Supporting Information

The Addition of Nitriles to a Molecular Digermene: Reversible Addition and Comparison to Surface Reactivity**

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**Identification of 5 and 6**

The key spectral features which led to the structural assignment of 5 included a molecular ion (M + H⁺) located at m/z 664 (\(^{72}\text{Ge}^{74}\text{Ge}\)) in the ESI-TOF mass spectrum of 5, which is consistent with a 1:1 adduct between CH₃CN and digermene 4 (plus a hydrogen), a signal at 2.46 ppm (s, 3H, CH₃) in the \(^1\text{H}\) NMR spectrum of 5, and signals at 32.93 (CH₃) and 201.86 ppm (C=N) in the \(^{13}\text{C}\) NMR spectrum of 5. The appropriate correlations were observed in the \(^1\text{H}-^{13}\text{C}\) gHSQC and gHMBC spectra of 5. The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectral data of 5 are comparable to those of the analogous silicon derivative A (\(^1\text{H}\): 2.55 ppm (CH₃); \(^{13}\text{C}\): 33.35 (CH₃) and 214.76 ppm (C=N)),\(^{[1]}\) which supports the assigned structure of 5 (Chart S1).

\[
\begin{array}{ccc}
\text{Mes}_2\text{Si-SiMes}_2 & \text{Mes}_2\text{Si-SiMes}_2 & \text{Ar}_2\text{Si-SiAr}_2 \\
\text{A} & \text{B} & \text{E} \\
\text{R} & \text{R'} = \text{H} & \text{R'} = \text{CH}_3 \\
\text{R} = \text{CH}_3 & \text{C} & \text{D} \\
\text{R} = \text{CH}_3\text{CH}_2 & & \\
\end{array}
\]

**Chart S1**

The \(^1\text{H}\) NMR spectrum of 6 revealed a broadened signal at 4.58 ppm (s, 1H, NH) and two sharp signals at 4.54 and 4.46 ppm (both are s, 1H, \(=\text{CH}\)), which are similar to the \(^1\text{H}\) chemical shifts of the \(\text{H}_2\text{C}=\text{C}-\text{NH}\) moiety of B (\(^1\text{H}\): 4.70 (\(=\text{CH}\)), 4.62 (=CH), and 4.53 ppm (NH)) (Chart S1).\(^{[1]}\) In the \(^1\text{H}-^{13}\text{C}\) gHSQC spectrum of 6, the signals at 4.54 and 4.46 ppm (=CH₂) in the \(^1\text{H}\) dimension showed a correlation to a signal at 88.7 ppm in \(^{13}\text{C}\) dimension. Although a \(^{13}\text{C}\) signal was not observed in the \(^{13}\text{C}\) NMR spectrum at 88.7 ppm, this chemical shift is similar to the \(^{13}\text{C}\) chemical shift assigned to the \(=\text{CH}_2\) carbon of B (92.95 ppm),\(^{[1]}\) and therefore, the \(=\text{CH}_2\) carbon of 6 was assigned to this signal. Furthermore, the \(^1\text{H}-^{13}\text{C}\) gHMBC spectrum of 6 revealed a
correlation between the signal at 4.54 ppm in the $^1$H dimension and 166.8 ppm in $^{13}$C dimension. Although a $^{13}$C signal was not observed in the $^{13}$C NMR spectrum at 166.8 ppm, this chemical shift is similar to the $^{13}$C chemical shift assigned to the $=$C-NH carbon of B (160.17 ppm),[1] and therefore, the $=$C-NH carbon of 6 was assigned to this signal. The $=$CH$_2$ and $=$C-NH carbons of 6 are likely not observed in the 1-dimensional $^{13}$C NMR spectrum of 6 due to the low concentration of 6 in the sample.

