

## Varied Reactivity of the Germene Mes<sub>2</sub>Ge=CR<sub>2</sub> toward Nitriles

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The germene Mes<sub>2</sub>Ge=CR<sub>2</sub> (**1**, CR<sub>2</sub> = fluorenylidene) shows varied behavior toward nitriles. It reacts as a 1,2-dipole with *t*-BuCN giving a four-membered ring heterocycle, 2-aza-3-germacyclobut-1-ene, as a 1,4-dipole with PhCN, leading to a six-membered ring heterocycle, 3,4-dihydro-3-germaisoquinoline, and as a base, abstracting the α-H of R'CH<sub>2</sub>CN to give α-cyanogermanes (R' = H, 2-thienyl, 2-FC<sub>6</sub>H<sub>4</sub>, 4-FC<sub>6</sub>H<sub>4</sub>).

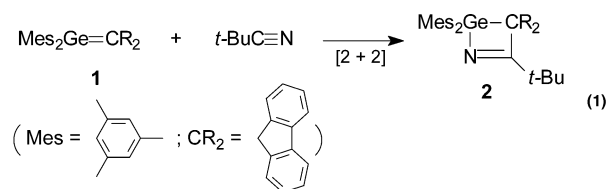
### Introduction

The synthesis of the first stable compound containing a Si=C double bond, the silene (Me<sub>3</sub>Si)<sub>2</sub>Si=C(OSiMe<sub>3</sub>)-Ad,<sup>1</sup> was a milestone in organometallic chemistry. Other silenes and some germenes >Ge=C< and stannenes >Sn=C< have been prepared since this date.<sup>2</sup> Despite the great steric hindrance necessary for their stabilization as monomers, a flourishing chemistry of these organometallic alkenes has been developed. Their reactions with various unsaturated compounds showed them to be, among others, valuable sources of metalated heterocycles difficult to obtain by other routes. To the best of our knowledge, in the case of nitriles, only the [2+4] cycloadduct of the silene Me<sub>2</sub>Si=C(SiMe<sub>3</sub>)<sub>2</sub> with PhC≡N has been reported so far,<sup>3a</sup> while Me<sub>2</sub>Si=CH<sub>2</sub>, generated by pyrolysis of the corresponding silacyclobutane, inserted into a CH bond of acetonitrile.<sup>3b</sup> Silenes (Me<sub>3</sub>Si)<sub>2</sub>Si=C(OSiMe<sub>3</sub>)R gave a [2+2] cycloadduct with the C=C bond of acrylonitrile.<sup>3c</sup> In the case of germenes, only one recent paper reported the reactions of an acetylene-bridged bis(germene) with dinitrile compounds.<sup>4</sup>

Thus, we became interested in investigating the reactivity of nitriles with the germene Mes<sub>2</sub>Ge=CR<sub>2</sub> (**1**)<sup>5</sup> (Mes = 2,4,6-trimethylphenyl, CR<sub>2</sub> = fluorenylidene), in which the Ge=C unsaturation is conjugated with the fluorenylidene unit. Interestingly, three kinds of products were obtained in this study, depending on the nitrile used.

### Results and Discussion

Germene **1** reacted at 140 °C as a 1,2-dipole with trimethylacetone nitrile, giving 2-aza-3-germacyclobut-1-ene (**2**), a four-membered ring derivative with both a heavy group 14 element and a C=N double bond<sup>6</sup> (eq 1).



The observed regioselectivity (N bonded to germanium) in this [2+2] cycloaddition between the Ge=C and C≡N unsaturation was expected from the Ge<sup>δ+</sup>=C<sup>δ-</sup> polarity of the germanium–carbon double bond. The structure of **2** was evidenced by mass spectroscopy (besides the molecular peak, the main fragment was the starting germene obtained by a [4 → 2+2] cycloreversion) and particularly by NMR spectroscopic analysis

(5) (a) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411–4412. (b) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828–829.

