Organometallics **1994,** *13,* 631–634

Thermolysis of Hexamesitylsiladigermirane or Hexamesitylcyclotrigermane in the Presence of 2,3-Dimethylbutadiene or Water

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Received September 21, 1993⊗

The thermolysis of hexamesitylsiladigermirane and hexamesitylcyclotrigermane in the presence of 2,3-dimethylbutadiene (DMB) or water has been investigated. Thermolysis of hexamesitylsiladigermirane (1) in the presence of DMB results in the formation of two major compounds: 1,1-dimesityl-3,4-dimethyl-1-germacyclopent-3-ene (**3**) and 1-mesityl-1-(trimesitylsilyl)-3,4-dimethyl-1-germacyclopent-3-ene (**4**). Compounds **3** and **4** are most probably formed by initial thermal regioselective cleavage of the siladigermirane to give tetramesitylgermasilene and dimesitylgermylene, which is immediately trapped by the diene. The germasilene does not appear to react with DMB but rather, under the reaction conditions, undergoes a 1,2-mesityl shift at a faster rate to give a silylgermylene, which is subsequently trapped by the diene. Similarly, thermolysis of hexamesitylcyclotrigermane (**5**) in the presence of DMB yields compounds **3** and 1-mesityl-1-(trimesitylgermyl)-3,4-dimethyl-1-germacyclopent-3-ene (**6**), in contrast to an earlier report. Again, the intermediate digermene rearranges to a germylgermylene, which is the species trapped, at a faster rate than reaction with DMB. Thermolysis of **1** or **5**, in the presence of water, results in the formation of products clearly derived from the addition of water across the double bond of the intermediate germasilene or digermene. Unlike the addition of methanol, the addition of water across the germasilene is not completely regioselective. The synthetic utility and mechanistic implications of this reaction are discussed.

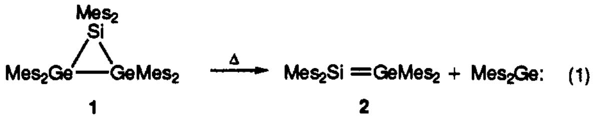
Introduction

Dienes, such as butadiene, 1,4-diphenylbutadiene, and 2,3-dimethylbutadiene, have long been used as trapping agents for intermediate silenes[1,2] and disilenes.[2] The isolation of a Diels–Alder type adduct, a 1-sila- or a 1,2-disilacyclohexene, respectively, from the reaction between the diene and the doubly bonded silicon compound is taken as solid evidence for the intermediacy of a silene or disilene. Dienes have also been used as trapping agents for germenes and digermenes,[3] albeit less often.

The reaction between bulky, stable group 14 homodimetalenes and dienes, particularly 2,3-dimethylbutadiene (DMB), is not straightforward and is illustrative of the discrepancies apparent in the literature concerning the reactivity of a series of group 14 dimetalenes. For example, $Mes_2Si{=}SiMes_2$ (Mes = mesityl = 2,4,6-trimethylphenyl) does not react with DMB even upon heating in decalin at 150–175 °C.[4] Consistent with this observation is the report that $Dmp_2Si{=}SiDmp_2$ (Dmp = 2,6-dimethylphenyl) also does not react with DMB.[5] In contrast is the finding that $Mes_2Ge{=}GeMes_2$ does react with the same diene to give a Diels–Alder type adduct in good yield;[6] however, $Dep_2Ge{=}GeDep_2$[7] (Dep = 2,6-diethylphenyl) and (*Z*)-Dip(Mes)Ge=GeDip(Mes)[8] (Dip = 2,6-diisopropylphenyl) are unaffected by the presence of 2,3-dimethylbutadiene. These disparate results led us to investigate the reaction between $Mes_2Si{=}GeMes_2$, which we have recently synthesized,[9,10] and 2,3-dimethylbutadiene. It was not certain whether the germasilene would behave in the same manner as $Mes_2Ge{=}GeMes_2$ and react with DMB or if it would not react with the diene, following the behavior of $Mes_2Si{=}SiMes_2$. Furthermore, if the germasilene did not react with the diene, it was expected that the germasilene would rearrange to a silylgermylene, as has been reported by us,[10] which would react with the diene, providing additional evidence for the germasilene-to-silylgermylene rearrangement. In the course of this study, we had reason to reinvestigate the thermolysis of hexamesitylcyclotrigermane in the presence of DMB and the results of this study are also reported. The results of the thermolysis of hexamesitylsiladigermirane and hexamesitylcyclotrigermane in the presence of water are also discussed.

