The Reaction of Group 14 Dimetallenes with Alkenes: Electron-Poor Alkenes

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Received July 28, 1997⊗

The addition reactions of tetramesitylgermasilene with methyl vinyl ketone (MVK), crotonaldehyde, and acrylonitrile were studied. When tetramesitylgermasilene was allowed to react with MVK, [2 + 4] cycloaddition and nonregioselective carbonyl [2 + 2] cycloaddition products were isolated. When tetramesitylgermasilene was allowed to react with crotonaldehyde, the carbonyl [2 + 2] adduct was produced exclusively. The regiochemistry was not determined. The addition of acrylonitrile to tetramesitylgermasilene yielded a germasilacyclobutane, which is the formal [2 + 2] cycloadduct between the germasilene and the C−C double bond of acrylonitrile. Tetramesityldisilene was also found to yield a formal [2 + 2] adduct with acrylonitrile. However, tetramesityldigermene rearranges to a germylgermylene at a faster rate than acrylonitrile addition.

Introduction

The chemistry of stable and relatively stable tetraaryldisilenes and -digermenes has been extensively documented,[1] and the reactivity of tetramesitylgermasilene, the first relatively stable germasilene, has been demonstrated to closely follow that of its homonuclear analogs tetramesityldisilene and tetramesityldigermene. In many cases, these heavier analogs of olefins have displayed an increased reactivity toward many reagents relative to alkenes. For example, tetramesityldisilene,[2] -digermene,[3] and -germasilene[3] smoothly add alcohols across the double bond without need of a catalyst. This increased level of reactivity of the heavier group 14 double bonds, relative to the C−C double bond, is responsible for some interesting behavior that has no direct parallel in carbon chemistry. For example, the C−O double bond of ketones and aldehydes reacts rapidly with the M_1−M_2 double bond of tetramesityldisilene,[2] -digermene,[4] and -germasilene,[5] in a formal [2 + 2] manner, to fashion the corresponding metallaoxetane.

Surprisingly, stable and relatively stable tetraaryldimetallenes have proven to be, for the most part, unreactive toward conjugated dienes. For example, tetramesityldisilene,[2] -digermene,[6] and -germasilene[6] are each unreactive toward 2,3-dimethylbutadiene. However, tetramesityldisilene and -germasilene will add styrene in a formal [2 + 2] manner.[7] [2 + 2] cycloaddition products have also been isolated from reactions between tetramesitylgermasilene and *trans*-1-methoxybutadiene[7] as well as between tetra-*tert*-butyldisilene and 2,2′-dipyridine,[8] *o*-methylstyrene,[9] or furan.[10] In each case where reaction between the dimetallene and the alkene is observed, the alkene reacting has been electron-rich. To our knowledge, the only electron-poor alkene that has been allowed to react with a dimetallene, namely tetramesityldisilene, has been an α,*β*-unsaturated ketone. Although the reactivity of dimetallenes toward ketones and aldehydes is well-known, the effect of the C−C double bond in conjugation with the carbonyl on this observed reactivity was not. When tetramesityldisilene was allowed to react with acrolein, methyl vinyl ketone, or ethyl vinyl ketone, the only products isolated were the corresponding disilaoxetanes from addition of the carbonyl moiety to the Si−Si double bond.[11] Apparently, the presence of the C−C double bond in conjugation with the carbonyl did not affect the reactivity between the disilene and the ketone.

To further explore what effect substitution of an electron-withdrawing group on an alkene may have on its reactivity with tetramesitylgermasilene, three electron-poor alkenes were selected for study. The results of the reactions between tetramesitylgermasilene and methyl vinyl ketone, crotonaldehyde, or acrylonitrile are reported in this paper. Also reported are the results of the reactions between tetramesityldisilene and -digermene and acrylonitrile.

Results and Discussion

Photolysis of hexamesitylsiladigermirane (**1**) in the presence of methyl vinyl ketone (MVK) at 22 °C yielded compounds **3**−**5** in a 8:1:4 ratio (Scheme 1). Compounds

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) For example see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1015. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (e) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, *J. Coord. Chem. Rev.* **1994**, *130*, 427.

