Addition of Phenylacetylene to Germasilenes

Kim M. Baines,* Craig E. Dixon, Jonathon M. Langridge, Hui Wen Liu, and Fagen Zhang

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received December 15, 1998

Phenylacetylene has been found to add regioselectively to both tetramesitylgermasilene and Si,Si-di-*tert*-butyldimesitylgermasilene to give the 3-phenyl-1-sila-2-germacyclobut-3-enes, exclusively. The regioselectivity of the adducts was established by nucleophilic cleavage of the Si−Ge bond using sodium methoxide or hydroxide, respectively, to give the (methoxy- or hydroxysilyl)germylethenes.

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Published on May 6, 1999 on http://pubs.acs.org | doi: 10.1021/om981017h

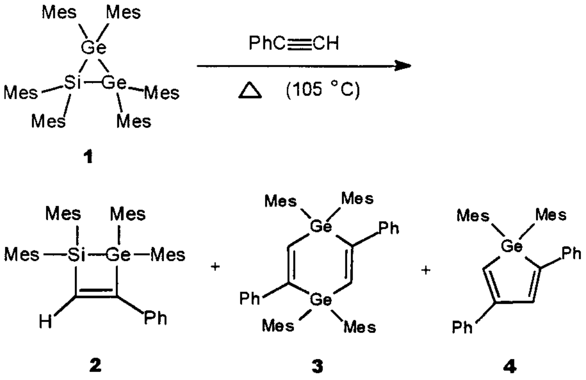
Introduction

The addition of alkynes to both stable (and relatively stable) disilenes,[1−6] and digermenes,[7−11] yields disilacyclobutenes and digermacyclobutenes, respectively. Whereas only phenylacetylene has been reacted with stable digermenes, a variety of alkynes, ranging from the unsubstituted acetylene[5] to a diyne[6] have been reacted with disilenes. The addition of alkynes to disilenes is believed to occur in a stepwise manner,[2,5] although there has been some debate over the nature of the intermediate. The fact that tetramesityldisilene only reacts with polar terminal alkynes is evidence for a zwitterionic intermediate;[5] however, a biradical intermediate has also been proposed.[2]

We have been successful in the synthesis of two heteronuclear group 14 dimetallenes, namely, tetramesitylgermasilene[12,13] and Si,Si-di-*tert*-butyldimesitylgermasilene.[14] The germasilenes provide an opportunity to examine the regiochemistry of the addition of an unsymmetrical alkyne, and thus, the addition of phenylacetylene to both germasilenes has been examined.

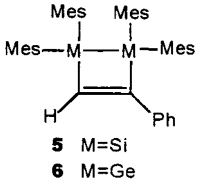
Results

Thermolysis of *cyclo*-$SiGe_2Mes_6$ in the presence of phenylacetylene was carried out in (or without) dry toluene at 105 °C. Under these conditions, the siladigermirane cleaves to give tetramesitylgermasilene and dimesitylgermylene, regioselectively.[12] Compounds **2**, **3**, and **4** were isolated from the reaction mixture (eq 1).



(1)

The ^{1}H NMR spectral data of compound **2** are remarkably similar to those of the phenylacetylene adducts of $Mes_2Si{=}SiMes_2$, **5**,[1] and $Mes_2Ge{=}GeMes_2$, **6**.[7] The chemical shift of the vinylic hydrogen is quite diagnostic at 7.87 ppm for **2** compared to 8.08 ppm for **5**[1] and 8.07 ppm for **6**.[7,15] Only one isomer of **2** was formed. An attempt was made to determine the regiochemistry of the adduct by spectroscopic means; however, the results were ambiguous. To identify the regiochemistry of the adduct, **2** was treated with sodium methoxide followed by treatment with water (eq 2). The reaction was remarkably clean, giving essentially one product, **7**, which was identified by NMR spectroscopy and mass spectrometry. The absence of the typically shielded ^{13}C resonance of a RO−C═C moiety and the absence of a geminal or a vicinal alkenyl coupling pattern in the ^{1}H NMR spectrum of **7** led us to conclude