(6) Rather similar 1-aza-2,3-disilacyclobut-1-enes have been obtained by thermolysis or photolysis of cyclotrisilanes (R<sub>2</sub>Si)<sub>3</sub> in the presence of nitriles. Although in a formal sense they are the product of a [2+2] cycloaddition reaction between the disilene R<sub>2</sub>Si=SiR<sub>2</sub> and a nitrile, their formation is likely to proceed via initially generated azasilacyclopropenes followed by ring expansion with a second silylene R<sub>2</sub>Si: (a) Weidenbruch, M.; Meiners, F.; Saak, W. *Can. J. Chem.* **2000**, *78*, 1469–1473. (b) Belzner, J.; Ihmels, H.; Noltemeyer, M. *Tetrahedron Lett.* **1995**, *36*, 8187–8190.

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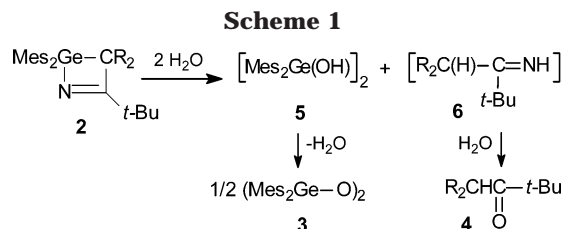
<sup>‡</sup> Université Paul Sabatier.

(1) Brook, A. G.; Abdekassen, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191–192.

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(3) (a) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518–3532. (b) Bush, R. D.; Golino, C. M.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1973**, *59*, C17–C20. (c) Brook, A. G.; Hu, S. S.; Saxena, A. K.; Lough, A. J. *Organometallics* **1991**, *10*, 2758–2767.

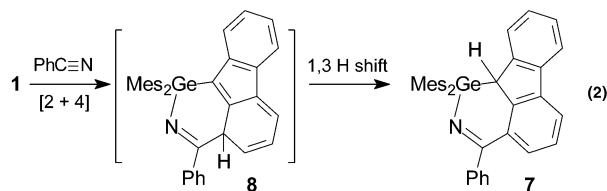
(4) Meiners, F.; Haase, D.; Koch, R.; Saak, W.; Weidenbruch, M. *Organometallics* **2002**, *21*, 3990–3995.



( $\delta^{13}C$  (C=N) = 198.41 ppm). In the  $^1H$  NMR spectrum, a very broad singlet, characteristic of a cyclic structure,<sup>7</sup> was observed for the *ortho*-methyl groups of equivalent mesityl groups due to their slow rotation caused by the large steric hindrance, which confers to **2** a surprisingly high thermal stability.

The structure of **2** was confirmed chemically by its hydrolysis, which gave a nearly quantitative yield of tetramesityldigermoxane (**3**)<sup>8</sup> and fluorenyl(*tert*-butyl)-ketone (**4**).<sup>9</sup> Their formation resulted from the initial cleavages of the Ge–C and Ge–N bonds, giving first the dihydroxygermane **5**<sup>8a,10</sup> (which slowly converts to **3**) and the transient imine **6** ( $\delta^{13}C$  NMR (C=N) = 189.1 ppm), which undergoes further hydrolysis to **4** (Scheme 1).

The behavior of **1** toward benzonitrile is completely different, giving compound **7** (eq 2). The structure of **7** was established by an X-ray diffraction (Figure 1).



The first step of the reaction probably was the formation of **8** by [2+4] cycloaddition between the C≡N moiety and the Ge=C–C=C dienic system of **1**, followed by rearomatization via a 1,3-sigmatropic shift of H, leading to 3,4-dihydro-3-germaisoquinoline (**7**). This a priori surprising diene behavior of **1** can, however, be understood both from its cisoid structure and from the conjugation of the Ge=C double bond with the fluorenylidene unit.<sup>11</sup> Usually, one of the features of Diels–Alder reactions with nitriles as dienophiles is the extremely high reaction temperature required, often above 200 °C.<sup>12</sup> Therefore, the formation of **7** in 78% yield at room temperature was rather unexpected and confirmed the high reactivity of **1**.

(7) In the four-membered ring 1-oxa-2-germacyclobutane, obtained from **1** and benzophenone, a similar very broad signal was observed for the *ortho*-methyl groups of the mesityl substituents: Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Dräger, M. *Organometallics* **1991**, *10*, 1771–1778.

