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Reaction of Group 14 Dimetallenes with Alkenes: Electron-Rich Alkenes

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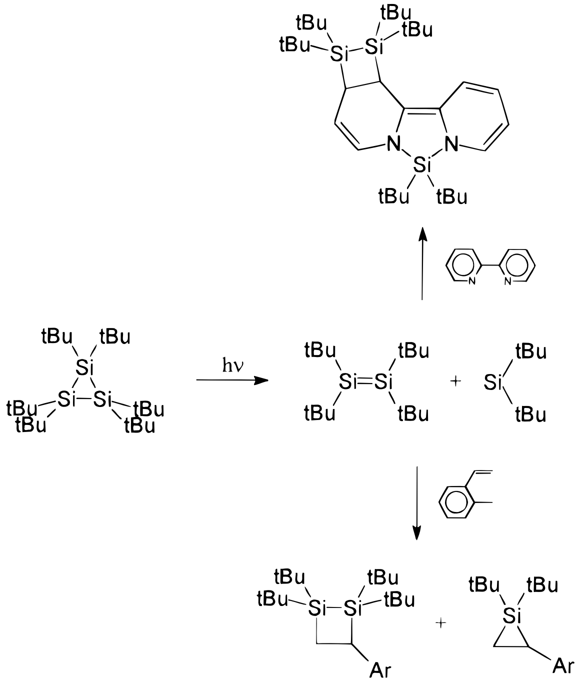
The addition reactions of tetramesitylgermasilene with 1-methoxybutadiene, ethyl vinyl ether, vinyl acetate, or styrene were studied. When tetramesitylgermasilene was allowed to react with 1-methoxybutadiene or styrene, formal [2+2] addition products were isolated. The addition of styrene to tetramesitylgermasilene was determined to be completely regioselective. In the presence of ethyl vinyl ether or vinyl acetate, tetramesitylgermasilene undergoes a 1,2-mesityl shift yielding a silylgermylene, at a faster rate than addition to either alkene. Tetramesityldisilene was also found to yield a formal [2+2] adduct with styrene. However, tetramesityldigermene rearranges to a germylgermylene at a faster rate than styrene addition.

Introduction

Tetramesityldisilene[1] and tetramesityldigermene[2] are now well-known examples of stable group 14 dimetallenes. Although both compounds require bulky substituents to gain kinetic stability, the presence of these sterically demanding groups does not greatly diminish the reactivity of these species. In fact, it has been shown that these heavier analogs of alkenes are frequently more reactive than alkenes. Stable disilenes and digermenes react with a variety of compounds to give a number of previously unknown compounds.[3] However, early in the development of this chemistry, it was demonstrated that hindered tetraaryldisilenes did not react with nonpolar alkenes or conjugated dienes. For example, tetramesityldisilene does not react with 2,3-dimethylbutadiene[4] or isoprene.[5]

Although hindered tetraaryldisilenes appear to be unreactive with alkenes or conjugated dienes, hindered tetraalkyldisilenes have been shown to give addition products with certain alkenes. Weidenbruch has reported that tetra-*tert*-butyldisilene will add, in a formal [2+2] manner, to 2,2′-dipyridine[6] or *o*-methylstyrene[7] to yield a disilacyclobutane (see Scheme 1). Tetraalkyldisilenes have also been observed to react in a formal [2+4] manner with conjugated dienes. For example, tetrakis(1-ethylpropyl)disilene[8] and tetra-*tert*-butyldisilene[9] give the expected Diels−Alder adducts with 2,3-dimethylbutadiene. Tetra-*tert*-butyldisilene also reacts in a formal [2+4] fashion with cyclopentadiene and furan.[10]

Scheme 1



Only one reaction between a digermene and an alkene or conjugated diene has been reported. Tetramesityldigermene has been shown to rearrange via a 1,2-mesityl shift to give a germylgermylene at a rate faster than addition of 2,3-dimethylbutadiene. The germylgermylene is subsequently trapped by the diene.[11]

The chemistry of tetramesitylgermasilene has been shown to be similar in some respects to that of hindered tetraaryldisilenes and -digermenes. For example, tetramesitylgermasilene does not appear to react with

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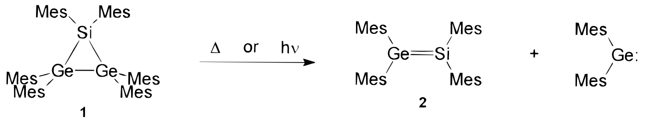
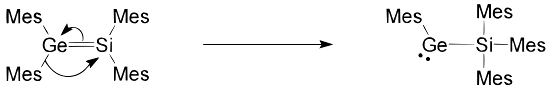
Scheme 2



Scheme 3



conjugated dienes such as 2,3-dimethylbutadiene, at least at a rate faster than the thermal rearrangement to a silylgermylene.[11] While investigating what, if any, effect changing the electronic character of the diene may have on the addition reactions of tetramesitylgermasilene, it was found that tetramesitylgermasilene yields a formal [2+2] cycloaddition product with 1-methoxybutadiene.[12] This result, along with the reports of tetra-*tert*-butyldisilene reacting in a formal [2+2] manner with 2,2′-dipyridine and *o*-methylstyrene, prompted us to examine the reaction of tetramesitylgermasilene with a number of substituted alkenes. This paper reports the results of the reactions between tetramesitylgermasilene and 1-methoxybutadiene, ethyl vinyl ether, vinyl acetate, or styrene. Also reported are the results for the reactions of tetramesityldisilene and tetramesityldigermene with styrene.