**Identification of 7 and 8**

The ESI-TOF mass spectrum of 7 and 8 revealed a molecular ion (M + $^1$H$^+$) located at m/z 678 ($^{72}$Ge$^{74}$Ge), which is consistent with a 1:1 adduct between CH$_3$CH$_2$CN and digermene 4 (plus a hydrogen). The CH$_3$CH$_2$C=N moiety of 7 was characterized by signals at 1.21 (t, 3H, CH$_3$) and 2.79 ppm (q, 2H, CH$_2$) in the $^1$H NMR spectrum of 7 and signals at 10.12 (CH$_3$), 38.58 (CH$_2$), and 205.10 ppm (C=N) in the $^{13}$C NMR spectrum of 7. The appropriate correlations were observed in the gCOSY, $^1$H-$^1$C gHSQC and gHMBC spectra of 7. The $^1$H and $^{13}$C NMR spectral data of 7 are comparable to those of C ($^1$H: 1.23 (CH$_3$) and 2.87 ppm (CH$_2$); $^{13}$C: 9.50 (CH$_3$), 38.07 (CH$_2$), and 217.12 ppm (C=N)),[1] which supports the structural assignment of 7 (Chart S1).

The presence of a CH$_3$(H)C=C-NH moiety in 8 was clearly apparent from the NMR data. The $^1$H NMR spectrum of 8 revealed signals at 1.64 (d, 3H, CH$_3$), 4.60 (s, 1H, NH), and 4.92 (q, 1H, $=$CH) ppm and the $^{13}$C NMR spectrum of 8 revealed signals at 10.95 (CH$_3$), 97.97 (=CH), and 158.56 ppm (=C-NH). The appropriate correlations were observed in the gCOSY, $^1$H-$^1$C gHSQC and gHMBC spectra of 8. The $^1$H and $^{13}$C NMR spectral data of 8 are comparable to those of D ($^1$H: 1.56 (CH$_3$), 4.56 (NH), and 5.15 (=CH); $^{13}$C: 11.28 (CH$_3$), 102.06 (=CH), and 151.52 ppm (=C-NH)), which supports the assigned structure of 8. Unlike D, only one isomer of
8 was observed. Due to reduced steric interactions, 8 likely has the E-configuration; however, this has not been confirmed.

**Identification of 9**

The ESI-TOF mass spectrum of 9 revealed a molecular ion (M + H+) at m/z 676 (72Ge74Ge), which is consistent with a 1:1 adduct between acrylonitrile and digermene 4 (plus a hydrogen). The 1H NMR spectrum of 9 revealed two types of mesityl groups and the H2C=CH-C=N moiety was apparent from the NMR data. The 1H NMR spectrum of 9 revealed three signals within the vinyl region of the spectrum at 6.84, 5.79, and 5.18 ppm. Each 1H signal was a doublet of doublets and integrated to 1H. The 1H chemical shifts and multiplicities were similar to those of acrylonitrile and, in the gCOSY spectrum of 9, all three 1H signals correlated to each other, indicating the presence of a H2C=CH group. The 13C NMR spectrum of 9 revealed three signals at 199.84, 142.21, and 121.46 ppm. In the 1H-13C gHSQC spectrum of 9, the 1H signal at 6.84 ppm showed a correlation to the 13C signal at 142.21 ppm, which was assigned to the HC=CH2 carbon, and the 1H signals at 5.79 and 5.18 ppm showed correlations to the 13C signal at 121.46 ppm, which was assigned to the HC=CH2 carbon. In the 1H-13C gHMBC spectrum of 9, the 1H signals at 6.84, 5.79, and 5.18 ppm showed correlations to the 13C signal at 199.84 ppm. The 13C chemical shift of 199.84 ppm is similar to the chemical shifts of the C=N carbons of 5 (201.86 ppm) and 7 (205.10 ppm), and thus, was assigned to the C=N carbon of 9. Although 9 was contaminated with Mes2Ge(H)Ge(OH)Mes2, the IR spectrum of the mixture was obtained. The IR spectrum of 9 revealed bands at 1602 and 1556 cm\(^{-1}\), which are similar in position to the two bands observed in the IR spectrum of E (Chart S1; 1590 and 1555 cm\(^{-1}\))[2] and which may be assigned to the C=N/C=C stretching vibrations. Together, the data support the assigned structure of 9.
**General Experimental Details**

