 (s, 4 H, Mes H), 5.90 (s, 1 H, GeH), 2.28 (s, 12 H, Mes oCH_3), 2.25 (s, 12 H, Mes oCH_3), 2.10, 2.09 (each s, 12 H total, Mes pCH_3), 1.30 (s, 3 H, GeCH_3); ^{13}C NMR (ppm) 143.77, 143.57, 138.44, 137.91, 137.84, 136.11 (Mes C), 129.56, 129.07 (Mes CH), 24.59, 21.00, 20.89 (Mes CH_3), 7.84 (GeCH_3); MS (m/z) 637 ($\text{M}^+ - \text{H}$, 0.3), 623 ($\text{M}^+ - \text{CH}_3$, 0.2), 431 (Mes₃Ge, 18), 327 (Mes₂GeCH₃, 100), 313 (Mes₂GeH, 14), 191 (MesGe, 14); high-resolution MS calcd for $\text{C}_{37}\text{H}_{47}^{74}\text{Ge}^{72}\text{Ge}$ ($\text{M}^+ - \text{H}$) 637.2110, found 637.2098.

Thermolysis of Hexamesitylsiladigermirane in the Presence of Methylmagnesium Bromide. $\text{SiGe}_2\text{Mes}_6$ (100 mg, 0.11 mmol) and approximately 2 mL of 3.1 M CH_3MgBr in diethyl ether (excess) were dissolved in toluene (4 mL) and heated in an oil bath at 110°C for 18 h. A cream-colored precipitate was observed. The reaction mixture was then hydrolyzed with a saturated NH_4Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with ether/toluene. The combined organic extracts were dried over MgSO_4 . Filtration to remove the MgSO_4 followed by evaporation of the solvent yields **9** (40 mg, 95%). Compound **9** can be purified by chromatography.

(Dimesitylmethylsilyl)dimethylgermane (9): IR (thin film, cm^{-1}) 2001 (m, GeH); ^1H NMR (ppm) 6.69 (s, 4 H, Mes H), 4.15 (septet, 1

H, $J = 4$ Hz, GeH), 2.33 (s, 12 H, Mes oCH₃), 2.09 (s, 6 H, Mes pCH₃), 0.82 (s, 3 H, SiCH₃), 0.30 (d, 6 H, $J = 4$ Hz, GeCH₃); ¹³C NMR (ppm) 143.18, 138.34, 133.98, 129.53 (Mes C), 24.53, 20.97 (Mes CH₃), 3.71 (SiCH₃), -4.95 (GeCH₃); ²⁹Si NMR (ppm) -20.20; MS (m/z) 386 (M⁺, 2), 281 (Mes₂SiCH₃, 100), 161 (MesSiCH₃ - H, 13); high-resolution MS calcd for C₂₁H₃₁SiGe (M⁺ - H) 385.14068, found 385.14072.

The reaction was repeated (15 mg of SiGe₂Mes₆). The thermolysis was carried out in C₆D₆ for 18 h at 105 °C in the presence of excess MeMgBr in ether. The reaction mixture was quenched with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with deuterated benzene. The combined organic extracts were dried over MgSO₄ and then analyzed by ¹H NMR spectroscopy. Mesitylene was found to be present as confirmed by spiking the sample with authentic material.

The reaction was repeated (30 mg of SiGe₂Mes₆ contaminated with Ge₃Mes₆). The reaction was hydrolyzed with D₂O and then worked up in the usual manner. The product was purified by chromatography (1:9 CH₂Cl₂/hexanes) to give a mixture of **16** and (dimesitylmethylgermyl)deuteriodimethylgermane.

(Dimesitylmethylsilyl)deuteriodimethylgermane (16): ¹H NMR (ppm) 6.71, 6.69, 2.33, 2.10, 2.09, 0.90, 0.81, 0.32, 0.29 (all singlets); ²H{¹H} NMR (C₆H₆, ppm) 4.34 (s, GeD of (dimesitylmethylgermyl)deuteriodimethylgermane), 4.17 (GeD of **16**).