Results and Discussion

The thermolysis or photolysis of hexamesitylsiladigermirane (**1**) has been shown to give tetramesitylgermasilene (**2**) and dimesitylgermylene, regioselectively[13] (Scheme 2). Although the germasilene is stable in solution at −78 °C, at higher temperatures it rearranges via a 1,2-mesityl shift to give the corresponding silylgermylene[13] (Scheme 3). Thus, the relative rate of reaction of the germasilene with a selected trap versus the rate of rearrangement to the silylgermylene determines the products observed. For example, when tetramesitylgermasilene is generated in the presence of alcohols,[14] aldehydes, or ketones,[15] the germasilene reacts exclusively with each trap. However, in the presence of 2,3-dimethylbutadiene[11] or triethylsilane,[13] the only products detected are those derived from the silylgermylene. By changing the electronic properties of the alkene or conjugated diene used in reaction with tetramesitylgermasilene, we reasoned that the rate of reaction of the alkene with the Si−Ge double bond of the germasilene may be increased relative to the rearrangement of the germasilene to the silylgermylene. Thus, the reaction between tetramesitylgermasilene and 1-methoxybutadiene was investigated.

Thermolysis of **1** at 110 °C in the presence of *trans*-1-methoxybutadiene yielded three compounds. Compounds **3** and **4** were each characterized by IR and ^{1}H, ^{13}C, and ^{29}Si NMR (for **4**) spectroscopy and mass spectrometry. Compound **5** was produced in low yield and proved to be unstable in solution and, as a result, was characterized solely by ^{1}H NMR correlation spectroscopy (Scheme 4). Compound **3** appears to be derived from reaction between 1-methoxybutadiene and dimesitylgermylene, consistent with the previously observed chelotropic [2+4] addition of dimesitylgermylene to 2,3-dimethylbutadiene[11] yielding a germacyclopentene. Under the thermal conditions of reaction, tetramesitylgermasilene readily rearranges to give the silylgermylene, which reacts with 1-methoxybutadiene to give compound **4** as a mixture of diastereomers. Interestingly, compound **5** appears to be the formal [2+2] cycloaddition product between tetramesitylgermasilene and 1-methoxybutadiene. The presence of four different mesityl groups in the ^{1}H NMR spectrum of **5** is consistent with a substituted germasilacyclobutane ring, as is the multiplet observed at 2.95−3.10 ppm, which may be assigned to the CH of the germasilacyclobutane. In addition, two alkenyl resonances, which integrate for two hydrogen atoms, are observed in the chemical shift range consistent with an alkoxy-substituted vinyl moiety (5.03 and 6.15 ppm) indicating that the terminal double bond of 1-methoxybutadiene has added to the Ge−Si double bond of the germasilene. The coupling constant between these two alkenyl hydrogen atoms (12.5 Hz) suggests a trans geometry for the double bond. Taken together, these data support the structural assignment given for compound **5**, which represents the first example of a formal [2+2] cycloaddition product between tetramesitylgermasilene and an alkene. The regiochemistry of the addition is unknown.

In contrast to 2,3-dimethylbutadiene, which reacts exclusively with the silylgermylene, 1-methoxybutadiene seems to react with the germasilene to some degree. However, the reaction of 1-methoxybutadiene with the silylgermylene is still the predominant reaction pathway. The concurrent formation of the silylgermylene and the rapid subsequent reaction with the conjugated diene, polar or not, apparently limits the yield of the formal [2+2] cycloaddition product. Since germylenes do not readily add to alkene π-bonds,[16] three polar alkenes, ethyl vinyl ether, vinyl acetate, and styrene, were selected for reaction with tetramesitylgermasilene in an attempt to maximize the yield of any formal [2+2] product.

Photolysis of **1** at −70 °C in the presence of Et_3SiH produces a solution of tetramesitylgermasilene. Subsequent addition of ethyl vinyl ether and slow warming of the reaction mixture to room temperature produced compounds **6** and **7** in approximately a one to one ratio as determined by ^{1}H NMR spectroscopy (Scheme 5). Compounds **6** and **7** were readily identified by comparison to literature data.[13] Apparently, the rearrangement of tetramesitylgermasilene to the corresponding silylgermylene occurs at a faster rate than any reaction with ethyl vinyl ether. Thermolysis of **1** in the presence of ethyl vinyl ether gave a very complex reaction mixture which yielded no identifiable products. Cophotolysis of **1** with vinyl acetate and Et_3SiH yielded mainly a mixture of compounds **6** and **7**. Again, the 1,2-mesityl rearrangement appears to occur at a rate greater than reaction with the alkene. Two additional products were isolated from the reaction mixture: (triethylsilyl)mesi-