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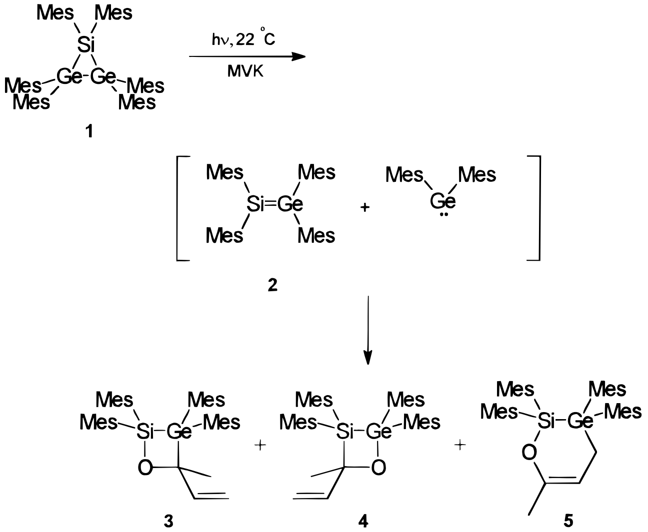
S0276-7333(97)00638-9 CCC: $14.00

Scheme 1

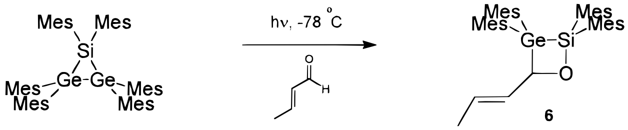


3 and **5** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopy and mass spectrometry. Compound **4** could not be isolated free of compound **3** and as a result was characterized soley by ^{1}H NMR spectroscopy, as a mixture of **3** and **4**.

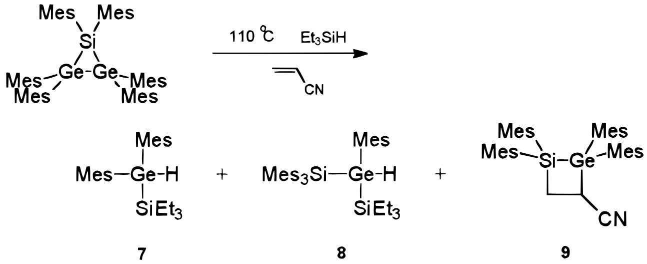
Compounds **3** and **4** appear to be the [2 + 2] adducts of tetramesitylgermasilene, generated by photolysis of the siladigermirane,[12] and the carbonyl group of MVK. Consistent with this assignment, as determined by thorough ^{1}H NMR spectroscopic examination of **3**, is the presence of four nonequivalent mesityl groups, a single resonance, and the characteristic splitting pattern for a terminal vinyl moiety: three doublets of doublets at 6.32, 5.19, and 4.82 ppm with $J_{\mathrm{trans}} = 16.9$ Hz, $J_{\mathrm{cis}} = 10.7$ Hz, and $J_{\mathrm{gem}} = 1.92$ Hz. Furthermore, the 25.45 ppm signal in the ^{29}Si NMR spectrum is consistent with the 2-sila-3-germaoxetane structure.[5] Although the regiochemistry of **3** was not determined, we are confident that **3** is the major regioisomer on the basis of molecular structure determinations of similar adducts. Acetone and pivalaldehyde each gave a [2 + 2] adduct with tetramesitylgermasilene and were shown to give a single regioisomer: the 2-sila-3-germaoxetane.[5] Compound **5** is the [2 + 4] cycloadduct of tetramesitylgermasilene and MVK. Consistent with this assignment are the two distinct mesityl groups, as determined by ^{1}H NMR spectroscopy, as is the presence of a triplet at 4.50 ppm ($J = 6.5$ Hz), corresponding to the vinyl moiety. The regiochemistry of the molecule was not determined. No product derived from the reaction between dimesitylgermylene and MVK was detected.

The reactivity of metallenes and dimetallenes with ethylenic ketones has been shown to follow a certain order, loosely based upon the polarity of the reacting double bond. For example, nonpolar disilenes[11] exclusively undergo [2 + 2] additions with the carbonyl double bond, whereas the more polar germenes undergo [2 + 4] cycloadditions, regioselectively, as the sole mode of reaction.[13] The reactivity of tetramesitylgermasilene toward MVK falls between the observed reactivity of disilenes and digermenes, which would be consistent with the slight polarity of the silicon−germanium double bond.