Thermolysis of Hexamesitylcyclotrimergermane in the Presence of Methylmagnesium Bromide. (1) Ge₃Mes₆ (100 mg, 0.11 mmol) and approximately 2 mL of 3.1 M CH₃MgBr in diethyl ether (excess) were dissolved in toluene (3 mL) and heated in an oil bath at 80 °C for 4 h. A white precipitate was observed to form. The reaction mixture was then hydrolyzed with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with ether. The combined organic extracts were dried over MgSO₄ and filtered, and the solvents were evaporated. Analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed the presence of **8**¹⁶ and **11**. Chromatographic separation (8:92 CH₂Cl₂/hexanes) yielded **11** (52 mg, 0.098 mmol, 89%). Compound **8** was not isolated.

(2) Ge₃Mes₆ (60 mg, 0.066 mmol) and approximately 1.5 mL of 3.1 M CH₃MgBr in diethyl ether (excess) were dissolved in toluene (4 mL) and heated in an oil bath at 105 °C for 18 h. Following this time, the reaction mixture was hydrolyzed with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with ether. The combined organic extracts were dried over MgSO₄ and filtered, and the solvents were evaporated. Analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed the presence of **10** and **11** in a 1:1.3 ratio, respectively. Chromatographic separation (Chromatotron; eluent varied from 8% CH₂Cl₂ in hexanes to 25%) of the reaction mixture gave **11** (17 mg, 0.033 mmol, 50%). Compound **10** was not isolated from this reaction mixture.

1,1,2-Trimesityl-1,2-dimethyldigermane (11): IR (thin film cm⁻¹) 2967 (s), 2919 (s), 2030 (m, GeH), 1602 (m), 1557 (m), 1454 (s), 1289 (w), 1235 (w), 1027 (w), 849 (s), 803 (s), 780 (s); ¹H NMR (ppm) 6.72 (s, Mes H), 6.70 (s, Mes H), 6.69 (s, Mes H), 5.19 (q, $J = 4.1$ Hz, GeH), 2.31 (s, Mes oCH₃), 2.19 (s, Mes oCH₃), 2.18 (s, Mes oCH₃), 2.11 (s, Mes pCH₃), 2.09 (s, Mes pCH₃), 0.97 (s, GeCH₃), 0.75 (d, $J = 4.1$ Hz, GeCH₃); ¹³C NMR (ppm) 144.09, 143.21, 142.89, 139.29, 138.53, 138.25, 138.03, 137.96, 134.87, 129.68, 129.57, 129.13, 25.21, 25.07, 24.98, 21.36, 21.28, 21.25, 5.55, -1.68; MS (m/z) 550 (4), 533 (M⁺, 3), 327 (Mes₂GeCH₃, 100), 312 (Mes₂Ge, 13), 221 (MesGe(CH₃)₂, 23), 206 (MesGeCH₃, 21), 191 (MesGe, 16), 119 (Mes, 55).

Photolysis of Hexamesitylsiladigermirane in the Presence of Methylmagnesium Iodide Followed by Thermolysis. SiGe₂Mes₆ (50 mg, 0.058 mmol) and approximately 0.25 mL of 4 M CH₃MgI (excess) were dissolved in toluene (4 mL) and photolyzed at -60 °C for 4 h. The reaction mixture was then warmed to -10 °C and allowed to stand for 12 h. After standing at -10 °C, a small portion (approximately 1 mL) of the reaction mixture was removed and hydrolyzed with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with hexanes (10 mL total). The combined organic extracts were dried over MgSO₄ prior to filtration and solvent evaporation, which yielded a white solid residue. Examination of this residue showed it to be a 1:1 mixture of

(dimesitylmethylsilyl)dimesitylgermane (**5**) and dimesitylmethylgermane¹⁶ (**8**). The original reaction mixture was heated to 110 °C (from -10 °C) for 6 h. The remaining reaction mixture was then hydrolyzed with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with hexanes (20 mL total). The combined organic extracts were dried over MgSO₄ prior to filtration and solvent evaporation, which yielded a white solid residue. The crude reaction mixture was purified by preparative thin-layer chromatography (1:9 CH₂Cl₂/hexanes) to yield (dimesitylmethylsilyl)-dimethylgermane (**9**) as the only identifiable product.