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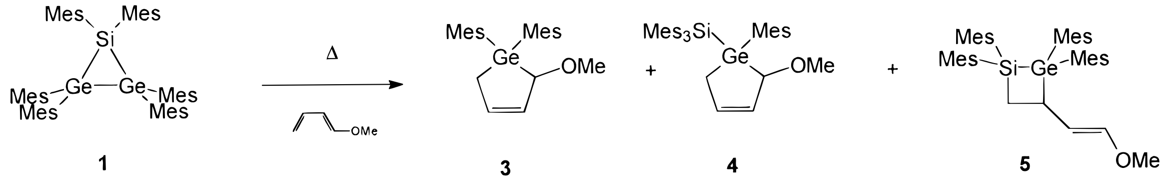
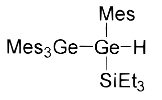
Scheme 4



(regiochemistry uncertain)

tyl(trimesitylgermyl)germane (**8**) and 4-(2-methylethenyl)tetramesitylsilagermoxetane (**9**). Compound **8** appears to be derived from tetramesityldigermene, which is a known photoproduct of hexamesitylcyclotrigermane,[2] a common byproduct in the synthesis of hexamesitylsiladigermirane.[14] Under the thermal conditions of the reaction, the digermene undergoes a 1,2-mesityl shift to give the germylgermylene which is subsequently trapped by Et_3SiH.[17] Compound **9** appears to be the cycloadduct of tetramesitylgermasilene and crotonaldehyde. The regiochemistry of the addition was not determined; the assigned structure is based upon the known regiochemistry of the addition of acetone and pivalaldehyde to tetramesitylgermasilene.[15] Crotonaldehyde is believed to be generated in small amounts during the purification of vinyl acetate by distillation from Li(t-BuO)$_3$AlH.



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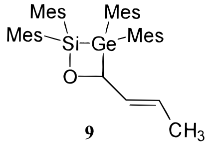

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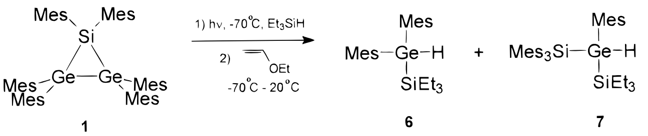
Photolysis of **1** at −70 °C in the presence of Et_3SiH, followed by the addition of styrene and subsequent warming to room temperature, gave products **6** and **10** in a one to one ratio as determined by ^1H NMR spectroscopy (Scheme 6). Compound **10** appears to be the formal [2+2] cycloaddition product between tetramesitylgermasilene and styrene. Consistent with this assignment is the appearance of four mesityl groups and an ABX spin pattern in the ^1H NMR spectrum of **10**. The ^{13}C NMR, DEPT, HETCOR, and COSY spectra also support the assignment. Unlike ethyl vinyl ether and vinyl acetate, it appears that the addition of styrene to tetramesitylgermasilene occurs at a faster rate than the 1,2-mesityl rearrangement yielding the formal [2+2] cycloaddition product, **10**, completely regioselectively.

The regiochemistry of the adduct was determined by nucleophilic cleavage of **10** with NaOMe. When a solution of **10** in THF was refluxed in the presence of NaOMe, one product, **11**, was isolated (Scheme 7). The ^1H NMR spectrum of **11** shows one doublet in the Si/Ge−H region of the spectrum indicating that methoxide attacked selectively at the atom adjacent to the CH_2 moiety and not the CHPh of the germasilacyclobutane ring. The IR spectrum shows an absorbance at 2046 cm^{-1}, which is consistent with a Ge−H stretching vibration. The $^1H-^{29}Si$ HMBC experiment shows a correlation between the signal at 1.90 ppm in the ^{29}Si dimension with the OCH_3 at 2.78 ppm in the ^1H dimension, which suggests a structure with the ^1H bonded directly to the Ge atom. Furthermore, there were no 1-bond correlations observed in the standard $^1H-^{29}Si$ HMQC spectra. Taken together, these data support the structure as assigned for **11**. Thus, the addition of styrene to tetramesitylgermasilene is completely regioselective with the germanium atom of the germasilene becoming bonded to the substituted end of the alkene. Furthermore, attack of methoxide on **10** occurs exclusively at the silicon atom.