Scheme 2



Scheme 3



Interestingly, crotonaldehyde, despite its structural similarity to MVK, failed to produce a similar product mixture when allowed to react with tetramesitylgermasilene. Photolysis of hexamesitylsiladigermirane in the presence of crotonaldehyde, at −78 °C, yielded one product, **6**, the formal [2 + 2] cycloaddition product between the carbonyl moiety of crotonaldehyde and tetramesitylgermasilene (Scheme 2). Compound **6** was previously isolated as a minor byproduct from the photolysis of $SiGe_2Mes_6$ in the presence of vinyl acetate distilled from LiAlH(O-*t*-Bu)$_3$.[7] The spectroscopic data for compound **6** agree completely with the literature data.[7] The regiochemistry of the adduct was not determined; the assigned structure is based on the known regiochemistry for the addition of pivalaldehyde and acetone to the germasilene.[5] It is noteworthy to mention that another product is observed in the ^{1}H NMR spectrum of the crude reaction mixture, which is presumably derived from the reaction between dimesitylgermylene and crotonaldehyde. However, compound **6** was the only compound isolated from the reaction mixture, indicating that the germylene-derived product may have decomposed during chromatography. In fact, compounds derived from reaction between dimesitylgermylene and ketones or aldehydes have been found to be notoriously difficult to purify by conventional chromatographic techniques; therefore, this observed decomposition is not unexpected.[14] The observed reactivity of tetramesitylgermasilene with MVK or crotonaldehyde is consistent with the reactivity observed between tetramesityldisilene and α,*β*-unsaturated ketones or aldehydes. Not surprisingly, the cycloaddition of the germasilene to the carbonyl moiety of MVK or crotonaldehyde occurs preferentially over reaction with the C−C double bond.

Thermolysis of hexamesitylsiladigermirane at 110 °C, in the presence of Et_3SiH and acrylonitrile, yielded compounds **7**−**9** in a 3:1:2 ratio, as determined by ^{1}H NMR spectroscopy (Scheme 3). Compounds **7** and **8** are the products obtained by trapping dimesitylgermylene and mesityl(trimesitylsilyl)germylene (from rearrangement of $Mes_2Ge{=}SiMes_2$) with Et_3SiH, respectively, and were identified by comparison to the literature data.[12] Compound **9** is the cycloaddition product between tetramesitylgermasilene and the C−C double bond of acrylonitrile. Consistent with this assignment is the

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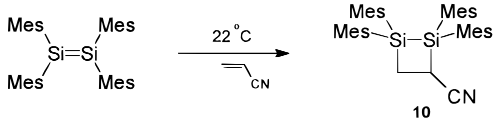
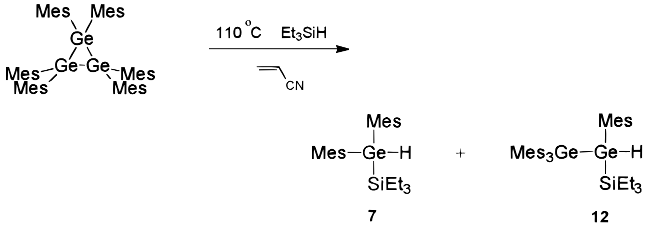
Scheme 4



Scheme 5



appearance of four mesityl groups and an ABX spin pattern in the ^{1}H NMR spectrum of **9**. The IR spectrum shows an absorbance at 2217 cm^{-1}, which is assigned to the CN stretching vibration. The ^{13}C (spin sort method), COSY, HSQC (heteronuclear spin quantum coherence; ^{1}H/^{13}C), and HMBC (heteronuclear multiple bond correlation; ^{1}H/^{13}C and ^{1}H/^{29}Si) NMR spectra also support the assignment. The ^{1}H/^{29}Si HMBC spectrum shows a two-bond correlation between the signal at 10.1 ppm in the ^{29}Si dimension and the methylene protons at 2.48 and 2.57 ppm in the ^{1}H dimension, which suggests the regiochemistry of compound **9** is that which is shown. There is also evidence to suggest the presence of another regioisomer of **9**. There appears to be an additional four lines in the ^{1}H NMR spectrum (3.04 ppm), consistent with an ABX spin system. Furthermore, the ^{29}Si NMR spectrum shows a second signal very close to that which was assigned to **9** (approximately 10.1 ppm). The ratio of these two regioisomers is approximately 8:1, with the major component being **9**.