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10.1021/om981017h CCC: $18.00 © 1999 American Chemical Society
Publication on Web 05/06/1999

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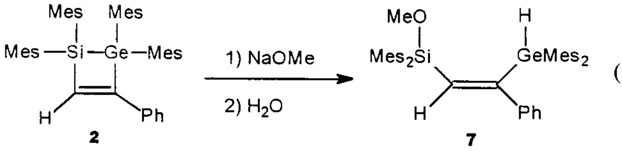
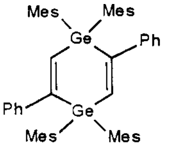


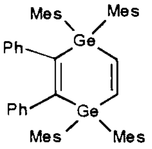
(2)

that cleavage had indeed occurred at the Si−Ge bond and not the Si−C or Ge−C bond. The signal at 5.86 ppm in the ^{1}H NMR spectrum can be assigned to a MH moiety. The absence of a large coupling in the ^{1}H-coupled ^{29}Si NMR spectrum of **7** allowed us to assign the MH signal as a GeH, and thus, the methoxide anion appears to have become attached to the silicon atom. Consistent with this conclusion, the base peak in the mass spectrum of **7** occurs at *m*/*z* 297, corresponding to $[Mes_2SiOCH_3]^+$. The regiochemistry of the cleavage of this Si−Ge bond is in agreement with the regiochemistry of other nucleophilic cleavage reactions of silylgermanes.[16] Most importantly, the absence of any splitting of the Ge−H signal indicates that the vinylic hydrogen atom is vicinal to the germanium atom and not geminal. Thus, the terminal carbon of the phenylacetylene is attached to the silicon atom of the germasilene, and the phenyl group is attached to the carbon atom adjacent to the germanium.

The yield of digermin **3** was low. In both the ^{1}H ($CDCl_3$ and C_6D_6) and the ^{13}C NMR spectra, there is only one kind of mesityl group present in the molecule. The ratio of the vinyl hydrogen atoms to the phenyl group and mesityl aryl hydrogen atoms is 1:5:4. From the MS, the highest mass ion was found at 826.2830. There are two structures consistent with these data:



3

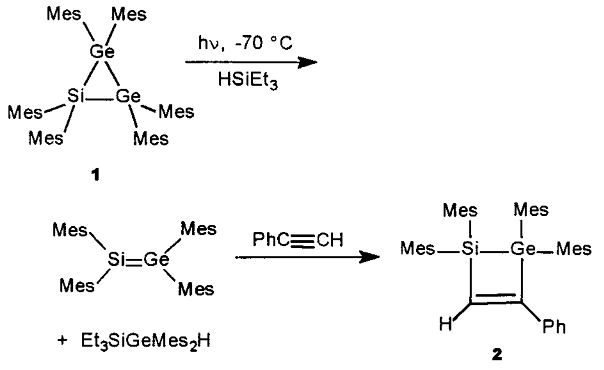


3a

A fragment corresponding to $Mes_2GePhCCPh$ or PhC-CPh was not apparent in the mass spectrum of **3**. Furthermore, only the loss of PhCCH (and not PhCCPh) was observed. Considering the known reactivity of Me_2Ge: toward phenylacetylene and other alkynes (in particular cyclooctyne), where structures analogous to **3** but not **3a** have been isolated,[17] the structure **3** is assigned to the compound.

With toluene as the reaction solvent, only traces of the germole **4** were observed in the ^{1}H NMR spectrum of the product mixture. By using phenylacetylene itself as the reaction solvent,[17] a small amount of compound **4** could be isolated. The ^{1}H NMR spectrum of compound **4** has one type of mesityl group in a 1:1 ratio with the phenyl group. There are two correlated doublets at 6.20 and 5.68 ppm with a coupling constant of 1.7 Hz, consistent with a homovinylic long-range coupling. The highest mass ion was found at 516.1884. From these data, the structure of **4** has been assigned. The ^{13}C NMR data and the MS fragmentation pattern are also consistent with the structure as shown.