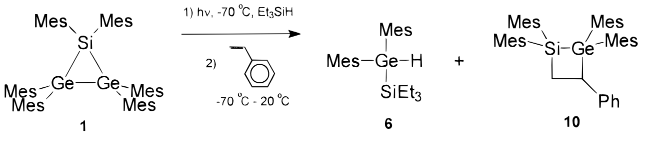
It is interesting to compare the chemistry of the heteronuclear dimetallene to that of the homonuclear analogs, disilenes and digermenes. Photolysis of hexamesitylcyclotrigermane[18] at −70 °C, in the presence of Et_3SiH, followed by addition of styrene and subsequent warming to room temperature yielded two major compounds, **6** and **8**, in a one to one ratio as ascertained by ^1H NMR spectroscopy (Scheme 8). Tetramesityldigermene has been shown to undergo a thermal 1,2-mesityl rearrangement, similar to that observed with tetramesitylgermasilene, to give the corresponding germylgermylene.[17] Compound **8** is the result of insertion of mesityl(trimesitylgermyl)germylene into the Si−H bond of Et_3SiH. Unlike tetramesitylgermasilene, tetramesityldigermene does not appear to add styrene at a rate faster than the 1,2-mesityl shift. A possible explanation may be an increased rate of the 1,2-mesityl rearrangement for the digermene, relative to the germasilene. The increased rate is perhaps due to the decrease in steric crowding around the germanium atom in the germylgermylene, compared to the silicon atom in the corresponding silylgermylene.

When styrene is added to a solution of tetramesityldisilene[1] in benzene and heated to 60 °C for several hours, compound **12** is formed, which is the first

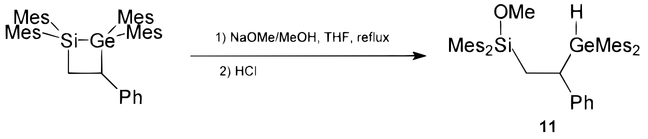
Scheme 5



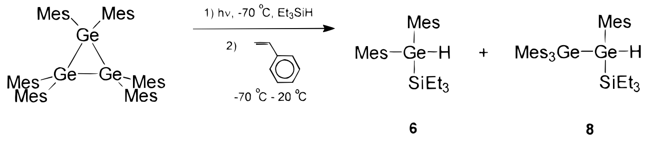
Scheme 6



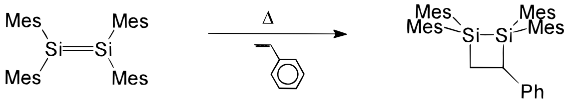
Scheme 7



Scheme 8



Scheme 9



12

example of a formal [2+2] cycloaddition product between tetramesityldisilene and an alkene (Scheme 9). Again, the ^1H, ^{13}C NMR, DEPT, HETCOR, and COSY spectra all support the assigned structure for **12**. Thus, similar to tetramesitylgermasilene, tetramesityldisilene adds styrene in a formal [2+2] fashion.

In summary, we have shown that tetramesitylgermasilene yields a formal [2+2] cycloaddition product in reaction with 1-methoxybutadiene or styrene. It has been demonstrated that the addition of styrene to tetramesitylgermasilene is completely regioselective. In the presence of ethyl vinyl ether or vinyl acetate, however, it appears that the 1,2-mesityl rearrangement of tetramesitylgermasilene occurs at a faster rate than the cycloaddition of either alkene. Furthermore, it has also been shown that tetramesityldisilene, like tetramesitylgermasilene, adds styrene in a formal [2+2] manner. In contrast, tetramesityldigermene rearranges to the corresponding germylgermylene at a faster rate than styrene addition. We believe that these preliminary investigations point to a stepwise radical mechanism for the addition of alkenes to tetramesitylgermasilene, and we are currently exploring this idea.

Experimental Section

All experiments were carried out in flame-dried glassware under an atmosphere of argon. Toluene and benzene were freshly distilled from sodium/benzophenone. Pentane was distilled from $LiAlH_4$ prior to use. Styrene was obtained from BDH and used without any further purification. Ethyl vinyl ether was obtained from Aldrich Chemical Co. and distilled from lithium aluminum hydride prior to use. Vinyl acetate was obtained from Aldrich Chemical Co. and distilled from lithium tri-*tert*-butoxyaluminum hydride prior to use. Chromatography was carried out using a Chromatotron (Harrison Research) or on conventional silica gel preparative plates.

NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C), an XL-300, a Varian Gemini 300 (299.9 MHz for ^1H, 75.4 MHz for ^{13}C, 59.6 MHz for ^{29}Si), or a Bruker Avance DRX-500 using benzene-d_6 as a solvent, unless otherwise noted. The standards were as follows: residual C_6D_5H 7.15 ppm for ^1H spectra; C_6D_6 or $CDCl_3$ central transition for ^{13}C NMR spectra; 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). The 2-D spectra were acquired using standard techniques.[19−21]

Photolyses were carried out at 350 nm, unless otherwise stated, using a Rayonet Photochemical Reactor.

Thermolysis of $SiGe_2Mes_6$ in the Presence of 1-Methoxybutadiene. $SiGe_2Mes_6$ (50 mg, 0.056 mmol) and *trans*-1-methoxybutadiene (3 drops, ∼ 40 mg, 0.48 mmol) were dissolved in toluene (2.0 mL). The reaction mixture was placed in an oil bath at 105 °C for 4 h. The reaction mixture became light yellow in color soon after heating began. After 3 h, the mixture became clear and colorless. The solvents were evaporated leaving a light yellow viscous residue. The product mixture was separated by preparative thin-layer chromatography using 50% CH_2Cl_2/hexane as the eluent to give at least five fractions: Fraction 1, unidentified, appears to be a mixture of cylcloadducts; fraction 2, compound **5** (3.5 mg, 10%); fraction 3, compound **4** (8 mg, 22%); fraction 4, compound **3** (21 mg, 95%). Compound **5** decomposes if left in solution over a period of time.