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques\(^3\) or a glove box. Acetonitrile, hexanes, and THF were purified using standard procedures.\(^4\) Propionitrile was distilled from CaH\(_2\), degassed, and stored over 4 Å molecular sieves prior to use. C\(_6\)D\(_6\) was distilled from LiAlH\(_4\), degassed, and stored over 4 Å molecular sieves prior to use. Acrylonitrile and [D\(_8\)]THF were stored over 4 Å molecular sieves. All other chemicals were purchased from commercial sources and used without further purification. Ge\(_3\)Mes\(_6\)\(^5\) and Mes\(_2\)Ge=GeMes\(_2\)\(^6\) were prepared according to literature procedures.

NMR spectra were recorded on a Varian Mercury 400, Inova 400 or 600 MHz NMR spectrometer using C\(_6\)D\(_6\) as the solvent. The NMR standards used are as follows: \(^1\)H NMR spectra were referenced to residual internal C\(_6\)D\(_5\)H (7.15 ppm); \(^1\)C\(_{\{1\}H}\) NMR spectra were referenced to the central transition of C\(_6\)D\(_6\) (128.00 ppm); \(^29\)Si NMR spectra (\(^1\)H-\(^29\)Si gHMBC) were externally referenced to SiMe\(_4\) (0 ppm). All \(^1\)H and \(^1\)C NMR signals were assigned using the appropriate combinations of gCOSY, \(^1\)C-\(^1\)H gHSQC and gHMBC NMR spectroscopy. FTIR spectra were recorded (cm\(^{-1}\)) as thin films using either a Bruker Vector 33 or Tensor 27 FTIR spectrometer. FT-Raman spectra were recorded (cm\(^{-1}\)) as powders using a Bruker RFS 100/S. ESI-TOF mass spectra were obtained on a Micromass LCT instrument. Mass spectral data are reported in mass-to-charge units, m/z, with ion identity and peak intensities (%) in parentheses. Photolyses of Ge\(_3\)Mes\(_6\) were performed in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with 350 nm lamps using Pyrex glassware. Unless otherwise noted, solutions of Ge\(_3\)Mes\(_6\) were cooled during irradiation using a Dry Ice/acetone slurry, respectively. Melting point data are uncorrected.
**Addition of CH₃CN to Digermene 4**

CH₃CN (1 mL, excess) was added to the bright yellow solution of digermene 4 (made from Ge₃Mes₆ (38 mg, 0.04 mmol) dissolved in THF (10 mL)) and the solution was stirred at room temperature overnight. The color of the solution slowly faded to pale yellow. The solvent was removed under vacuum; a pale yellow solid was obtained. ¹H NMR spectroscopic analysis of the crude product revealed the presence of 5, 6, and Mes₂Ge(H)Ge(OH)Mes₂,⁷ in a ratio of ~105:1:4, respectively. The ratio of the products did not change at room temperature under an inert atmosphere or upon exposure to trace amounts of atmospheric moisture (sample in an NMR tube sealed only with Parafilm). However, 5 and 6 decomposed upon prolonged exposure to atmospheric moisture; therefore, 5 and 6 were characterized as a mixture. Mes₂Ge(H)Ge(OH)Mes₂ was identified by comparison of the ¹H NMR spectral data to the values reported in the literature⁷ and was likely formed by the addition of adventitious water to digermene 4.