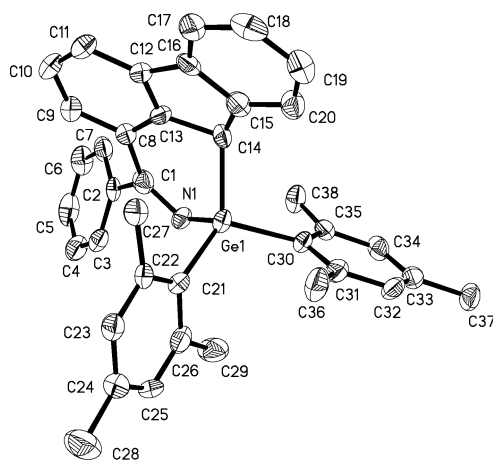
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(9)  $^1H$  NMR data were in accordance with those found in: Meyers, C. Y.; Wahner, A. P.; Manohar, S. K.; Carr, S. E.; Chan-Yu-King, R.; Robinson, P. D. *Acta Crystallogr.* **1991**, *C47*, 1236–1239.

(10) Slow decomposition of **5** to **3** was observed previously: (a) El Baz, F.; Rivière-Baudet, M.; Chazalotte, C.; Gornitzka, H. *Phosphorus, Sulfur Silicon* **2000**, *163*, 121–142. (b) Rivière-Baudet, M.; El Baz, F.; Satgé, J.; Khallaayoun, A.; Ahra, M. *Phosphorus, Sulfur Silicon* **1996**, *112*, 203–217.

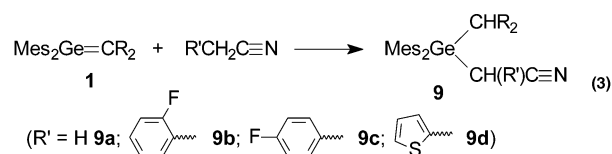
(11) The unique precedent diene behavior of **1** was postulated in its reaction with *t*-BuC≡P at 170 °C: Lazraq, M.; Escudié, J.; Couret, C.; Bergsträsser, U.; Regitz, M. *Chem. Commun.* **1993**, 569–570.

(12) Hamer, J. *1,4-Cycloaddition Reactions*; Academic Press: New York, 1967; pp 97–125.



**Figure 1.** Molecular structure of **7** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–N1, 1.855(4); C1–N1, 1.306(6); Ge1–C30, 1.979(4); Ge1–C21, 1.964(5); Ge1–C14, 1.990(5); C13–C14, 1.516(6); C8–C13, 1.395(6); C1–C8, 1.496(7); N1–Ge1–C14, 98.74(19); N1–Ge1–C21, 101.16(19); N1–Ge1–C30, 111.19(17); C21–Ge1–C30, 112.6(2); C1–N1–Ge1, 122.8(3); N1–C1–C8, 124.5(4).

In contrast, with nitriles of type  $R'CH_2C\equiv N$  with  $R'$  groups of various electronic effects, **1** preferentially reacted at the hydrogen  $\alpha$  to the C≡N bond. These reactions occurred at room temperature in Et<sub>2</sub>O solutions to afford  $\alpha$ -cyanogermenes **9a–d** in quantitative yield, regioselectively with exclusive formation of the  $Ge^{\delta+}=C^{\delta-}$  polarity (eq 3). Thus germene **1** contains a strongly basic fluorenylidene unit.



Such electrophilic addition of acidic HA compounds to the Ge=C double bond of **1** has previously been reported to occur only with the more “acidic” hydrogens of alcohols, water, thiols, and imines containing an NH bond to give  $Mes_2Ge(A)C(H)R_2$  adducts.<sup>5a,13</sup>

## Experimental Section

**General Procedures.** All manipulations were carried out under N<sub>2</sub> or Ar using standard Schlenk techniques with solvents freshly distilled from sodium benzophenone.  $^1H$  and  $^{13}C$  NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AC 250 instrument at 250.1 MHz and a Bruker Avance 300 instrument at 75.48 MHz, respectively. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope heating stage 250. IR were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed by the “Service de Microanalyse de l’Ecole de Chimie de Toulouse”.

The carbon atoms of the fluorenyl group are numbered as shown in Figure 1.

**Synthesis of 2.** Germene **1** was prepared as previously described<sup>5</sup> by addition of 1 molar equiv of *tert*-butyllithium (1.7

(13) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Soufiaoui, M. *Organometallics* **1991**, *10*, 1140–1143.