The formation of compounds **2**−**4** can be explained by initial thermal degradation of *cyclo*-$SiGe_2Mes_6$ to give $Mes_2Si{=}GeMes_2$ and Mes_2Ge:. $Mes_2Si{=}GeMes_2$ undergoes a cycloaddition reaction with PhC≡CH, yielding only one isomer, the 2,3-silagermacyclobutene, regioselectively. To confirm that **2** is indeed the product from the direct reaction of the germasilene with the alkyne, a solution of the germasilene was generated by photolysis of the siladigermirane in the presence of Et_3SiH at −70 °C.[13] Phenylacetylene was then added to the germasilene in the cold, and the solution was warmed to room temperature. In addition to the expected $Et_3SiGeHMes_2$, **2** was isolated (eq 3).

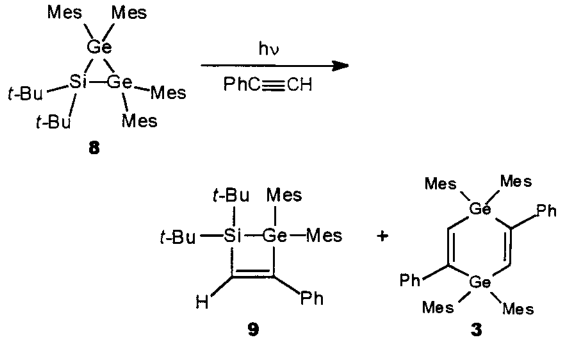


(3)

If the formation of the dimetallacyclobutene ring occurs in two steps via a biradical or a zwitterionic intermediate, the regiochemistry is most likely governed by the preferential formation of a germanium-centered radical or ion and stabilization of a vinylic radical or ion by the phenyl substituent.

The formation of 1,4-digermins and germoles such as **3** and **4**, respectively, from the reaction between germylenes and alkynes is well-known.[17] Although the mechanism for the formation of both the digermin and the germole is still open to scrutiny, the initial formation of a transient germirene followed by either dimerization to give the digermin or reaction with a second equivalent of alkyne to give the germole has been proposed.[17]

To investigate not only the generality of the addition of phenylacetylene to germasilenes but also the regiochemistry of the reaction, the addition of phenylacetylene to Si,Si-di-*tert*-butyldimesitylgermasilene[14] was investigated. Cophotolysis of Si,Si-di-*tert*-butyltetramesitylsiladigermirane (**8**) and phenylacetylene at ambient temperatures also gave three compounds (eq 4).



(4)

Compound **3** was isolated in 28% yield from the reaction mixture. A second compound, also believed to

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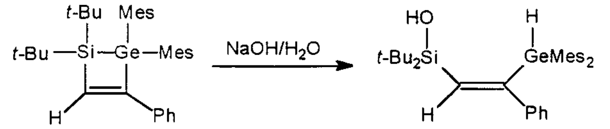
be derived from the addition of phenylacetylene to Mes_2-Ge:, was obtained in low yield but could not be identified.

Only one compound derived from reaction between phenylacetylene and the germasilene was isolated in high yield. The silagermacyclobutene structure was apparent from the singlet at 7.08 ppm in the ^{1}H NMR spectrum of **9**. An attempt was made to determine the regiochemistry of the adduct by cleavage of the Si−Ge bond with sodium methoxide; however, the cleavage of the dimetallacyclobutene was not clean. The bulk of the *tert*-butyl groups on silicon may hinder the approach of the methoxide nucleophile, leading to a less selective cleavage. Hence, a smaller nucleophile, sodium hydroxide, was employed (eq 5). In this case, the reaction was quantitative, with only a trace of impurities being visible in the crude reaction mixture by ^{1}H NMR analysis. The presence of a signal assignable to a hydroxyl hydrogen and the absence of any signals with a geminal or a vicinal alkenyl coupling in the ^{1}H NMR spectrum of **10** led to the conclusion that cleavage of the Si−Ge bond occurred. The ^{1}H-coupled ^{29}Si NMR spectrum of **10** lacked any large coupling, leading to the assignment of the signal at 6.43 ppm in the ^{1}H NMR spectrum to a GeH. The regiochemistry of the cleavage is the same as was observed previously. The GeH signal is a singlet, confirming that the benzylidenylic carbon is adjacent to the germanium atom. It follows that the regiochemistry shown for compound **9** is correct.