⁴Δ 2,2,3,3-Tetramesityl-4-methyl-1,2,3-azadigermetine, 5: ¹H NMR (C₆D₆, 600 MHz) δ 6.69 (s, 4H, Mes m-H), 6.66 (s, 4H, Mes m-H), 2.52 (br s, 12H, Mes o-CH₃), 2.46 (s, 3H, CH₃), 2.25 (s, 12H, Mes o-CH₃), 2.08 and 2.07 (each s, 12H total, Mes p-CH₃);¹³C{¹H} NMR (C₆D₆, 150 MHz) δ 201.86 (C=N), 143.37 (Mes o-C), 142.42 (Mes o-C), 138.75, 138.73 (Mes p-C, Mes i-C), 138.58 (Mes p-C), 138.32 (Mes i-C), 129.17 (Mes m-C x 2), 32.93 (CH₃), 24.14 (Mes o-CH₃), 24.12 (Mes o-CH₃), 20.99 (Mes p-CH₃), 20.96 (Mes p-CH₃).

2,2,3,3-Tetramesityl-4-methylidene-1,2,3-azadigermetidine, 6: ¹H NMR (C₆D₆, 600 MHz) δ 4.58 (s, 1H, NH), 4.54 (s, 1H, =CH), 4.46 (s, 1H, =CH);¹³C{¹H} NMR (C₆D₆, 600 MHz) δ 166.8 (=C-NH),⁸ 88.7 (=CH₂).⁸
**5/6:** IR (cm\(^{-1}\)) 3019 (m), 2961 (m), 2920 (s), 2863 (w), 1602 (m), 1555 (w), 1451 (s), 1408 (w), 1378 (w), 1289 (w), 1029 (w), 847 (s), 737 (w), 663 (w); ESI-TOF MS m/z 664 (M + H\(^+\), \(^{72}\)Ge\(^{74}\)Ge, 94 %), 431 (Mes\(^{74}\)Ge, 27 %), 215 (100 %), 208 (79 %); High-Resolution ESI-TOF MS for C\(_{38}\)H\(_{48}\)\(^{70}\)Ge\(_2\)N (M + H\(^+\)) (m/z) calcd 658.2272, found 658.2289.

**Addition of CH\(_3\)CH\(_2\)CN to Digermene 4**

CH\(_3\)CH\(_2\)CN (1 mL, excess) was added to the bright yellow solution of digermene 4 (made from Ge\(_3\)Mes\(_6\) (50 mg, 0.05 mmol) dissolved in THF (10 mL)) and the reaction mixture was allowed to stir at room temperature overnight. The color of the solution slowly faded to pale yellow. The solvent was then removed under vacuum; a pale yellow solid was obtained. \(^1\)H NMR spectroscopic analysis of the crude product revealed the presence of 7, 8, and Mes\(_2\)Ge(H)Ge(OH)Mes\(_2\)\[^7\] in a ratio of ~32:10:1, respectively, as well as small amounts of an unknown product. The ratio of products did not change at room temperature under an inert atmosphere. Compounds 7 and 8 slowly decomposed upon exposure to atmospheric moisture; therefore, 7 and 8 were characterized as a mixture.

\(^4\)Δ 2,2,3,3-Tetramesityl-4-ethyl-1,2,3-azadigermetine, 7: \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz) \(\delta\) 6.69 (s, 4H, Mes \(m\)-H), 6.67 (s, 4H, Mes \(m\)-H), 2.79 (q, 2H, CH\(_2\), \(J = 7.2\) Hz), 2.52 (br s, 12H, Mes \(o\)-CH\(_3\)), 2.26 (s, 12H, Mes \(o\)-CH\(_3\)), 2.074, 2.071 (both s, 12H, Mes \(p\)-CH\(_3\)), 1.21 (t, 3H, CH\(_3\), \(J = 7.2\) Hz); \(^13\)C \({}^1\)H NMR (C\(_6\)D\(_6\), 100 MHz) \(\delta\) 205.10 (C=N), 143.38 (Mes \(o\)-C), 142.42 (Mes \(o\)-C), 139.09 (Mes \(i\)-C), 138.71, 138.52 (Mes \(p\)-C),\[^9\] 138.45 (Mes \(i\)-C), 129.17 (Mes \(m\)-C), 129.16 (Mes \(m\)-C), 38.58 (CH\(_2\)), 24.19 (Mes \(o\)-CH\(_3\)), 24.14 (Mes \(o\)-CH\(_3\)), 20.99 (Mes \(p\)-CH\(_3\)), 20.96 (Mes \(p\)-CH\(_3\)), 10.12 (CH\(_3\)).