M in pentane) to a solution of the fluorogermane Mes<sub>2</sub>Ge(F)CHR<sub>2</sub> (1.00 g, 2.02 mmol) in Et<sub>2</sub>O (20 mL) cooled at -78 °C. Warming to room temperature afforded an orange solution of **1**, which is nearly quantitatively produced along with a precipitate of LiF. Crude solutions of **1** were used without further purification. The mixture of Mes<sub>2</sub>Ge=CR<sub>2</sub> and *t*-BuCN (0.17 g, 2.02 mmol) was heated in a sealed tube at 140 °C for 15 h. After filtration to remove LiF and evaporation of solvents in vacuo, crystallization from pentane at -20 °C afforded 0.54 g of **2**: white crystals; mp 228 °C; yield 48%; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.83 (s, 9H, *t*-Bu), 2.01 (br s, 12H, *o*-Me), 2.24 (s, 6H, *p*-Me), 6.75 (s, 4H, arom CH of Mes), [7.01 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 7.10 and 7.33 (2t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 × 2H), 7.85 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), H of CR<sub>2</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 20.98 (*p*-Me), 23.20 (*o*-Me), 28.68 (C(CH<sub>3</sub>)<sub>3</sub>), 42.79 (C(CH<sub>3</sub>)<sub>3</sub>), 73.77 (CR<sub>2</sub>), 120.03, 123.80, 125.89 and 126.42 (CH of CR<sub>2</sub>), 126.70 (*m*-CH of Mes), 132.90 (*ipso*-C of Mes), 138.30, 139.50, 143.39, and 144.38 (*o*- and *p*-C of Mes, quat. C of CR<sub>2</sub>), 198.41 (C=N); IR (KBr) 1542.0 cm<sup>-1</sup> (νC=N); MS, *m/z* (%) 559 (M, 4), 502 (M - *t*-Bu, 2), 476 (Mes<sub>2</sub>Ge=CR<sub>2</sub>, 42), 440 (M - Mes, 2), 311 (Mes<sub>2</sub>Ge - 1, 100), 192 (MesGe - 1, 38). Anal. Calcd for C<sub>36</sub>H<sub>39</sub>GeN: C, 77.45; H, 7.04. Found: C, 77.21; H, 7.25.

**Hydrolysis of 2.** Compound **2** slowly hydrolyzed when left in wet CDCl<sub>3</sub> solution at room temperature. After 3 days, the NMR signals of **2** disappeared and new signals assigned to dihydroxygermane **5** and imine **6** were observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra.

**5:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.84 (s, 2H, OH), 2.28 (s, 6H, *p*-Me), 2.45 (s, 12H, *o*-Me), 6.83 (s, 4H, arom. H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 21.12 (*p*-Me), 23.14 (*o*-Me), 129.32 (*m*-C), 133.20 (*ipso*-C), 140.08 (*p*-C), 143.10 (*o*-C).

**6:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.49 (s, 9H, *t*-Bu), 5.09 (s, 1H, CHR<sub>2</sub>), [7.26 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 7.35 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 7.38 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 7.78 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), CR<sub>2</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 27.98 (C(CH<sub>3</sub>)<sub>3</sub>), 40.78 (C(CH<sub>3</sub>)<sub>3</sub>), 52.78 (CR<sub>2</sub>), 120.08, 124.34, 127.53 and 127.71 (CH of CR<sub>2</sub>), 140.10 and 142.00 (quat. C of CR<sub>2</sub>), 189.08 (C=N).

**5** and **6** were not isolated. After 2 weeks, NMR analysis of this solution showed the nearly quantitative formation of **3**<sup>8</sup> and **4**.

**3:** <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 21.12 (*p*-Me), 23.14 (*o*-Me), 129.32 (*m*-C of Mes), 133.20 (*ipso*-C), 140.08 (*p*-C of Mes), 143.10 (*o*-C of Mes).