It is interesting to compare the chemistry of the heteronuclear dimetallene to that of the homonuclear analogs, disilenes and digermenes. When acrylonitrile is added to a solution of tetramesityldisilene in benzene and this mixture is allowed to stand at 22 °C for several hours, compound **10** is formed (Scheme 4). The ^{1}H, ^{13}C (spin sort method), COSY, HSQC (^{1}H/^{13}C), and HMBC (^{1}H/^{13}C and ^{1}H/^{29}Si) NMR spectra all support the assigned structure for **10**. Thus, similar to the case for tetramesitylgermasilene, tetramesityldisilene adds acrylonitrile in a formal [2 + 2] fashion.

Thermolysis of hexamesitylcyclotrigermane in the presence of Et_3SiH and acrylonitrile yielded compounds **7** and **12**, which were readily identified by referral to the literature data[15] (Scheme 5). Tetramesityldigermene has been shown to undergo a thermal 1,2-mesityl shift to give the corresponding germylgermylene.[15] Compound **12** results from insertion of mesityl(trimesitylgermyl)germylene into the Si–H bond of Et_3SiH. Unlike tetramesitylgermasilene and tetramesityldisilene, tetramesityldigermene does not appear to add acrylonitrile at a faster rate than the 1,2-mesityl shift to the corresponding germylgermylene.

In summary, we have shown that tetramesitylgermasilene yields formal [2 + 2] and [2 + 4] cycloaddition products in reaction with the C–O double bond of MVK and that the [2 + 2] reaction does not occur entirely regioselectively. In the presence of crotonaldehyde, however, tetramesitylgermasilene yields the formal [2 + 2] cycloaddition product in reaction with the C–O double bond, exclusively. Furthermore, it has also been shown that tetramesitylgermasilene and -disilene add across the C–C double bond of acrylonitrile in a formal [2 + 2] manner. In the case of tetramesitylgermasilene the addition of acrylonitrile is not entirely regioselective, with the major regioisomer produced being **9**. In contrast, tetramesityldigermene rearranges to the corresponding germylgermylene at a faster rate than addition of acrylonitrile, perhaps a reflection of the greater ease for migration of the mesityl group across the Ge–Ge double bond in comparison to the germasilene system.

In combination with the results of our previous investigations,[7] tetramesitylgermasilene and/or -disilene react with the following alkenes: 1-methoxybutadiene, styrene, and acrylonitrile. However, no reaction was observed between the germasilene and ethyl vinyl ether, vinyl acetate, allyltrimethylsilane, *trans*-phenylvinylcyclopropane, and 2,3-dimethylbutadiene. The reactions between the germasilene and α,β-unsaturated carbonyl compounds such as crotonaldehyde and methyl vinyl ketone are dominated by reaction with the carbonyl moiety. As a result, we cannot consider these alkenes in our examination of the reactivity of dimetallenes toward alkenes. We believe that this trend in reactivity suggests a mechanism of addition which proceeds through a biradical intermediate. We will report on our findings in due course.

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. Acrylonitrile was obtained from BDH and used without any further purification. Crotonaldehyde was base-washed, dried and filtered from $MgSO_4$, and distilled prior to use. MVK was simply distilled under an atmosphere of argon prior to 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.

NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C), an XL-300, a Varian Gemini 300 (299.9 MHz for ^{1}H, 75.4 MHz for ^{13}C, 59.6 MHz for ^{29}Si), or a Bruker Advance DRX-500 using benzene-d_6 as a solvent. The standards were as follows: residual C_6D_5H 7.15 ppm for ^{1}H spectra; C_6D_6 central transition for ^{13}C NMR spectra; Me_4Si as an external standard, 0 ppm for ^{29}Si. The 2-D spectra were acquired using standard techniques.[16–18] 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 $SiGe_2Mes_6$ in the Presence of Methyl Vinyl Ketone (MVK). A solution of $SiGe_2Mes_6$ (75 mg, 0.084 mmol) and freshly distilled MVK (0.75 mL, excess) in dry toluene was photolyzed for 6.5 h at 22 °C. During the photolysis, the reaction mixture developed a yellow color which faded as the reaction proceeded. Following the photolysis, the solvent was removed, yielding a tan semisolid. Trituration of

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this mixture with either hexanes or diethyl ether caused precipitation of a white, intractable solid. Removal of the solvent from the triturate yielded a mixture of both regioisomers of 4-methyl-2,2,3,3-tetramesityl-4-vinylgermasilaoxetane (**3** and **4**) and 5-methyl-2,2,3,3-tetramesitylgermasilacyclohex-1-ene (**5**). Separation of the components was accomplished using preparative thin-layer chromatography (Chromatotron) with hexanes/CH_2Cl_2 as the eluent. Compounds **3** and **5** were isolated in 38% and 18% yields, respectively. The minor isomer, **4**, could not be separated from the major isomer, **3**. Compound **5** contained traces of, perhaps, a regioisomeric compound. No product derived from the reaction of MVK with Mes_2Ge: was detected.