Discussion

The thermolysis of hexamesitylsiladigermirane (**1**) has been shown to give tetramesitylgermasilene (**2**) and dimesitylgermylene, regioselectively.[9] Thermolysis of **1**



(1)

in the presence of DMB yielded two major compounds.

⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1994.

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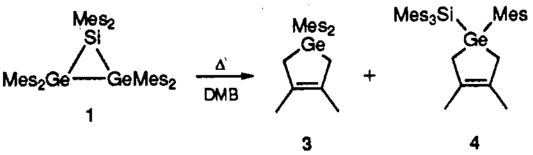
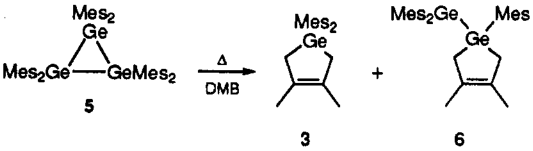
Compound **3** was readily identified by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry and by comparison with literature data.[11] Compound **4** was identified by NMR spectroscopy. The presence of two different mesityl groups in a ratio of 1:3 was evident from the ^{1}H NMR spectrum of **4**. By use of the DEPT pulse sequence[12] and ^{1}H–^{13}C shift correlation spectroscopy the methylene carbon atom was found to be correlated to two geminally coupled hydrogen atoms. The chemical shift of the silicon atom in **4** (−21.62 ppm) falls within the same chemical shift range as the chemical shift of the silicon atom of the $SiMes_3$ moiety (−19.85 ppm) in the related compound $(Mes_3Si)MesGeH(SiEt_3)$.[10] Taken together, these data are consistent with the structure shown for compound **4** rather than a Diels–Alder type adduct.



(2)

The formation of compounds **3** and **4** can most easily be explained by consideration of the known reactivity of dimesitylgermylene and $Mes_2Si{=}GeMes_2$, the products from thermal degradation of the siladigermirane. Dienes are well-known to be efficient traps of germylenes,[13] and formation of compound **3** is most likely the result of trapping dimesitylgermylene with 2,3-dimethylbutadiene. Compound **4** also appears to be derived from trapping of a germylene. Apparently, $Mes_2Si{=}GeMes_2$ rearranges under the reaction conditions to give the silylgermylene at a faster rate than a Diels–Alder type addition reaction with 2,3-dimethylbutadiene (see Scheme 1; M = Si). The germylene is trapped by the diene to give the germacyclopentene. Since $Mes_2Ge{=}GeMes_2$ was reported to react with 2,3-dimethylbutadiene, we were surprised that the germasilene did not react at all with the diene. For this reason, we reinvestigated the thermolysis of hexamesitylcyclotrigermane in the presence of 2,3-dimethylbutadiene.[6]

Thermolysis of hexamesitylcyclotrigermane (**5**) in the presence of DMB either in toluene for 4 h at 110 °C or in refluxing benzene (15 h; the same conditions used by Ando and co-workers[6]) gave the same mixture of products. There were two major products formed. In each case compound **3** was formed. The second compound was identified by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry as compound **6**. The spectroscopic data were clearly not consistent with a Diels–Alder type adduct of $Mes_2Ge{=}GeMes_2$ and DMB: the compound had a 3:1 ratio of mesityl groups, and the methylene hydrogen atoms were not equivalent. Since bulky group 14 dimetalenes have been shown to be unreactive toward DMB, we conclude that $Mes_2Ge{=}GeMes_2$ also does not yield a Diels–Alder type adduct with DMB. Under the reaction conditions, the digermene appears to undergo a 1,2-mesityl shift to give mesityl(trimesitylgermyl)germylene rather than addition to DMB (see Scheme 1; M = Ge). The germylene is the species trapped by the diene.