**4** was also identified by an independent synthesis.<sup>9</sup> <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 26.57 (CMe<sub>3</sub>), 45.64 (CMe<sub>3</sub>), 57.11 (HCR<sub>2</sub>), 120.36, 124.43, 127.32 and 127.81 (CH of CR<sub>2</sub>), 142.38 and 143.60 (quat. C of CR<sub>2</sub>), 213.18 (CO); MS (EI, *m/z*, %) 250 (M, 10), 192 (M - *t*-Bu - 1, 3), 165 (R<sub>2</sub>CH, 30), 57 (*t*-Bu, 100).

**Synthesis of 7.** One equivalent of PhCN (0.21 g, 2.02 mmol) was added to a solution of **1**, prepared as previously described,<sup>5</sup> cooled at -78 °C. The reaction mixture gradually turned from orange to light yellow after overnight stirring at room temperature. LiF was then filtered, and the solvents were removed in vacuo. Recrystallization of the crude material from pentane at -20 °C afforded white crystals of **7** (0.91 g, yield 78%, mp 200–201 °C): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.85 (s, 3H, *p*-Me), 1.97 (br s, 6H, *o*-Me), 2.15 (s, 3H, *p*-Me), 2.52 (s, 6H, *o*-Me), 4.55 (s, 1H, CH-Ge), 6.43 and 6.81 (2s, 2 × 2H, arom H of Mes), 7.10–7.29 (m, 7H, *m*- and *p*-H of C<sub>6</sub>H<sub>5</sub> and 4H of CR<sub>2</sub>), 7.51, 7.71, and 7.81 (3d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 3 × 1H, 3H of CR<sub>2</sub>), 7.88–7.92 (m, 2H, *o*-H of C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 20.42 and 20.75 (*p*-Me), 22.80 and 24.68 (*o*-Me), 41.25 (CHR<sub>2</sub>), 120.43, 121.20, 124.44, 125.95, 126.37, 126.90, 127.36 (CH of CR<sub>2</sub>), 127.68, 128.00, 128.52, and 129.08 (*m*-CH of Mes, *o*- and *m*-CH of Ph), 129.16 (*p*-CH of Ph), 129.81, 135.47, 136.05, 138.55, 138.75, 141.15, 141.20, 141.96, 142.25, 143.25, 143.99, and 145.47 (*ipso*-C of Ph, *ipso*-, *o*-, and *p*-C of Mes, C<sub>12,13,15,16</sub>), 171.35 (C=N); IR (KBr) 1556 cm<sup>-1</sup> (νC=N); MS, *m/z* (%) 579 (M, 9), 564 (M - Me, 3), 460 (M - Mes, 3), 341 (M - 2Mes, 10), 311 (Mes<sub>2</sub>Ge - 1, 100), 267 (M - Mes<sub>2</sub>Ge, 18), 190 (M - Mes<sub>2</sub>Ge

- Ph, 17). Anal. Calcd for C<sub>38</sub>H<sub>35</sub>GeN: C, 78.93; H, 6.10. Found: C, 78.75; H, 6.05.

**Crystal data for 7:** C<sub>38</sub>H<sub>35</sub>GeN, *M* = 578.26, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.701(3) Å, *b* = 15.722(4) Å, *c* = 16.171(4) Å, β = 91.083(4)°, *V* = 2974.3(12) Å<sup>3</sup>, *Z* = 4, *T* = 193(2) K. 11 756 reflections (4208 independent, *R*<sub>int</sub> = 0.1054) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97),<sup>14</sup> and all non hydrogen atoms were refined anisotropically using the least-squares method on *F*<sup>2</sup>.<sup>15</sup> Largest electron density residue: 0.683 e Å<sup>-3</sup>, *R*<sub>1</sub> (for *I* > 2σ(*I*)) = 0.0488 and *wR*<sub>2</sub> = 0.0972 (all data) with *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>| and *wR*<sub>2</sub> = (Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)/Σ*w*(*F*<sub>o</sub><sup>2</sup>))<sup>0.5</sup>.

**Reaction of Mes<sub>2</sub>Ge=CR<sub>2</sub> with Nitriles R'CH<sub>2</sub>C≡N: Formation of α-Cyanogermanes 9.** To a crude solution of **1** prepared as previously described<sup>5</sup> from 1.00 g (2.02 mmol) of Mes<sub>2</sub>Ge(F)CHR<sub>2</sub> in Et<sub>2</sub>O (20 mL) cooled at -78 °C was added 1 equiv of the nitrile R'CH<sub>2</sub>-C≡N. The reaction mixture was allowed to warm to room temperature, during which time it slowly turned from orange to pale yellow. After overnight stirring, solvent was removed in vacuo and replaced by 15 mL of pentane. Crystallization at -20 °C afforded pure **9a–d** as crystalline compounds.