Photolysis of Hexamesitylcyclotrimergermane in the Presence of Methylmagnesium Iodide Followed by Thermolysis. Ge₃Mes₆ (50 mg, 0.054 mmol) and approximately 0.25 mL of 4 M CH₃MgI (excess) were dissolved in toluene (5 mL) and photolyzed at -70 °C for 9 h. A small portion (approximately 1 mL) of the reaction mixture was removed and hydrolyzed with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with hexanes (10 mL total). The combined organic extracts were dried over MgSO₄ prior to filtration and solvent evaporation, which yielded a white solid residue. Examination of this residue showed it to be a 1:1 mixture of (dimesitylmethylgermyl)dimesitylgermane (**7**) and dimesitylmethylgermane¹⁶ (**8**). The original reaction mixture was heated to 110 °C (from -70 °C) for 4 h. The reaction mixture was then hydrolyzed with a saturated NH₄Cl solution. The aqueous and organic layers were separated, and the aqueous phase was extracted with hexanes (20 mL total). The combined organic extracts were dried over MgSO₄ prior to filtration and solvent evaporation, which yielded a white solid residue. The crude reaction mixture consisted mainly of (dimesitylmethylgermyl)dimethylgermane (**10**) as determined by ¹H NMR spectroscopy.

Thermolysis of Hexamesitylcyclotrimergermane in the Presence of Methylmagnesium Iodide and GC-MS Analysis of Headspace Gas. Ge₃Mes₆ (70 mg, 0.075 mmol) and approximately 0.3 mL of 4 M CH₃MgI (excess) were dissolved in toluene (5 mL) and heated to 110 °C for 12 h. Following this time, 100 μL of the headspace gas was withdrawn from the reaction vessel and injected into a Varian Saturn 4D GC-MS (-40 °C). Once the reference GC-MS trace was obtained, the reaction was quenched by injecting 1 mL of a saturated NH₄Cl solution into the sealed reaction vessel. When the exothermic reaction due to quenching subsided, a second 100 μL of the headspace gas was injected into the GC-MS. With the GC-MS analysis complete, the aqueous and organic layers of the hydrolyzed reaction mixture were separated, and the aqueous phase was extracted with hexanes. The combined organic extracts were dried over MgSO₄ prior to filtration and solvent evaporation. Analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed the presence of **10** as the major product. Preparative thin-layer chromatography (5:95 CH₂Cl₂/hexanes) gave **7** (21 mg, 60%) in pure form.

1,1-Dimesityl-1,2,2-trimethyldigermane (10): IR (thin film, cm⁻¹) 3032 (m), 2972 (s), 2920 (s), 2875 (m), 2008 (s, GeH), 1611 (m), 1563 (m), 1454 (m), 1417 (m), 1035 (m), 852 (m), 837 (m); ¹H NMR (ppm) 6.71 (s, 4 H, Mes H), 4.32 (septet, 1 H, $J = 3.9$ Hz, GeH), 2.33 (s, 12 H, Mes oCH₃), 2.10 (s, 6 H, Mes pCH₃), 0.90 (s, 3 H, GeCH₃), 0.32 (d, 6 H, $J = 3.9$ Hz, GeCH₃); ¹³C NMR (ppm) 142.57, 137.71, 137.66, 129.30, 24.56, 20.96, 3.83, 1.40; MS (m/z) 430 (M⁺, 4), 415 (M⁺ - CH₃, 1.6) 327 (Mes₂GeCH₃, 100), 221 (MesGe(CH₃)₂, 19), 193 (MesGe, 17), 119 (Mes, 17), 105 ((CH₃)₂GeH, 8); high-resolution MS calcd for C₂₁H₃₂Ge⁷⁴ 430.0937, found 430.0948.

Trimethylgermane: MS (m/z) 206 (10), 118 (85), 104 (100), 89 (50), 74 (15).