9 **10** (5)

In summary, the regioselective addition of phenylacetylene to germasilenes appears to be a general reaction. We continue to design experiments to help us determine the factors controlling the regiochemistry of the reaction.

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. Phenylacetylene was obtained from the Aldrich Chemical Co. and distilled before use. 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. Hexamesitylsiladigermirane[12] and Si,-Si-di-*tert*-butyltetramesitylsiladigermirane[14] were synthesized according to published procedures.

NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C), an XL-300, or a Varian Gemini 300 (299.9 MHz for ^{1}H, 75.4 MHz for ^{13}C, 59.6 MHz for ^{29}Si) using benzene-d_6 as solvent, unless otherwise noted. The standards were as follows: residual C_6D_5H 7.15 ppm for ^{1}H 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 peak intensities relative to the base peak and the ion identity in parentheses).

Thermolysis of *cyclo*-$SiGe_2Mes_6$ in the Presence of Phenylacetylene. *cyclo*-$SiGe_2Mes_6$ (50 mg, 0.056 mmol) and phenylacetylene (0.25 mL, 45× excess) were placed in toluene (2.5 mL). The mixture was heated to 105 °C for 5 h. Shortly after the thermolysis was started, the mixture turned yellow in color. After 3−4 h, the color faded to light yellow. After 4 h, the solvents were evaporated, leaving a yellow, viscous oil. The product mixture was separated by preparative thin-layer chromatography (Chromatotron; 10% CH_2Cl_2/hexane) to yield two major compounds, compound **2** (19 mg, contaminated with a trace of an unknown compound) and compound **3** (10 mg, 43%), and a trace amount of compound **4** (<2 mg). When neat phenylacetylene is used as the solvent, the following yields were obtained: compound **2** (23 mg, 61%), compound **3** (14 mg, 61%), and compound **4** (6 mg, 21%).

3-Phenyl-1,1,2,2-tetramesityl-1-sila-2-germacyclobut-3-ene (2): white solid; mp 82−84 °C; IR (thin film, cm^{-1}) 3047 (m), 2971 (s), 2920 (s), 2857 (m), 1603 (s), 1558 (m), 1542 (m), 1507 (m), 1450 (s), 1412 (m), 1380 (m), 1291 (m), 1237 (w), 1194 (w), 1062 (w), 1038 (m), 879 (m), 850 (s), 815 (m), 753 (s), 696 (m); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.63 (s, 1 H, vinyl-H), 7.15 (m, 5 H, Ph-H), 6.67 (s, 4 H, Mes-H), 6.64 (s, 4 H, Mes-H), 2.22 (s, 12 H, Mes-CH_3), 2.19 (bs, 12 H, Mes-CH_3), 1.99 (s, 12 H, Mes-CH_3); ^{1}H NMR (C_6D_6, 200 MHz, ppm) 7.87 (s, 1 H, vinyl-H), 7.4−7.0 (2m, 5 H, H−Ph), 6.66 (s, 8 H, Mes-H), 2.41 (s, 12 H, CH_3), 2.29 (s, 12 H, CH_3), 2.06 (s, 12 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 153.89 (H*C*═CPh), 174.11, 145.31, 144.05, 143.10, 139.15, 138.59, 137.65, 133.32 (Ar-C and vinyl C═), 128.70, 128.44 (Mes-H), 127.89, 126.62, 126.31 (Ph-H), 24.74, 24.56 (*o*-CH_3), 21.02, 20.97 (*p*-CH_3); ^{29}Si NMR ($CDCl_3$, ppm) −2.79, J_{Si-H} = 11 Hz; MS (*m*/*z*) 680 (59, M$^+$), 561 (6, M$^+$ − Mes), 533 (8, M$^+$ − SiMes), 412 (16, M$^+$ − $SiMes_2$ − 2H), 385 (100, $SiMes_3$), 367 (58, M$^+$ − $GeMes_2$ − H), 312 (24, $GeMes_2$), 279 (11), 235 (8), 192 (28, GeMes − H), 147 (12, SiMes), 125 (14); high-resolution MS calcd for $C_{44}H_{50}Si^{74}Ge$ 680.2894, found 680.2896.