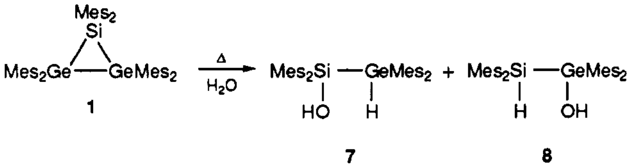
(3)

We are unable to satisfactorily explain the different results obtained by Ando and co-workers[6] and ourselves. A comparison of the data reported for the DMB Diels–Alder type adduct of $Mes_2Ge{=}GeMes_2$ and **6** reveals that although the melting points are different, the ^{1}H NMR and the mass spectral data are strikingly similar. Since we were unable, using the same conditions reported, to isolate a compound corresponding to the DMB Diels–Alder adduct of $Mes_2Ge{=}GeMes_2$, we believe that the structural assignment for the compound isolated by Ando and co-workers from the reaction between $Mes_2Ge{=}GeMes_2$ and DMB is incorrect. We believe the correct assignment is that of compound **6**.

Thus, we have firmly established that bulky, aryl-substituted germasilenes and digermenes do not react at an observable rate under mild thermal conditions with a relatively nonpolar diene such as 2,3-dimethylbutadiene. Rearrangement to the corresponding germylene appears to be favored. To understand more completely the behavior of bulky dimetalenes toward dienes, we are continuing to investigate the reactivity of these systems toward other dienes.

Thermolysis of $SiGe_2Mes_6$ (1) and Ge_3Mes_6 (5) in the Presence of Water. During the course of this study, and in other studies related to the addition reactions of $Mes_2Si{=}GeMes_2$, we have often observed trace amounts of what appear to be products arising from the addition of water across the double bond. Thus, we felt it was necessary to investigate the addition of water to both $Mes_2Si{=}GeMes_2$ and $Mes_2Ge{=}GeMes_2$.

Thermolysis of $SiGe_2Mes_6$ (**1**) in wet toluene cleanly yielded two isolable compounds identified as water adducts of **2**. A third compound, tentatively identified as $(Mes_2GeH)_2O$ and presumably the product derived from the reaction of $Mes_2Ge{:}$ with water, was also detected in the crude reaction mixture, but we were unable to isolate this compound in pure form. The same product mixture was obtained upon photolysis (350 nm) of **1** at −78 °C. Surprisingly, unlike the addition of methanol to the germasilene,[9] the addition of water is not completely regioselective. Both regioisomers are formed, with the (hydroxysilyl)germane **7** being the major isomer formed in preference over the (hydroxygermyl)silane **8** in an approximate ratio of 7:1. The ratio of isomers is independent of temperature; the same ratio is obtained at 110 °C in toluene (by thermal decomposition of the siladigermirane) or at −78 °C in toluene (by photochemical cleavage of the siladigermirane). No interconversion of the isomers was observed under the reaction conditions.



(4)

Little is known about the mechanism for the addition of water to disilenes[2] or digermenes.[3] The addition of

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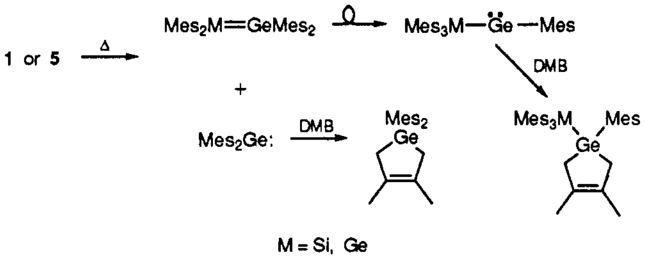
Scheme 1



water to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene yields a mixture of diastereomers, suggesting a stepwise mechanism.[14] More is known about the mechanism for the addition of water and alcohols to silenes. The addition is completely regioselective, with the hydroxy (alkoxy) moiety adding to the silicon end and the hydrogen atom adding to the carbon end of the double bond. The addition is believed to be nucleophilic in nature, with the first step being the formation of a silene Si—OHH(R) complex.[1,2,15] Recently, quantitative studies have provided evidence that the initial, rapid, reversible formation of the silene–alcohol (water) complex is followed by competing uni- and bimolecular proton transfer.[16] The rates of the different steps of the reaction mechanism and the stereochemical product ratios are dependent on the nucleophilicity, the acidity, and the concentration of the particular alcohol or water.