**9a:** white crystals; 0.96 g, yield 92%; mp 142–143 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.64 (s, 3H, CH<sub>2</sub>), 2.11 (s, 12H, *o*-Me), 2.27 (s, 6H, *p*-Me), 5.10 (s, 1H, CHR<sub>2</sub>), 6.81 (s, 4H, arom H of Mes), [7.15 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), 7.18 and 7.35 (2t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 × 2H), 7.83 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H), CR<sub>2</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 6.19 (CH<sub>2</sub>), 20.92 (*p*-Me), 24.20 (*o*-Me), 43.81 (CHR<sub>2</sub>), 119.43 (C≡N), 119.76, 125.12, 126.38, and 126.68 (CH of CR<sub>2</sub>), 129.69 (*m*-CH of Mes), 133.35, 139.13, 140.74, 142.64, and 143.55 (*ipso*-, *o*- and *p*-C of Mes and quat. C of CR<sub>2</sub>); IR (KBr) 2232 cm<sup>-1</sup> (νC≡N); MS, *m/z* (%) 517 (M, 1), 477 (M - CH<sub>2</sub>CN, 3), 352 (M - CHR<sub>2</sub>, 85), 311 (Mes<sub>2</sub>Ge - 1, 15), 192 (MesGe - 1, 20), 165 (CHR<sub>2</sub>, 100). Anal. Calcd for C<sub>33</sub>H<sub>33</sub>GeN: C, 76.78; H, 6.44. Found: C, 77.02; H, 6.55.

**9b:** white crystals; 1.01 g, yield 82%; mp 145 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.69 and 2.03 (2s, 2 × 6H, *o*-Me), 2.10 and 2.24 (2s, 2 × 3H, *p*-Me), 4.96 (s, 1H, CH-C≡N), 5.11 (s, 1H, CHR<sub>2</sub>), 6.39 and 6.68 (2s, 2 × 2H, arom H of Mes), 6.69–8.15 (m, 12H, arom H of C<sub>6</sub>H<sub>4</sub>F and CR<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 20.71 and 20.86 (*p*-Me), 23.57 (d, <sup>3</sup>J<sub>CF</sub> = 1.1 Hz, CHC≡N), 24.38 and 24.90 (*o*-Me), 46.67 (d, <sup>5</sup>J<sub>CF</sub> = 1.5 Hz, CHR<sub>2</sub>), 114.90 (d, <sup>2</sup>J<sub>CF</sub> = 21.9 Hz, CH-CF), 119.75 and 119.76 (CH of CR<sub>2</sub>), 121.96 (d, <sup>2</sup>J<sub>CF</sub> = 15.1 Hz, *ipso*-C of C<sub>6</sub>H<sub>4</sub>F), 122.26 (C≡N), 124.27 (d, *J*<sub>CF</sub> = 3.3 Hz, CH of C<sub>6</sub>H<sub>4</sub>F), 124.68, 124.81, 124.94, 126.04, 126.21, 126.36, 128.65, and 129.48 (*m*-CH of Mes and CH of CR<sub>2</sub>), 128.39 (d, *J*<sub>CF</sub> = 8.3 Hz, CH of C<sub>6</sub>H<sub>4</sub>F), 131.00 (d, *J*<sub>CF</sub> = 3.5 Hz, CH of C<sub>6</sub>H<sub>4</sub>F), 130.92, 132.81, 138.16, 138.71, 141.29, 141.58, 142.78, 143.42, 143.69, and 144.43 (*ipso*-, *o*-, and *p*-C of Mes and quat. C of CR<sub>2</sub>), 159.67 (d, <sup>1</sup>J<sub>CF</sub> = 244.5 Hz, CF); <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ -39.0; MS, *m/z* (%) 477 (Mes<sub>2</sub>GeCHR<sub>2</sub>, 2), 446 (M - CHR<sub>2</sub>, 4), 312 (Mes<sub>2</sub>Ge, 10), 192 (MesGe - 1, 41), 165 (CHR<sub>2</sub>, 100). Anal. Calcd for C<sub>39</sub>H<sub>36</sub>FGeN: C, 76.75; H, 5.95. Found: C, 76.51; H, 6.05.