1,1-Dimesityl-2-methoxy-1-germacyclopent-3-ene (3): Mp 80−82 °C; IR (thin film, cm^{-1}) 3015 (s), 2922 (s), 2811 (s), 2730 (w), 1603 (s), 1557 (m), 1456 (s), 1411 (m), 1375 (m), 1358 (m), 1087 (s), 1028 (m), 950 (m), 930 (m), 847 (s), 804 (m), 701 (m); ^1H NMR (ppm) 6.72, 6.71 (each s, 4 H total, Mes CH), 2.41 (s, 6 H, Mes o-CH_3), 2.34 (s, 6 H, Mes o-CH_3), 2.12 (s, 3 H, Mes p-CH_3), 2.08 (s, 3 H, Mes p-CH_3), 3.10 (s, 3 H, OCH_3), 4.77 (dddd, 1 H, $^3J = 3.2$ Hz, $^4J = 1.1$ Hz, $^5J = 1.1$ Hz, $^5J = 1.8$ Hz, C**H**OCH_3), 6.42 (dddd, 1 H, $^3J = 7.7$ Hz, $^4J = 1.9$ Hz, $^4J = 1.6$ Hz, $^3J = 3.2$ Hz, =C**H**$CHOCH_3$), 6.17 (dddd, 1 H, $^3J = 7.7$ Hz, $^3J = 3.2$ Hz, $^3J = 1.9$ Hz, $^4J = 1.1$ Hz, CH_2=C**H**), 2.49 (dddd, 1 H, $^2J = 17.2$ Hz, $^3J = 3.2$ Hz, $^4J = 1.6$ Hz, $^5J = 1.8$ Hz, CH_2), 1.73 (dddd, 1 H, $^2J = 17.2$ Hz, $^3J = 1.9$ Hz, $^4J = 1.9$ Hz, $^5J = 1.1$ Hz, CH_2); ^{13}C NMR ($CDCl_3$, ppm) 143.95, 142.42, 138.59, 138.15, 138.03, 133.26, (Mes C), 128.78, 128.65 (Mes CH), 134.82, 133.14 (=CH), 81.66 (**C**$HOCH_3$), 58.66 (OCH_3), 24.72 (CH_2), 24.39, 24.18, 20.94 (Mes CH_3); MS (m/z) 396 (M^+, 10), 312 ($GeMes_2$, 50), 192 (GeMes − H, 100), 119 (Mes, 26), 84 (CH_2=CHCH=$CHOCH_3$, 80); high-resolution MS for $C_{23}H_{30}O^{72}Ge$: calc, 394.1517; found, 394.1524.

1-Mesityl-2-methoxy-1-(trimesitylsilyl)-1-germacyclopent-3-ene (4): IR (thin film, cm^{-1}) 2921 (s), 1604 (s), 1448 (s), 1104 (m), 1082 (m), 1027 (m), 848 (s), 784 (s); ^1H NMR ($CDCl_3$, ppm) diastereomeric mixture, 6.62 (s, 6 H, Mes CH), 6.45 (s, 2 H, Mes CH), 6.12−6.21 (m, 1 H, =CH), 5.93−6.03 (m, 1 H, =CH), 4.56−4.63 (m, 1 H, C**H**OCH_3), 3.19 (d, 3 H, $J = 0.7$ Hz, OCH_3), 2.28−2.38 (m, 1 H, CH_2), 2.24 (s, 18 H, Mes CH_3), 2.18, 2.16 (each s, 15 H total, Mes CH_3), 2.09 (s, 3 H, Mes CH_3), 1.90−2.07 (m, 1 H, CH_2); signals for minor diastereomer apparent at 3.20, 2.25, 2.19, 2.17, 2.10; ^{13}C NMR ($CDCl_3$, ppm) 144.84, 143.90, 137.90, 136.77, 135.27, 134.59 (Mes C), 129.18, 128.10 (Mes CH), 133.57, 133.06 (=CH), 85.19 (**C**H-OCH_3), 58.62 (OCH_3), 24.92 (CH_2), 25.57, 24.99, 20.74 (Mes CH_3); ^{29}Si NMR ($CDCl_3$, ppm) −19.81; MS (m/z) 622 (M^+ − C_3H_4, 2), 578 (Mes_4GeSi, 10), 385 ($SiMes_3$, 100).