By extension, the addition of alcohols and water to germasilenes is presumably nucleophilic in nature as well and begins with the formation of a germasilene–alcohol (water) complex. In this case, however, the regiochemistry of the complex formation is most probably not well-defined. The difference in regioselectivity observed between the addition of water and methanol to $Mes_2Si{=}GeMes_2$ is most likely related to the same factors outlined above for addition of the same nucleophiles to silenes, i.e. nucleophilicity, acidity, and concentration. We note that the addition of water is less regioselective than the addition of methanol, but at low concentrations in acetone[17] only the major regioisomer of water addition, the (hydroxysilyl)germane, is formed. (Acetone also reacts with the germasilene; the results of this experiment will be published elsewhere.) Attempts to duplicate these results using wet tetrahydrofuran instead of acetone under similar conditions did not meet with success; both regioisomers were formed in the usual 7:1 ratio. We intend to pursue the mechanistic implications of our findings.

The thermolysis of the siladigermirane in the presence of water serves an additional synthetic purpose. The synthesis of $SiGe_2Mes_6$ is often accompanied by the formation of small amounts of Ge_3Mes_6.[9] As a result, after the thermolysis in the presence of water, trace quantities of the water adduct of the digermene, $Mes_2Ge(OH)GeHMes_2$ (**9**), are also often obtained in addition to the water adducts of the germasilene, depending on the amount of cyclotrigermane contaminant in the siladigermirane. The identity of **9** was confirmed by synthesizing it independently by thermolyzing Ge_3Mes_6 in wet toluene. We have previously described how the cyclotrigermane can be separated from the siladigermirane by taking advantage of the greater thermal lability of the cyclotrigermane compared to the siladigermirane.[9] Previously, we employed methanol as the trapping reagent. However, after partial thermolysis of the siladigermirane/cyclotrigermane mixture in the presence of methanol, the methanol adduct of the germasilene is inseparable from the siladigermirane by chromatographic techniques. As a result, although the cyclotrigermane is separated from the siladigermirane, the siladigermirane is still contaminated with the methanol adduct of the germasilene. Thermolysis of the siladigermirane/cyclotrigermane mixture in the presence of water circumvents this problem. Because of the greater polarity of the water adducts, the siladigermirane can be obtained completely free, after chromatographic separation, of the water adducts as well as the cyclotrigermane.

In summary, we have shown that $Mes_2Si{=}GeMes_2$ and $Mes_2Ge{=}GeMes_2$ appear to undergo a 1,2-Mes shift to give a germylene, which is trapped by DMB, at a faster rate than a Diels–Alder type reaction with the diene. Water adds across the double bond of $Mes_2Si{=}GeMes_2$ to yield two regioisomeric adducts. The addition of water to the germasilene is less regioselective than that of methanol.

Experimental Section

All experiments were carried out in flame-dried glassware under an atmosphere of argon. Toluene and benzene were distilled from sodium/benzophenone prior to use. $SiGe_2Mes_6$[9] and Ge_3Mes_6[18] were prepared according to literature procedures. 2,3-Dimethylbutadiene was obtained from the Aldrich Chemical Co. and used without further purification. Chromatography was carried out on silica gel plates using a Chromatotron (Harrison Research) or conventional preparative plates.

NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for ^1H), XL-300, or Gemini 300 (299.9 MHz for ^1H, 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 ^1H 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 DEPT[12] pulse sequence was used to assist in the ^{13}C NMR signal assignments. IR spectra were recorded on a Perkin-Elmer System 2000 FT infrared spectrometer; a Finnegan MAT Model 8230 was used with an ionizing voltage of 70 eV to obtain electron impact mass spectra (reported in mass-to-charge units, *m/z*, with ion identity and intensities of peaks relative to the base peak in parentheses). Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Thermolysis of $SiGe_2Mes_6$ (1) in the Presence of 2,3-Dimethylbutadiene. $SiGe_2Mes_6$ (1; 100 mg, 0.11 mmol) and 2,3-dimethylbutadiene (0.35 mL, 0.031 mol) were placed in toluene (2 mL). The mixture was heated to 105 °C for 8 h. Shortly after the thermolysis was started, the mixture turned bright yellow, but as the reaction progressed, the color faded, giving a clear, colorless solution. The crystals of $SiGe_2Mes_6$ were very slow to dissolve in the solution, taking 2–3 h at 105 °C to disappear. After completion of the reaction, the solvents were evaporated, leaving a yellow, viscous oil. The product mixture was separated by preparative thin-layer chromatography (Chromatotron; 95/5 hexanes/CH_2Cl_2) to yield two major compounds: compound **3** (30 mg, 67%) and compound **4** (25 mg, 34%).