2,2,3,3-Tetramesityl-4-ethylidene-1,2,3-azadigermetidine, 8: \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz) \(\delta\) 6.67 and 6.65 (s, together 8H, Mes \(m\)-H), 4.92 (q, 1H, =CH, \(J = 7\) Hz), 4.60 (s, 1H, NH), 2.42 (s,
12H, Mes $o$-CH$_3$), 2.33 (s, 12H, Mes $o$-CH$_3$), 2.06 and 2.05 (s, together 12H, Mes $p$-CH$_3$), 1.64 (d, 3H, CH$_3$, $J = 7$ Hz); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 100 MHz) $\delta$ 158.56 (C-NH), 143.30 (Mes $o$-C), 142.68 (Mes $o$-C), 140.08 (Mes $i$-C), 138.47 (Mes $p$-C),$^{[9]}$ 138.33 (Mes $p$-C),$^{[9]}$ 137.86 (Mes $i$-C), 129.37 (Mes $m$-C), 129.21 (Mes $m$-C), 97.97 (C=CH), 24.28 (Mes $o$-CH$_3$), 23.79 (Mes $o$-CH$_3$), 20.96 (Mes $p$-CH$_3$ x 2), 10.95 (CH$_3$).

7/8: ESI-TOF MS $m/z$ 718 (M + H$_2$O + Na$^+$, $^{72}$Ge$^{74}$Ge, 28 %), 678 (M + H$^+$, $^{72}$Ge$^{74}$Ge, 100 %); High-Resolution ESI-TOF MS for C$_{39}$H$_{50}$Ge$_2$N (M + H$^+$) ($m/z$) calcd 672.2428, found 672.2458.

**Addition of CH$_2$=CHCN to Digermene 4**

Two drops of CH$_2$=CHCN (~20 mg, 0.4 mmol) were added to the bright yellow solution of digermene 4 (made from Ge$_3$Mes$_6$ (50 mg, 0.05 mmol) dissolved in THF (10 mL)). The reaction mixture was allowed to stir at room temperature for ~24 hr; the color of the solution slowly faded to light yellow. The solvent was removed under vacuum; a yellow solid was obtained. The crude solid was washed with hexanes (three aliquots of 1 mL) to give a pale yellow solid (18 mg) identified as polymeric material (likely [Mes$_2$Ge]$_n$) by $^1$H NMR spectroscopy. The solvent washes were combined and the solvent was removed under vacuum to give a yellow solid, which consisted of 9 and Mes$_2$Ge(H)Ge(OH)Mes$_2$,$^{[7]}$ in a ratio of ~7:1, respectively, as estimated by $^1$H NMR spectroscopy. The product could not be purified by chromatography; therefore, 9 was characterized as a mixture with Mes$_2$Ge(H)Ge(OH)Mes$_2$.