Compound **2** can also be synthesized by addition of phenylacetylene to the preformed germasilene. A solution of *cyclo*-$SiGe_2Mes_6$ (150 mg, 0.17 mmol) dissolved in toluene (2 mL) and Et_3SiH (1 mL) was photolyzed at −70 °C for 8 h. Phenylacetylene (0.5 mL) was then added to the yellow solution in the cold. The color of the solution faded almost immediately. The solvent was removed in vacuo, and the product mixture was separated by chromatography (85:15 hexanes/CH_2Cl_2) to yield **2** (23 mg, 20%) in addition to Mes_2-GeH($SiEt_3$) and recovered siladigermirane.

2,5-Diphenyl-1,1,4,4-tetramesityl-1,4-digermacyclohexa-2,5-diene (3): white solid; mp 246−248 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.64 (s, 2 H, vinyl-H), 7.03−7.23 (m, 10 H, Ph-H), 6.55 (s, 8 H, Mes-H), 2.19 (s, 12 H, o-CH_3), 2.07 (s, 24 H, p-CH_3); ^{1}H NMR (300 MHz, C_6D_6, ppm) 7.89 (s, 2 H), 7.55−7.50, 7.05−6.85, (total 10 H), 6.59 (s, 8 H), 2.29 (s, 24 H), 2.08 (s, 12 H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) 147.68 (H*C*═CPh), 155.77, 144.02, 143.40, 137.70, 135.11 (Ar−C and vinyl C═), 128.88, 127.72, 127.19, 126.43 (Mes-H, Ph-H), 24.02, 20.98 (Mes-CH_3); MS (*m*/*z*): 825 (28, M$^+$ − H), 724 (63, M$^+$ − CHCPh), 707 (7, M$^+$ − Mes), 604 (11, M$^+$ − PhCCH − Mes), 533 (34, Mes_3GeCHCPh), 431 (72, $GeMes_3$), 413 (44, Mes_2-GeCCPh), 363 (28), 311 (48, $GeMes_2$ − H), 293 (24), 220 (24), 193 (100, GeMes), 120 (30, Mes + H); high-resolution MS calcd for $C_{52}H_{56}{}^{72}Ge^{74}Ge$ 826.2815, found 826.2841.

1,1-Dimesityl-2,4-diphenyl-1-germacyclopentadiene (4): white solid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.3−7.7 (m, Ph), 7.20 (s, Ph), 6.81 (s, 4 H, Mes), 6.20 (d, 1 H, *J* = 1.7 Hz), 5.68 (d, 1 H, *J* = 1.7 Hz, vinyl-H), 2.36 (s, 12 H, Mes-CH_3), 2.25 (s, 6 H, Mes-CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) 143.93, 141.96, 138.79, 133.48, 131.38, 129.86, 129.31, 128.11, 128.07, 127.99, 127.68, 127.61, 127.21, 24.32, 21.06; MS (*m*/*z*) 516 (38, M$^+$), 413 (100, Mes_2GeCCPh), 397 (10, M$^+$ − Mes), 295 (40,

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MesGe − CPhCH), 191 (52), 169 (52), 147 (34), 119 (82), 103 (90); high-resolution MS calcd for $C_{34}H_{34}{}^{74}Ge$ 516.1872, found 516.1884.

Reaction of Compound 2 with Sodium Methoxide. To a solution of compound **2** (20 mg, 0.0294 mmol) dissolved in THF (1 mL) was added a solution of NaOMe, prepared by dissolving Na (25 mg) in MeOH (1 mL). The solution was then refluxed overnight. The reaction mixture was then cooled and added to water (2 mL). The mixture was then extracted with diethyl ether, and the solvents were evaporated to yield a light yellow residue, which was then purified by preparative thin-layer chromatography (Chromatotron; 50% CH_2Cl_2/hexane) to yield one major product, compound **7** (19 mg, 91%).