1,1-Dimesityl-3,4-dimethyl-1-germacyclopent-3-ene (3): ^1H NMR (200 MHz, ppm)[11] 6.73 (s, 4 H, Mes H), 2.34 (s, 12 H, *o*-CH_3), 2.22 (s, 4 H, CH_2), 2.11 (s, 6 H, *p*-CH_3), 1.73 (s, 6 H, CH_3);

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^{13}C NMR (CDCl$_3$, ppm) 143.17, 137.81, 137.44, 130.81 (Mes C and =C), 128.68 (Mes CH), 32.02 (CH$_2$), 23.89, 20.88, 19.22 (CH$_3$); MS (*m/z* (%)) 394 (M$^+$, 10), 312 (GeMes$_2$, 70), 192 (GeMes − H, 100), 119 (Mes, 24), 105 (30).

1-Mesityl-3,4-dimethyl-1-(trimesitylsilyl)-1-germacyclopent-3-ene (4): mp 170–174 °C; IR (thin film, cm^{-1}) 2987 (s), 2933 (s), 2858 (s), 1608 (s), 1565 (m), 1452 (s), 1415 (m), 1373 (m), 1024 (m), 900 (m), 857 (m), 745 (m); ^{1}H NMR (300 MHz, ppm) 6.67 (s, 6 H, Mes H), 6.62 (s, 2 H, Mes H), 2.41 (s, 18 H, *o*-CH$_3$), 2.32 (d, J = 19 Hz, CH_AH$_B$ of an AB system), 2.20 (d, J = 19 Hz, CH$_A$$H_B$ of an AB system), 2.19 (s, *o*-CH$_3$) (total 10 H), 2.08 (s, *p*-CH$_3$), 2.07 (s, *p*-CH$_3$) (total 12 H), 1.67 (s, 6 H, =CCH$_3$); ^{13}C NMR (CDCl$_3$, ppm) 144.87, 143.54, 141.41, 137.72, 136.75, 134.78, 131.14, (Mes C and =C), 129.25, 128.23 (Mes CH), 34.02 (CH$_2$), 25.25, 24.87, 20.75, 20.73, 19.16 (CH$_3$); ^{29}Si NMR (ppm) −21.62; MS (*m/z* (%)) 431 (GeMes$_3$, 17), 385 (SiMes$_3$, 100), 266 (SiMes$_2$, 37), 193 (GeMes, 23), 147 (SiMes, 22), 105 (24); MS (*m/z*, CI, isobutane, (%)) 660 (M$^+$, 34), 622 (22), 593 (33), 578 (M$^+$ − C$_6$H$_{10}$, 100).

Thermolysis of Ge$_3$Mes$_6$ (5) in the Presence of 2,3-Dimethylbutadiene. Ge$_3$Mes$_6$ (29 mg, 0.031 mmol) and 2,3-dimethylbutadiene (0.5 mL, 0.044 mol) were placed in toluene (2 mL). The mixture was heated to 110 °C for 4 h. The solvent was then evaporated, and the crude product mixture was separated by preparative TLC using the Chromatotron and then traditional preparative TLC plates (90/10 hexanes/CH$_2$Cl$_2$) to yield compound **3** (5.5 mg, 45%) and compound **6** (9.2 mg, 42%). The same product mixture is obtained if the thermolysis is carried out in refluxing benzene for 15 h.