1,1,2,2-Tetramesityl-3 (or 4)-(*trans*-2-methoxyethenyl)-1,2-silagermacyclobutane (5): ^1H NMR (ppm) 6.74, 6.73, 6.71, 6.69 (each s, 8 H total, Mes CH), 6.15 (d, 1 H, $J = 12.5$ Hz, =C**H**OCH_3), 5.03 (dd, 1 H, $J = 12.5$ Hz, $J = 10.5$ Hz, C**H**=$CHOCH_3$), 3.13 (s, 3 H, OCH_3), 2.95−3.10 (m, 1 H, CH_2C**H**C=), 2.53 (s), 2.44 (bs), 2.43 (s), 2.30 (s), 2.20−2.60 (m, 25 H total, CH_2 and Mes o-CH_3), 2.14 (s, 3H, Mes p-CH_3), 2.11 (s, 3 H, Mes p-CH_3), 2.06 (s, 3 H, Mes p-CH_3), 2.03 (s, 3 H, Mes p-CH_3); MS (m/z) 578 (Mes_4GeSi, 18), 385 ($SiMes_3$, 100), 192 (GeMes, 4), 83 (C_5H_7O, 13).

Addition of Ethyl Vinyl Ether to Tetramesitylgermasilene. $SiGe_2Mes_6$ (50 mg, 0.062 mmol) and Et_3SiH (1 mL, excess) were dissolved in toluene (3 mL) and photolyzed for 6 h at −70 °C. After this time, ethyl vinyl ether (0.5 mL, excess) was added to the reaction mixture and the solution was allowed to warm to room temperature. After the solution was standing at room temperature for several hours, the yellow color of the germasilene had disappeared. Removal of the solvents and subsequent purification of the reaction mixture by preparative thin layer chromatography (20/80 CH_2Cl_2/hexanes) yielded compounds **6** (15 mg, 0.035 mmol, 56%) and **7** (17 mg, 0.025 mmol, 40%). There were no compounds identified as being derived from a reaction between tetramesitylgermasilene and ethyl vinyl ether.

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[22] While the isolated yield of the formal [2+2] adduct is relatively low, it appears as a major component in the crude reaction mixture as determined by ^1H NMR spectroscopy.

Photolysis of SiGe$_2$Mes$_6$ in the Presence of Vinyl Acetate. Vinyl acetate (1 mL, excess), triethylsilane (1 mL, excess), and SiGe$_2$Mes$_6$ (100 mg) were dissolved in toluene (5 mL). The reaction mixture was photolyzed for 8 h at −78 °C. Upon completion of the photolysis, the reaction mixture was allowed to warm slowly overnight. The product mixture was then separated by preparative thin layer chromatography to yield four products: dimesityl(triethylsilyl)germane (**6**, 31.2 mg), a mixture of mesityl(triethylsilyl)(trimesitylsilyl)germane (**7**) and mesityl(triethylsilyl)(trimesitylgermyl)germane (**8**) in a 1:3.4 ratio, and 4-(2-methylethenyl)tetramesitylsilagermaoxetane (**9**, 19.2 mg, regiochemistry unknown). When tetramesitylgermasilene was allowed to react with crotonaldehyde, compound **9** was isolated in good yield.

4-(2-Methylethenyl)tetramesitylsilagermoxetane (9): IR (thin film, cm^{-1}) 3020 (s), 2919 (s), 1604 (s), 1552 (m), 1448 (s), 1410 (m), 1376 (m), 1290 (w), 1233 (w), 1064 (m), 1028 (m), 964 (m), 933 (s), 847 (s), 829 (s), 773 (m), 739 (m); ^{1}H NMR (ppm) 6.72 (s, 2 H, Mes H), 6.71 (s, 2 H, Mes H), 6.68 (s, 2 H, Mes H), 6.64 (s, 2 H, Mes H), 5.85−6.05 (m, 2 H, CHCH=), 5.40−5.65 (m, 1 H, C**H**CH$_3$), 2.67 (s, 6 H, Mes *o*-CH$_3$), 2.44 (bs, 6 H, Mes *o*-CH$_3$), 2.35 (s, 6 H, Mes *o*-CH$_3$), 2.20 (s, 6 H, Mes *o*-CH$_3$), 2.11 (s, 6 H, Mes *p*-CH$_3$), 2.05 (s, 3 H, Mes *p*-CH$_3$), 2.03 (s, 3, Mes *p*-CH$_3$), 1.42−1.50 (m, 3 H, C=CCH$_3$); ^{13}C NMR (ppm) 144.37, 144.26, 143.61, 142.54, 141.03, 139.51, 139.38, 138.27, 138.18, 136.80, 134.65, 133.97 (Mes C), 134.30 (−**C**H=), 129.70, 129.28, 129.18, 128.83 (Mes CH), 122.83 (C=**C**H), 87.00 (O**C**HCH=), 24.96, 24.75, 24.20, 23.47 (Mes *o*-CH$_3$), 21.08, 20.96, 20.92, 20.85 (Mes *p*-CH$_3$), 17.48 (=CH**C**H$_3$); ^{29}Si NMR (ppm) 28.29 ppm; MS (EI) (*m*/*z*) 648 (M$^+$, 5), 593 (Mes$_4$GeSiO(−H), 25), 578 (Mes$_4$GeSi, 11), 475 (Mes$_3$GeSiO, 8), 385 (Mes$_3$Si, 100), 311 (Mes$_2$Ge − H, 11), 193 (MesGe, 9), 84 (SiOC$_3$H$_3$, 73); high-resolution MS calc for C$_{40}$H$_{50}$OSi^{74}Ge 648.2843, found 648.2861.