**9c:** white crystals; 1.06 g, yield 86%; mp 248 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.78 and 1.85 (2s, 2 × 6H, *o*-Me), 2.15 and 2.20 (2s, 2 × 3H, *p*-Me), 4.70 (s, 1H, CH-C≡N), 5.18 (s, 1H, CHR<sub>2</sub>), 6.48 and 6.60 (2s, 2 × 2H, arom H of Mes), 6.82–8.01 (m, 12H, arom H of C<sub>6</sub>H<sub>4</sub>F and CR<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 20.78 and 20.82 (*p*-Me), 24.79 and 24.98 (*o*-Me), 29.2 (CHC≡N), 45.84 (CHR<sub>2</sub>), 115.36 (d, <sup>2</sup>J<sub>CF</sub> = 21.1 Hz, *m*-CH of C<sub>6</sub>H<sub>4</sub>F), 119.97 and 120.00 (CH of CR<sub>2</sub>), 122.66 (C≡N), 124.32, 124.82, 125.84, 125.91, 126.18, 129.01, 129.37, 129.69, and 129.79 (*m*-CH of Mes, CH of CR<sub>2</sub>, *o*-CH of C<sub>6</sub>H<sub>4</sub>F), 130.03, 131.40, 131.80, 138.54, 138.72, 141.45, 142.98, 143.23, 143.91, and 144.15 (*ipso*-, *o*-, and *p*-C

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of Mes, quat. C of  $CR_2$ , *ipso*-C of  $C_6H_4F$ , 161.78 (d,  $^1J_{CF} = 246.0$  Hz, CF);  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$  -39.9; MS,  $m/z$  (%) 477 ( $Mes_2GeCHR_2$ , 19), 446 ( $M - CHR_2$ , 45), 312 ( $Mes_2Ge$ , 14), 192 ( $MesGe - 1$ , 48), 165 ( $CHR_2$ , 100). Anal. Calcd for  $C_{39}H_{36}FGeN$ : C, 76.75; H, 5.95. Found: C, 77.01; H, 5.80.

**9d**: light pink crystals; 0.95 g, yield 79%; mp 255 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.76 and 1.96 (2s,  $2 \times 6H$ , *o*-Me), 2.14 and 2.21 (2s,  $2 \times 3H$ , *p*-Me), 4.91 (s, 1H,  $CHR_2$ ), 5.31 (s, 1H,  $CH-C\equiv N$ ), 6.46 and 6.64 (2s,  $2 \times 2H$ , arom H of Mes), 6.50–8.01 (m, 11H, arom H of thienyl and  $CR_2$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  20.85 ( $CHC\equiv N$ ), 20.94 and 24.47 (*p*-Me), 25.06 and 25.32 (*o*-Me), 46.19 ( $CHR_2$ ), 97.54 ( $C\equiv N$ ), 119.94 and 120.23 (CH of  $CR_2$ ), 121.83 (CSCH) 123.95, 124.45, 124.77, 126.04, 126.12, 126.41, 127.25, and 127.64 (CH of  $CR_2$  and thienyl), 129.01 and 129.50 (*m*-CH of Mes), 131.11, 135.02, 138.47, 138.74, 141.40, 143.13,

143.55, 143.96, and 144.31 (quat. C of  $CR_2$ , *ipso*-, *o*- and *p*-C of Mes); IR (KBr)  $2222.7\text{ cm}^{-1}$  ( $\nu_{C\equiv N}$ ); MS,  $m/z$  (%) 477 ( $Mes_2GeCHR_2$ , 30), 434 ( $M - CHR_2$ , 22), 311 ( $Mes_2Ge - 1$ , 23), 192 ( $MesGe - 1$ , 41), 165 ( $CHR_2$ , 100). Anal. Calcd for  $C_{37}H_{35}GeNS$ : C, 74.27; H, 5.90. Found: C, 74.50; H, 6.02.

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**Supporting Information Available:** Table of bond lengths and bond angles for **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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