4-Methyl-2,2,3,3-tetramesityl-4-vinylgermasilaoxetane (3). IR (thin film, cm^{-1}): 2957 (s), 2919 (s), 1605 (s), 1553 (w), 1442 (s), 1410 (m), 1377 (w), 1070 (w), 1029 (w), 997 (w), 940 (m), 900 (w), 847 (s), 790 (w). ^1H NMR (ppm): 6.72, 6.71, 6.66, 6.64 (s, 8 H total, Mes H), 6.32 (dd, 1 H, C**H**=CH_2, $J_{cis} = 10.6$ Hz, $J_{trans} = 16.9$ Hz), 5.19 (dd, 1 H, CH=CH**H**$_{trans}$, $J_{gem} = 1.9$ Hz, $J_{trans} = 16.9$ Hz), 4.82 (dd, 1 H, CH=C**H**$_{cis}$H, $J_{gem} = 1.9$ Hz, $J_{cis} = 10.6$ Hz), 2.65 (bs), 2.46 (vbs), 2.37 (s), 2.19 (s) (24 H total, Mes *o*-CH_3), 2.118, 2.114 (6 H total), 2.06 (3 H), 2.01 (3 H) (each s, Mes *p*-CH_3), 1.62 (s, 3 H, CH_3). ^{13}C NMR (ppm): 148.01 (**C**H=CH_2), 143.90 (vbs), 142.76, 142.37, 141.69, 139.23, 137.95, 135.42, 134.55 (Mes C), 129.82 (bs), 129.24 (bs), 129.13, 128.91 (Mes CH), 108.03 (CH=**C**H_2), 94.38 (C—O), 30.53 (OC—**C**H_3), 26.65 (vbs), 24.93 (bs), 24.24, 23.92 (vbs) (*o*-CH_3), 21.06, 20.96, 20.92 (*p*-CH_3). ^{29}Si NMR (ppm): 25.45. MS (*m*/*z*): 648 (M^+, 9), 578 (Mes_4SiGe, 4), 528 ($M^+ -$ Mes, 8), 385 (Mes_3Si, 69), 312 (Mes_2Ge, 100), 265 (Mes_2Si, 6), 192 (MesGe, 21). High-resolution MS (*m*/*z*): calcd for $C_{40}H_{50}GeSiO$, 648.2843; found, 648.2828.

4-Methyl-2,2,3,3-tetramesityl-4-vinylgermasilaoxetane (4, Minor Isomer). ^1H NMR (ppm): 6.72, 6.71, 6.66, 6.62 (each s, Mes H), 6.39 (dd, 1 H, C**H**=CH_2, $J_{cis} = 10.7$ Hz, $J_{trans} = 16.9$ Hz), 5.37 (dd, 1 H, CH=CH**H**$_{trans}$, $J_{gem} = 2.0$ Hz, $J_{trans} = 16.9$ Hz), 4.91 (dd, 1 H, CH=C**H**$_{cis}$H, $J_{gem} = 2.0$ Hz, $J_{cis} = 10.7$ Hz), 2.65 (bs), 2.46 (vbs), 2.32 (s), 2.21 (s) (*o*-CH_3), 2.12, 2.09, 2.05, 2.03 (s, *p*-CH_3), 1.54 (s, CH_3).