Addition of Styrene to Tetramesitylgermasilene. SiGe$_2$Mes$_6$ (30 mg, 0.034 mmol) and Et$_3$SiH (0.5 mL, excess) were placed in toluene (3 mL) and photolyzed (350 nm) at −70 °C for 8 h. After this time, styrene (0.5 mL, excess) was added to the cold reaction mixture and the solution was allowed to warm to room temperature and stand for several hours. Following removal of the solvent, the products were separated by preparative thin layer chromatography (20/80 CH$_2$Cl$_2$/hexanes), to give two compounds: **10** (11 mg, 33%) and **6** (3 mg, 21%).[22]

1,1,2,2-Tetramesityl-4-phenylgermasilacyclobutane (10): Mp 66−70 °C; IR (thin film, cm^{-1}) 3022 (m), 2920 (s), 1603 (s), 1551 (w), 1491 (m), 1451 (s), 1047 (m), 1377 (w), 1291 (w), 1031 (m), 848 (s), 756 (s), 700 (s), 626 (s); ^{1}H NMR (ppm) 6.90−7.10 (m, 5 H, Ph H), 6.73 (s), 6.71 (bs, 6 H total, Mes H), 6.64 (s, 2 H, Mes H), 3.70 (X portion of ABX, 1 H, J_{AX} = 15.4 Hz, J_{BX} = 6.1 Hz, C**H**PhCH$_2$), 2.66, 2.59 (AB portion of ABX, J_{AB} = 13.5 Hz, CHPhC**H$_2$**), 2.57 (s, 8 H total, Mes *o*-CH$_3$), 2.46 (bs), 2.44 (s, 12 H total, Mes *o*-CH$_3$) 2.12, 2.11 (each s, 6 H total, *p*-CH$_3$), 2.06, 2.05 (each s, 6 H total, Mes *p*-CH$_3$), 1.93 (bs, 6 H, Mes *o*-CH$_3$); ^{13}C NMR (CDCl$_3$, ppm) 146.16, 145.13, 144.19, 143.59, 141.92, 138.80, 138.68, 137.60, 137.41, 136.33, 134.32, 132.41 (Mes and Ph C), 129.13, 128.89, 128.45, 128.23, 127.53, 127.13, 124.46 (Mes and Ph CH), 44.35 (**C**HPhCH$_2$), 30.82 (CHPh**C**H$_2$), 29.75, 24.84, 24.69, 24.54, 24.46, 21.06, 20.96 (bs, Mes CH$_3$); ^{29}Si NMR (ppm) −1.01; MS (*m*/*z*, CI, isobutane) 681 (M$^+$ − H, 0.8), 578 (M$^+$ − CH$_2$CHPh, 12), 371 (M$^+$ − Mes$_2$Ge, 28), 313 (M$^+$ − Mes$_2$SiCH$_2$CHPh, 8), 92 (C$_7$H$_8$, 100).

Addition of Styrene to Tetramesityldisilene. Mes$_2$Si(SiMe$_3$)$_2$ (100 mg, 0.24 mmol) was dissolved in pentane (10 mL) and photolyzed (254 nm) at −60 °C for 10 h. At this time, the pentane was removed, *in vacuo*, and replaced with benzene. To this solution was added styrene (0.5 mL, excess), and the mixture was heated to 60 °C for several hours. Following removal of the solvent, the reaction mixture was purified by preparative thin layer chromatography (20/80 CH$_2$Cl$_2$/hexanes) to give compound **12** (13.5 mg, 9%).[22]

1,1,2,2-Tetramesityl-3-phenyldisilacyclobutane (12): Mp 45−47 °C; IR (thin film, cm^{-1}) 3028 (m) 2962 (s), 2921 (s), 2865 (m), 1604 (s), 1548 (w), 1450 (s), 1409 (m), 1378 (m), 1261 (m), 1029 (s), 847 (s), 756 (s), 701 (s); ^{1}H NMR (ppm, 70 °C) 6.84−7.00 (m, 5 H, Ph H), 6.74 (s, 2 H, Mes H), 6.72 (s, 2 H, Mes H), 6.66 (s, 2 H, Mes H), 6.63 (s, 2 H, Mes H), 3.46 (X portion of ABX, 1H, J_{AX} = 10.7 Hz, J_{BX} = 12.1 Hz), 2.58 (s, 6 H, Mes *o*-CH$_3$), 2.51, 2.49 (AB portion of ABX, 2 H, J_{AB} = 13.7 Hz), 2.43 (s, 6 H, Mes *o*-CH$_3$), 2.39 (s, 6 H, Mes *o*-CH$_3$), 2.12 (s, 3 H, Mes *p*-CH$_3$), 2.10 (s, 3 H, Mes *p*-CH$_3$), 2.073, 2.068 (s, 6 H total, Mes *p*-CH$_3$), 1.99 (bs, 6 H, *o*-CH$_3$); ^{13}C NMR (CDCl$_3$, ppm) 146.21, 145.36, 143.71 (bs), 143.07 (bs), 138.50, 138.40, 138.34, 138.18, 136.38, 134.31, 132.79, 131.57 (Mes and Ph C), 129.07 (bs), 128.83 (bs), 128.53 (bs), 128.68, 127.55, 127.44, 124.47 (Ph and Mes CH), 39.88 (CH$_2$-**C**HPh), 30.09 (**C**H$_2$-CHPh), 24.96, 24.71 (bs), 21.03, 20.95, 20.93 (Mes CH$_3$); ^{29}Si (ppm) −11.06, 7.04; MS (*m*/*z*) 636 (M$^+$, 4), 532 (M$^+$ − CH$_2$-CHPh, 80), 413 (Mes$_3$Si$_2$, 17) 369 (M$^+$ − Mes$_2$Si, 100), 265 (Mes$_2$Si − H, 50), 147 (MesSi, 38); high-resolution MS for C$_{44}$H$_{52}$Si$_2$ calc 636.3608, found 636.3601.