1-Mesityl-3,4-dimethyl-1-(trimesitylgermyl)-1-germacyclopent-3-ene (6): mp 160–164 °C; IR (thin film, cm^{-1}) 3037 (m), 3018 (s), 2920 (s), 2854 (m), 1602 (m), 1552 (m), 1448 (s), 1406 (m), 1377 (m), 1288 (w), 1264 (w), 1172 (w), 1026 (w), 848 (s), 737 (m); ^{1}H NMR (200 MHz, CDCl$_3$, ppm) 6.67 (s, 6 H, Mes H), 6.59 (s, 2 H, Mes H), 2.19 (s, *o*-CH$_3$), 2.17 (s, *p*-CH$_3$) (total 27 H), 2.15 (s, 3 H, *p*-CH$_3$), 2.14 (d, J = 21 Hz, CH_AH$_B$ of an AB system), 2.02 (d, J = 21 Hz, CH$_A$$H_B$ of an AB system), 1.94 (s, 6 H, *o*-CH$_3$), 1.57 (s, 6 H, =CCH$_3$); ^{1}H NMR (200 MHz, ppm) 6.69 (s, 6 H, Mes H), 6.62 (s, 2 H, Mes H), 2.42 (s, 18 H, *o*-CH$_3$), 2.2–2.4 (m, 4 H), 2.16 (s, 6 H), 2.08 (s, 12 H), 1.65 (s, 6 H, =CCH$_3$); ^{13}C NMR (CDCl$_3$, ppm) 143.67, 143.58, 140.62, 139.84, 137.23, 137.01, 130.95 (Mes C and =C), 129.00, 128.25 (Mes CH), 33.62 (CH$_2$), 25.01, 24.65, 20.79, 20.71, 19.06 (CH$_3$); MS (*m/z*, CI, isobutane (%)) 705 (M$^+$ + H, 16), 622 (M$^+$ − C$_6$H$_{10}$, 8), 585 (M$^+$ − Mes, 44), 431 (GeMes$_3$, 100), 312 (GeMes$_2$, 18), 297 (78), 195 (36), 121 (56), 97 (60); high-resolution MS for C$_{42}$H$_{55}$^{74}Ge^{72}Ge (M$^+$ + H) (*m/z*) calcd 705.2736, found 705.2698. Anal. Calcd for C$_{42}$H$_{54}$Ge$_2$: C, 71.65; H, 7.73. Found: C, 68.99; H, 7.70.

Thermolysis of SiGe$_2$Mes$_6$ (1) in the Presence of Water. SiGe$_2$Mes$_6$ (49 mg, 0.055 mmol), which was contaminated with Ge$_3$Mes$_6$, was placed in toluene with 2 drops of water (excess). Argon was bubbled through the mixture for 5 min to remove dissolved O$_2$, and the vessel was sealed. The mixture was heated to 105 °C, whereupon it became bright green-yellow. After 16 h of heating with intermittent shaking, the mixture was clear and colorless. The solvent was removed, leaving a white, sticky film. The product mixture was separated by preparative thin-layer chromatography (Chromatotron; 50/50 hexanes/CH$_2$Cl$_2$), yielding two major fractions: one containing a mixture of Mes$_2$Si(OH)GeHMes$_2$ (**7**) and Mes$_2$SiHGe(OH)Mes$_2$ (**8**) in a 7:1 ratio (28 mg) as determined by ^{1}H NMR spectroscopy and a second fraction consisting solely of Mes$_2$Ge(OH)GeHMes$_2$ (**9**) (13 mg).

In a separate experiment, **7** could be obtained free from **8** by photolysis of **1** in toluene followed by the addition of acetone containing traces of water: SiGe$_2$Mes$_6$ (30 mg, 0.034 mmol) and Et$_3$SiH (3 drops, excess) dissolved in toluene (2.5 mL) were photolyzed (8 h, 350 nm, −70 °C). During this time, the mixture turned bright green-yellow, indicative of germasilene formation. Following photolysis, the reaction mixture was quenched with 1 mL of acetone (an attempt was made to dry the acetone by distillation from CaCl$_2$). Separation of the reaction mixture by preparative thin-layer chromatography (Chromatotron) yielded (hydroxydimesitylsilyl)dimesitylgermane (**7**) (2.5 mg, 12%), dimesityl(triethylsilyl)germane (8.7 mg, 63%), and acetone adducts of the germasilene.[17]

(Hydroxydimesitylsilyl)dimesitylgermane (7) (Major Component): IR (thin film, cm^{-1}) ca. 3400 (br), 2920 (s), 2024 (m, GeH), 1603 (s), 1558 (w), 1449 (s), 1028 (m), 847 (s), 802 (s); ^{1}H NMR (200 MHz, ppm, 21 °C) 6.74 (s, 4 H, Mes H), 6.63 (d, 4 H, Mes H, J = 0.9 Hz), 5.60 (s, 1 H, Ge—H), 2.36 (s, 12 H, *o*-CH$_3$), 2.31 (s, 12 H, *o*-CH$_3$), 2.15 (d, 1 H, OH, J = 0.9 Hz), 2.11 (s, 6 H, *p*-CH$_3$), 2.06 (s, 6 H, *p*-CH$_3$); ^{13}C NMR (CDCl$_3$, ppm) 143.84, 139.09, 137.49, 135.24, 133.35 (Mes C), 129.20, 128.21 (Mes CH), 24.24, 23.41, 20.96 (CH$_3$); ^{29}Si NMR (ppm) 0.89 (d, J = 16 Hz).