2-Methyl-4,4,5,5-tetramesityloxasilagermacyclohex-1-ene (5). IR (thin film, cm^{-1}): 3022 (s), 2976 (s), 2919 (s), 2731 (w), 1661 (m), 1604 (s), 1551 (m), 1449 (s), 1409 (s), 1376 (m), 1313 (m), 1289 (w), 1264 (m), 1210 (s), 1132 (s), 1063 (m), 1008 (s), 915 (m), 848 (s), 788 (w), 739 (s), 693 (s), 620 (m). ^1H NMR (ppm): 6.72 (s, 4 H, Mes H), 6.69 (s, 4 H, Mes H), 4.51 (dt, 1 H, C=CH, $J = 6.9$ Hz, $J = 0.9$ Hz), 2.55 (bs, 12 H total, Mes *o*-CH_3 and CH_2), 2.22 (s, 12 H, Mes *o*-CH_3), 2.09, 2.08 (each s, 12 H total, Mes *p*-CH_3), 1.70 (d, 3 H, CH_3, $J = 0.9$ Hz). ^{13}C NMR (ppm): 148.54 (CH_3**C**=CH), 144.80, 143.43, 139.34, 138.54, 137.45, 133.69 (Mes C), 129.82, 129.41 (Mes CH), 102.20 (CH_3C=**C**H), 25.06, 24.06 (Mes *o*-CH_3), 23.11 (CH_3), 20.96, 20.89 (Mes *p*-CH_3), 19.10 (CH_2). ^{29}Si NMR (ppm): −4.22. MS (*m*/*z*): 648 (M^+, 16), 578 (Mes_4SiGe, 2), 385 (Mes_3Si, 48), 312 (Mes_2Ge, 100), 267 (Mes_2Si, 13), 192 (MesGe, 48), 147 (MesSi, 14), 84 (53), 49 (60). High-resolution MS (*m*/*z*): calcd for $C_{40}H_{50}GeSiO$, 648.2843; found, 648.2857.

Photolysis of $SiGe_2Mes_6$ in the Presence of Crotonaldehyde. A solution of $SiGe_2Mes_6$ (48 mg, 0.054 mmol) and crotonaldehyde (1 mL, excess) in dry toluene (3 mL) was photolyzed for 6 h at −78 °C. The solution remained colorless during the given reaction time. After removal of the solvent, the oily mixture was separated by preparative thin-layer chromatography (Chromatotron) with a CH_2Cl_2/hexanes mixture as the eluent. Compound **6** was isolated as the major product (35 mg, 63%) and identified by comparison to the literature data.[5]

Thermolysis of $SiGe_2Mes_6$ in the Presence of Acrylonitrile. $SiGe_2Mes_6$ (40 mg, 0.045 mmol), acrylonitrile (0.5 mL, excess), and Et_3SiH (0.5 mL, excess) were placed in toluene (3 mL), and the mixture was heated to 110 °C for 8 h. The solvents were then removed to yield a yellow solid. This mixture was separated by preparative thin-layer chromatography (50/50 CH_2Cl_2/hexanes), to give compound **9** (3 mg, 6%).[19]

1,1,2,2-Tetramesityl-4-cyano-1-germa-2-silacyclobutane (9). IR (thin film, cm^{-1}): 3016 (m), 2964 (s), 2927 (s), 2860 (s), 2217 (m, CN), 1611 (s), 1458 (s), 1417 (m), 1383 (m), 1039 (m), 856 (m). ^1H NMR (ppm): 6.70 (s, 2 H, Mes H), 6.63 (s, 2 H, Mes H), 6.61 (s, 2 H, Mes H), 6.59 (s, 2 H, Mes H), 3.14 (X portion of ABX, 1 H, CH_2C**H**CN, $J_{AX} = 8$ Hz, $J_{BX} = 13$ Hz), 2.57, 2.48 (AB portion of ABX, C**H**$_2$CHCN, $J_{AB} = 15.1$ Hz), 2.35 (s, 6 H, Mes *o*-CH_3), 2.31 (s, 6 H, Mes *o*-CH_3), 2.24 (s, 6 H, Mes *o*-CH_3), 2.09 (s, 6 H, Mes *o*-CH_3), 2.07 (s, 3 H, Mes *p*-CH_3), 2.04 (s, 6 H, Mes *p*-CH_3), 2.01 (s, 3 H, Mes *p*-CH_3). ^{13}C NMR (ppm): 145.37, 144.58, 143.64, 142.25, 139.73, 139.52, 139.20, 138.54, 135.40, 130.87 (Mes C), 129.95, 129.79, 129.31, 129.24 (Mes CH), 124.44 (CN), 26.30 (CH_2), 25.41, 24.68, 24.36, 24.32 (Mes *o*-CH_3), 21.48 (CH), 21.05, 20.96, 20.87 (Mes *p*-CH_3). ^{29}Si NMR (ppm): 10.1. MS (*m*/*z*): 631 (M^+, 25), 616 ($M^+ - CH_3$, 39), 512 ($M^+ -$ Mes, 24), 385 (Mes_3Si, 100), 339 (Mes_2SiGe, 74), 310 (Mes_2Ge, 31), 265 (Mes_2Si − H, 36), 191 (MesGe, 55), 147 (MesSi, 68). High-resolution MS (*m*/*z*): calcd for $C_{39}H_{47}SiGeN$, 631.2683; found, 631.2690.