$^4$∆ 2,2,3,3-Tetramesityl-4-ethenyl-1,2,3-azadigermetine, 9: $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 6.84 (dd, 1H, H$_a$, $J = 17$ Hz, $J = 11$ Hz), 6.66 (s, 4H, Mes $m$-H), 6.64 (s, 4H, Mes $m$-H), 5.79 (dd, 1H, H$_c$, $J = 17$ Hz, $J = 2.0$ Hz), 5.18 (dd, 1H, H$_b$, $J = 10$ Hz, $J = 2.0$ Hz), 2.51 (s, 12H, Mes $o$-CH$_3$), 2.31 (s, 12H, Mes $o$-CH$_3$), 2.06 (s, 6H, Mes $p$-CH$_3$), 2.04 (s, 6H, Mes $p$-CH$_3$); $^{13}$C{$^1$H} NMR
(C₆D₆, 100 MHz) δ 199.84 (C=N), 143.47 (Mes o-C), 142.87 (Mes o-C), 142.21 (HCC=CH₂), 138.78 (Mes p-C), 138.75 (Mes p-C), 138.31 (Mes i-C), 138.18 (Mes i-C), 129.30 (Mes m-C), 129.19 (Mes m-C), 121.46 (HC=CH₂), 24.85 (Mes o-CH₃), 24.21 (Mes o-CH₃), 20.98 (Mes p-CH₃), 20.95 (Mes p-CH₃); IR (cm⁻¹) 3018 (w), 2958 (m), 2921 (s), 2857 (w), 1602 (m), 1556 (w, C=N), 1449 (s), 1407 (w), 1377 (w), 1290 (w), 1027 (w), 847 (s), 737 (w); ESI-TOF MS m/z 716 (M + H₂O + Na⁺, 72Ge74Ge, 67 %), 676 (M + H⁺, 72Ge74Ge, 100 %); High-Resolution ESI-TOF MS for C₃₉H₄₈⁷⁰Ge₂N (M + H⁺) (m/z) calcd 670.2272, found 670.2250.

Thermolysis of 5 in the Presence of DMB

Approximately 10 mg of a mixture consisting of 5 and trace amounts of 6 (as prepared by the method described above) was dissolved in [D₈]THF. 2,3-Dimethylbutadiene (~2 drops, excess) was then added to the solution. The clear, colorless solution was transferred to a Teflon screw-capped NMR tube (J. Young tube) and the NMR tube was then placed in an oil bath at 100 °C. The color of the solution became light yellow almost immediately and then bright yellow after 5 min of heating. The mixture was heated for an additional 13 hr; a clear, colorless solution was obtained. The ¹H NMR spectrum of the crude product revealed the presence of 1-mesityl-3,4-dimethyl-1-(trimesitylgermyl)-1-germacyclopent-3-ene (11)⁷ and 1,1-dimesityl-3,4-dimethyl-1-germacyclopent-3-ene (12)⁷ in a ratio of ~2:1, respectively and acetonitrile. Thermolysis of the 7/8 with DMB under the same conditions, also lead to the formation of 11 and 12 in a ratio of ~3:1 and proprionitrile and thermolysis of 9 with DMB under the same conditions, lead to the formation of 11 and 12 in a ratio of ~1:1 as well as acrylonitrile as determined by ¹H NMR spectroscopy.
**1H NMR Spectra of New Compounds**

![1H NMR spectrum of a mixture of 5 and 6](image)

**Figure S1.** 1H NMR spectrum (600 MHz) of a mixture of 5 and 6 (ratio 100:1) in C₆D₆. The signals assigned to 5 are labelled. The spectrum also contains traces of the water adduct. Expansion shows the diagnostic signals assigned to 6 (at increased intensity)
Figure S2. $^1$H NMR spectrum (600 MHz) of a mixture of 7 and 8 (ratio 3:1) in C$_6$D$_6$. 
Figure S3. Expansion of the $^1$H NMR spectrum (600 MHz) of a mixture of 7 and 8 (ratio 3:1) in C$_6$D$_6$ (4.4-6.8 ppm).
Figure S4. Expansion of the $^1$H NMR spectrum (600 MHz) of a mixture of 7 and 8 (ratio 3:1) in C$_6$D$_6$ (1.1-2.9 ppm).
Figure S5. $^1$H NMR spectrum (400 MHz) of 9 in C$_6$D$_6$. Traces of Mes$_2$Ge(OH)Ge(H)Mes$_2$ are indicated by an X.

References


[9] Due to overlap within the $^1$H-$^{13}$C gHMBC spectrum, the assignment is tentative.