Thermolysis of Dimesityl(methyl)germylmagnesium Iodide and (Dimesitylmethylgermyl)dimesitylgermylmagnesium Iodide in the Presence of 2,3-Dimethylbutadiene. Ge₃Mes₆ (50 mg, 0.054 mmol) and 0.32 mL of 0.33 M CH₃MgI (0.11 mmol) were dissolved in toluene (5 mL) and photolyzed at -70 °C for 4 h. Approximately 0.5 mL of the reaction mixture was then hydrolyzed with a saturated NH₄Cl solution. Following extraction, analysis of this aliquot by ¹H NMR spectroscopy showed a 1:1 mixture of **7** and **8**. Approximately 0.25 mL of 2,3-dimethylbutadiene was added to the remaining reaction mixture, which was then heated to 110 °C for 16 h. Following this time, the reaction mixture was quenched with NH₄Cl. The aqueous

and organic layers were separated, and the aqueous phase was extracted with hexanes. The combined organic extracts were dried over MgSO_4 prior to filtration and solvent evaporation. Separation of the reaction mixture by preparative thin-layer chromatography (12:88 CH_2Cl_2 /hexanes) gave **18** (10 mg, 0.017 mmol, 31%) and **19** (5 mg, 0.017 mmol, 32%), with the best results obtained if the preparative chromatography plate was eluted twice. In addition, **19** was very difficult to visualize on the preparative plate. Under these solvent and elution conditions, **19** has an R_f value of approximately 0.80.

1-(Dimesitylmethylgermyl)-1-mesityl-3,4-dimethyl-1-germacyclopent-3-ene (18): IR (thin film, cm^{-1}) 3024 (w), 2927 (s), 2845 (s), 1705 (w), 1608 (m), 1566 (m), 1503 (m), 1458 (m), 1409 (m), 1379 (w), 1058 (m), 882 (w), 852 (w), 834 (w); ^1H NMR (ppm) 6.75 (s, 2 H, Mes H), 6.69 (s, 4 H, Mes H), 2.28 (d, 2 H, AB of CH_AH_B , $J = 15$ Hz), 2.21 (s, 12 H, Mes CH_3), 2.15 (s, 9 H, Mes CH_3), 2.11 (s, 6 H, Mes CH_3), 2.05 (d, 2 H, AB of CH_AH_B , $J = 15$ Hz), 1.69 (s, 6 H, $=\text{C}-\text{CH}_3$), 0.98 (s, 3 H, GeCH_3); ^{13}C NMR (ppm) 143.53, 142.70, 139.31, 137.85, 137.45, 136.92, 131.37 (Mes C and $=\text{C}-\text{CH}_3$), 129.12, 128.73 (Mes CH), 31.14 ($=\text{C}-\text{CH}_2$), 25.06, 24.63, 21.07, 20.96, 19.16 (Mes CH_3), 5.03 (GeCH_3); MS (m/z) 598 (M^+ , 1.5), 518 ($\text{Mes}_2(\text{CH}_3)\text{-GeGeMes}$, 25), 480 ($\text{M}^+ - \text{Mes}$, 1.5), 431 (Mes_3Ge , 5) 327 ($\text{Mes}_2\text{-GeCH}_3$, 100), 193 (MesGe , 20); high-resolution MS calcd for $\text{C}_{34}\text{H}_{46}^{74}\text{-Ge}^{72}\text{Ge}$ 600.2032, found 600.1918.

1-Mesityl-1,3,4-trimethyl-1-germacyclopent-3-ene (19): IR (thin film, cm^{-1}) 3024 (w), 2927 (s), 2867 (m), 1615 (m), 1566 (m), 1499 (s), 1454 (m), 1413 (m), 1058 (m), 882 (w), 830 (w); ^1H NMR (ppm) 6.78 (s, 2 H, Mes H), 2.29 (s, 6 H, Mes oCH_3), 2.16 (s, 3 H, Mes pCH_3), 2.03 (d, 2 H, AB of CH_AH_B , $J = 15$ Hz), 1.75 (bs with fine splitting, 6 H, $=\text{C}-\text{CH}_3$), 1.68 (d, 2 H, AB of CH_AH_B , $J = 15$ Hz), 0.42 (s, 3 H, GeCH_3); ^{13}C NMR (ppm) 142.95, 130.45, 128.81, 29.95, 24.29, 21.06, 19.41, -1.13 ; MS (m/z) 290 (M^+ , 30), 208 (MesGeCH_3 , 30), 193 (MesGe , 100), 57 (C_4H_9 , 28); high-resolution MS calcd for $\text{C}_{16}\text{H}_{24}^{74}\text{Ge}$, 290.1090, found 290.1091.

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Supporting Information Available: ^1H NMR spectra of **6**, **7**, **9**, **10**, **11**, **18**, and **19** (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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