1-Dimesitylgermyl-2-(dimesitylmethoxysilyl)-1-phenylethene (7): white solid; ^1H NMR (300 MHz, $CDCl_3$, ppm) 7.2−6.5 (m, 5 H, Ph), 7.09 (s, 1 H, vinyl-H), 6.74 (s, 4 H, Mes-H), 6.66 (s, 4 H, Mes-H), 5.86 (s, 1 H, GeH), 2.92 (s, 3 H, OCH_3), 2.27 (s, 12 H, Mes-CH_3), 2.23 (s, 6 H, Mes-CH_3), 2.19 (s, 6 H, Mes-CH_3), 1.99 (s, 12 H, Mes-CH_3); ^1H NMR (C_6D_6) 7.5−6.8 (m, Ph), 6.73, 6.72, 6.24, 3.02, 2.43, 2.28, 2.12, 2.09; ^{13}C NMR (50 MHz, $CDCl_3$, ppm) 149.43 (vinyl-CH), 157.54, 147.82, 144.36, 143.24, 138.97, 137.51, 135.54, 132.13 (vinyl and ArC), 129.14, 128.22, 127.35, 127.19, 125.97 (ArCH), 50.05 (OCH_3), 24.16, 23.54, 21.08 (Mes-CH_3); ^{29}Si NMR ($CDCl_3$, ppm) −16.37 (bm); MS (*m*/*z*) 712 (1, M^+), 697 (1, $M^+ - CH_3$), 635 (<1, M^+ − Ph), 592 (40, M^+ − Mes), 577 (7, M^+ − Mes − CH_3), 547 (14, M^+ − Mes − CH_3 − CH_3O), 531 (11, M^+ − Mes − OCH_3 − $2CH_3$), 516 (5, M^+ − Mes − OCH_3 − $3CH_3$), 473 (4, M^+ − 2Mes), 457 (9, M^+ − 2Mes − CH_3), 413 (21, M^+ − Mes_2SiOCH_3), 399 (30, M^+ − Mes_2GeH), 368 (18, $Mes_2SiCPhCH$), 311 (31, Mes_2Ge − H), 297 (100, Mes_2SiOCH_3), 279 (24, Mes_2SiCH), 265 (20, Mes_2Si − H), 193 (12 MesGe), 105 (9), 59 (18); high-resolution MS calcd for $C_{54}H_{54}OSi^{73}Ge$ 711.3179, found 711.3149.

Photolysis of *cyclo*-Si(*t*-Bu)$_2$Ge$_2$Mes$_4$ in the Presence of Phenylacetylene. A solution of *cyclo*-Si(*t*-Bu)$_2$Ge$_2$Mes$_4$ (50 mg, 0.065 mmol) and phenylacetylene (0.5 mL) in toluene (2 mL) was photolyzed (350 nm) 18 h at room temperature. Within 1 h, the pale yellow cloudy reaction mixture became dark yellow in color. At the end of the photolysis, the reaction mixture was a bright orange, clear solution. The solvent was removed under vacuum to give a viscous orange oil, which became a dark orange solid when a stream of argon was blown over it for 1.5 h. The product mixture was separated by preparative thin-layer chromatography (Chromatotron) using 1:9 CH_2Cl_2/hexanes as the eluent. The polarity of the eluent was gradually changed to 25:75 CH_2Cl_2/hexanes. Three products were isolated and identified, **9**, which was purified by recrystallization from pentane (27.8 mg, 77%), (7.7 mg, 29%), and a third compound observed in low yield, which appeared to be derived from the addition of Mes_2Ge: to phenylacetylene. However, this third compound could not be unambiguously identified.