Addition of Styrene to Tetramesityldigermene. Ge$_3$Mes$_6$ (50 mg, 0.054 mmol) and Et$_3$SiH (1 mL, excess) were dissolved in toluene (2 mL) and photolyzed for 8 h at −70 °C. After this time, styrene (1 mL, excess) was added to the reaction mixture, and the solution was allowed to warm to room temperature. After the solution was standing at room temperature for several hours, the yellow color of the digermene had disappeared. Removal of the solvents and subsequent analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed approximately a 1:1 mixture of compounds **6** and **10**.

Nucleophilic Cleavage of 1,1,2,2-Tetramesityl-4-phenylgermasilacyclobutane (10). Na (20 mg, 0.87 mmol) was added to MeOH (5 mL) and allowed to stir until all visible reaction had subsided. **10** (6 mg, 0.008 mmol) was dissolved in THF (5 mL) and added, in one shot, to the MeONa/MeOH solution, and the reaction mixture was refluxed for 24 h. Following the addition of 1 M HCl (approximately 5 mL), extraction of the aqueous layer with Et$_2$O (3×, 25 mL total), and removal of the solvents, a white solid was isolated. Analysis by ^{1}H NMR spectroscopy showed the solid to be compound **11** (5.8 mg, 0.007 mmol, 94%) in relatively pure form. Preparative thin-layer chromatography (10/90 CH$_2$Cl$_2$/hexanes) offered only marginal improvement in purity as determined by ^{1}H NMR spectroscopy.

1-(Dimesitylgermyl)-1-phenyl-2-(dimesityl(methoxy)silyl)ethane (11): IR (thin film, cm^{-1}) 2926 (s), 2861 (m), 2046 (w), 1605 (m), 1494 (s), 1451 (m), 1404 (m), 1262 (w), 1050 (m), 825 (m); ^{1}H NMR (ppm) 6.88−7.08, 7.40−7.44 (m, 5 H total, Ph CH), 6.74 (s, 2 H, Mes CH), 6.71 (s, 2 H, Mes CH), 6.59 (s, 2 H, Mes CH), 6.56 (s, 2 H, Mes CH), 5.82 (d, 1 H, *J* = 6.1 Hz, Ge-H), 3.49 (4 lines of ABX, 1 H, CH$_2$C**H**Ph), 2.78 (s, 3 H, OCH$_3$), 2.38 (s, 6 H, Mes *p*-CH$_3$), 2.34 (s, 6 H, Mes *p*-CH$_3$), 2.30, 2.29 (each s, 12 H total, Mes *p*-CH$_3$), 2.17−2.27 (m, AB of ABX, C**H**$_2$-CHPh), 2.13 (s, 3 H, Mes *o*-CH$_3$), 2.10 (s, 3 H, Mes *o*-CH$_3$), 2.04 (s, 3 H, Mes *o*-CH$_3$), 1.99 (s, 3 H, Mes *o*-CH$_3$); ^{13}C NMR (ppm) 146.07, 144.50, 144.04, 143.86, 143.35, 138.87, 138.83, 138.32, 138.04, 135.13, 134.50, 132.45, 131.67 (Ph and Mes C), 129.80, 129.69, 129.24, 129.14, 128.97, 124.97 (Ph and Mes CH), 49.28 (OCH$_3$), 34.10 (CH$_2$CHPh), 24.87, 24.11, 24.09, 24.02, 23.61, 21.03, 20.95, 20.85 (CH$_2$ and Mes CH$_3$); ^{29}Si NMR (ppm) 1.90; MS (*m*/*z*) 713 (M$^+$ − H, 12), 595 (M$^+$ − Mes, 24), 312 (GeMes$_2$, 36), 297 (Mes$_2$SiOCH$_3$, 100); high-resolution MS for C$_{45}$H$_{55}$SiGeO calc 713.3234, found 713.3177.

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Supporting Information Available: NMR spectra for compounds **4**, **5**, and **10** and the experimental details for the 2-D NMR experiments (49 pages). Ordering information is given on any current masthead page.

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