(Dimesitylsilyl)hydroxydimesitylgermane (8) (Minor Component): ^{1}H NMR (200 MHz, ppm) 6.71 (s, Mes H), 6.63 (s, Mes H), 5.63 (s, Si—H), 2.38 (s, *o*-CH$_3$), 2.30 (s, *o*-CH$_3$), 2.10 (s, *p*-CH$_3$), 2.07 (s, *p*-CH$_3$); ^{29}Si NMR (ppm) −55.52 (d, J = 178 Hz).

Mixture (7 and 8 in a 7:1 Ratio): IR (thin film, cm^{-1}) 3351 (br), 2963 (s), 2136 (w, SiH), 2025 (m, GeH), 1603 (s), 1551 (m), 1451 (s), 1410 (m), 1064 (w), 1029 (w), 847 (s), 801 (s); MS (*m/z* (%)) 596 (3, M$^+$), 476 (2, M$^+$ − MesH), 312 (22, Mes$_2$Ge), 283 (100, Mes$_2$SiOH), 265 (7, Mes$_2$SiH), 163 (8, MesSiO), 119 (5, Mes); high-resolution MS for C$_{36}$H$_{46}$OSiGe (M$^+$) (*m/z*) calcd 596.2530, found 596.2528.

Thermolysis of Ge$_3$Mes$_6$ (5) in the Presence of Water. Ge$_3$Mes$_6$ (25 mg, 0.027 mmol) was placed in a screw-cap NMR tube with 2 mL of toluene and 2 drops of distilled water (excess). The mixture was degassed, placed under argon, and heated to 105 °C for 16 h, with periodic shaking during the first 6 h. The reaction mixture became bright green-yellow upon heating and faded to clear and colorless at completion. The solvent was removed, leaving a white, sticky film. Mes$_2$Ge(OH)GeHMes$_2$ (**9**) (16 mg, 0.025 mmol, 92%) was isolated by preparative thin-layer chromatography (Chromatotron; 50/50 hexanes/CH$_2$Cl$_2$).

(Hydroxydimesitylgermyl)dimesitylgermane (9): mp 205–208 °C; IR (thin film, cm^{-1}) ca. 3500 (br), 2921 (s), 2028 (s), 1601 (s), 1552 (m), 1450 (s), 847 (s); ^{1}H NMR (200 MHz, ppm) 6.72 (s, 4 H, Mes H), 6.64 (s, 4 H, Mes H), 5.86 (s, 1 H, GeH), 2.39 (s, 12 H, *o*-CH$_3$), 2.36 (s, 12 H, *o*-CH$_3$), 2.09 (s, 6 H, *p*-CH$_3$), 2.06 (s, 6 H, *p*-CH$_3$), 1.08 (s, 1 H, OH); ^{13}C NMR (CDCl$_3$, ppm) 143.81, 142.88, 138.67, 138.09, 137.24, 134.12 (Mes C), 129.06, 128.47 (Mes CH), 24.14, 23.16, 21.04, 21.01 (CH$_3$); MS (*m/z* (%)) 640 (16, M$^+$), 431 (25, Mes$_3$Ge), 329 (100, Mes$_2$GeOH), 312 (36, Mes$_2$Ge), 192 (24, MesGeH), 119 (14, Mes); high-resolution MS for C$_{36}$H$_{46}$O^{74}Ge$_2$ (M$^+$) (*m/z*) calcd 642.1972, found 642.1978.

Purification of SiGe$_2$Mes$_6$ (1). A mixture of SiGe$_2$Mes$_6$/Ge$_3$Mes$_6$ (43 mg) was thermolyzed in wet toluene at 90 °C for 6 h. The reaction mixture was then separated by preparative chromatography using the Chromatotron (80/20 hexanes/CH$_2$Cl$_2$) to yield the siladigermirane (22 mg; 51% weight recovery) free from any cyclotrigermane and water adducts.

Note Added in Proof. After a reinvestigation, Ando and co-workers agree with our findings: Ando, W. Personal communication.

Acknowledgment. We thank the NSERC (Canada) and the University of Western Ontario for financial support.

OM930656J