Addition of Acrylonitrile to Tetramesityldisilene. $Mes_2Si(SiMe_3)_2$ (100 mg, 0.24 mmol) was dissolved in pentane (8 mL) and photolyzed (254 nm) at −60 °C for 12 h. At this time, the pentane was removed, in vacuo, and replaced with toluene. To this solution was added acrylonitrile (0.25 mL, excess), and the mixture was allowed to stand at 22 °C for 12 h. Following removal of the solvent, the reaction mixture was purified by preparative thin-layer chromatography (50/50 CH_2Cl_2/hexanes) to give compound **10** (14 mg, 10%).[19]

1,1,2,2-Tetramesityl-4-cyano-1,2-disilacyclobutane (10). Mp: 178−180 °C. IR (thin film, cm^{-1}): 3032 (m), 2965 (s), 2920 (s), 2224 (m, CN), 1611 (s), 1555 (w), 1454 (s), 1413 (m), 1379 (w), 1293 (w), 1271 (w), 1237 (w), 1064 (w), 1036 (m), 856 (s). ^1H NMR (ppm): 6.69 (s, 2 H, Mes CH), 6.65 (s, 2 H, Mes CH), 6.58 (s, 2 H, Mes CH), 6.57 (s, 2 H, Mes CH), 3.04 (X portion of ABX, 1 H, CH_2C**H**CN, $J_{AX} = 8.2$ Hz, $J_{BX} = 13.6$ Hz), 2.45, 2.35 (AB portion of ABX, C**H**$_2$CHCN, $J_{AB} = 14.8$ Hz), 2.38 (s, 6 H, Mes *o*-CH_3), 2.35 (s, 6 H, Mes *o*-CH_3), 2.27 (s, 6 H, Mes *o*-CH_3), 2.08 (s, 3 H, Mes *p*-CH_3), 2.06 (s, 6 H, Mes *o*-CH_3), 2.024 (s, Mes *p*-CH_3), 2.018 (s, Mes *p*-CH_3) (9 H total). ^{13}C NMR (ppm): 146.15, 145.45, 143.81, 143.47, 140.15, 139.39, 139.275, 139.265, 136.25, 135.82, 131.43, 129.07 (Mes C), 130.02, 129.85, 129.31 (Mes CH), 123.76 (CN), 25.75 (Mes *o*-CH_3), 25.13 (CH_2), 24.69, 24.53, 24.47 (Mes *o*-CH_3), 21.00, 20.89, 20.80 (Mes *p*-CH_3), 20.15 (CH). ^{29}Si NMR (ppm): 7.50 (SiCHCN), −1.60 ($SiCH_2$). MS (*m*/*z*): 585 (M^+, 25), 570 ($M^+ - CH_3$, 74), 466 ($M^+ -$ Mes, 15), 293 (Mes_2Si_2 − H, 95), 266 (Mes_2Si, 34), 147 (MesSi, 100). High-resolution MS (*m*/*z*): calcd for $C_{39}H_{47}Si_2N$, 585.3247; found, 585.3243.

Thermolysis of Ge_3Mes_6 in the Presence of Acrylonitrile. Ge_3Mes_6 (50 mg, 0.054 mmol) and Et_3SiH (1 mL, excess) were dissolved in toluene (2 mL), and the mixture was heated to 110 °C for 8 h. After this time, the solvents were removed and subsequent analysis of the crude reaction mixture by ^1H NMR spectroscopy showed a mixture of compounds **7** and **12** as the major product. There were no products detected from a reaction between tetramesityldigermene and acrylonitrile.

Acknowledgment. We thank the NSERC (Canada) for financial support and Dr. D. W. Hughes (McMaster University) for assistance in obtaining the 2-D spectra.

Supporting Information Available: NMR and mass spectra for compounds **3**, **5**, **9**, and **10** and IR spectra for **5**, **9**, and **10** (27 pages). Ordering information is given on any current masthead page.

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[19] While the isolated yield of the cycloadduct is low, it appears as a major component of the crude reaction mixture, as determined by ^1H NMR spectroscopy. Loss of material appears to occur during the separation and purification of the compounds.