3-Phenyl-1,1-di-*tert*-butyl-2,2-dimesityl-1-sila-2-germacyclobut-3-ene (9): white solid; mp 190−193 °C; IR (thin film, cm^{-1}) 3060 (w), 3020 (w), 2960 (s), 2920 (s), 2860 (s), 1600 (m), 1460 (s), 1290 (s), 1280 (s), 1180 (w), 1140−980 (br, s), 880 (w), 850 (m), 860 (m), 800 (s), 750 (s), 700 (s); ^1H NMR (C_6D_6, 300 MHz, ppm) 7.28−7.23, 7.14−7.00 (m, 5 H, Ph), 7.08 (s, 1 H, CH═), 6.75 (s, 4 H, Mes-CH), 2.50 (s, 12 H, *o*-CH_3), 2.09 (s, 6 H, *p*-CH_3), 1.14 (s, 18 H, *t*-Bu); ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.27−7.15, 7.11−7.06 (m, 5 H, Ph), 7.05 (s, 1 H, CH═), 6.74 (s, 4 H, Mes-CH), 2.31 (s, 12 H, *o*-CH_3), 2.21 (s, 6 H, *p*-CH_3), 1.08 (s, 18 H, *t*-Bu); ^{13}C NMR ($CDCl_3$, ppm): 181.15 (HC═*C*Ph), 150.26 (H*C*═CPh), 146.23, 142.56, 139.00, 137.40 (Ar-C), 128.54, (d, Mes-CH), 127.72, 126.32, 126.20 (Ph-CH), 29.48, 25.13, 20.92 (CH_3), 23.00 ($C(CH_3)_3$); ^{29}Si NMR (ppm) 30.79; MS (*m*/*z*) 556 (35, M^+), 499 (100, M − *t*-Bu), 311 (34, $GeMes_2$ − H), 281 (25), 193 (88, GeMes), 105 (36), 91 (69), 73 (70); high-resolution MS calcd for $C_{34}H_{46}Si^{74}Ge$ 556.2581, found 556.2587.

Reaction of Compound 9 with Sodium Hydroxide. A solution of compound **9** (30 mg, 0.054 mmol) in 1,4-dioxane (8 mL) was added dropwise to a clear, colorless, homogeneous solution of NaOH (2 pellets; approximately 75 mg) in aqueous dioxane (8 mL, approximately 40% H_2O). The solution was heated for 20 h, after which time the reaction mixture was a clear yellow in color. After the reaction cooled to room temperature, water (5 mL) was added and the reaction mixture was left to stir for 25 min. The reaction mixture was then extracted with hexanes. The solvent was removed from the combined organic layers to give a sticky white solid, **10** (24 mg, 77%). If left for any period of time, or if chromatographed, compound **10** is slowly converted to a new compound whose structure has not yet been determined.

2-(Di-*tert*-butylhydroxysilyl)-1-(dimesitylgermyl)-1-phenylethene (10): IR (thin film; cm^{-1}) 3608 (OH); ^1H NMR (C_6D_6, 300 MHz, ppm) 7.34−7.39, 6.88−7.03 (m, 6 H, Ph-H and CH═), 6.69 (s, 4 H, Mes-CH), 6.43 (s, 1 H, GeH), 2.39 (s, 12 H, *o*-Me), 2.04 (s, 6 H, *p*-Me), 1.54 (s, 1 H, OH), 1.13 (s, 18 H, *t*-Bu); ^{13}C NMR ($CDCl_3$, ppm) 161.78, 146.71, 143.56, 142.83, 138.65, 134.02, 128.90, 127.52, 127.25, 126.53, 28.06, 23.99, 21.12, 21.04; ^{29}Si NMR (^1H-coupled, ppm) 3.13 (bm); MS (*m*/*z*) 574 (6, M^+), 517 (50, M^+ − *t*-Bu), 455 (46, M^+ − Mes), 397 (100, M^+ − *t*-Bu − Mes − H), 313 (33, Mes_2GeH), 277 (30), 193 (25, MesGe), 163 (23), 119 (12), 84 (52).

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada in the form of a Summer Research Assistantship to J.M.L. and a grant to K.M.B. is gratefully acknowledged.

Supporting Information Available: ^1H and ^{13}C NMR spectra of **2**−**4**, **7**, **9**, and **10**, and ^{29}Si NMR spectra of **2**, **7**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM981017H