Novel Stable Germanimines: Synthesis and Characterization of Dimesitylgermanimine Derivatives of Methyl Anthranilate and *N,N*-Dimethylanthranilamide

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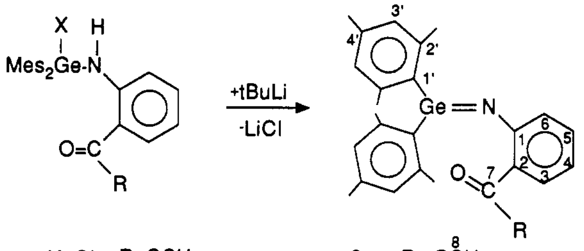
*Summary: The title compounds (**2a** and **2b**) are novel, thermally stable germanimines formed by dehydrohalogenation of the corresponding precursor halogermylamines with tert-butyllithium; each undergoes protic dipolar addition and 1,3-cycloaddition reactions, characteristic of germanium–nitrogen double bonds.*

Ever since the first reports[1,2] of transient intermediates having germanium doubly bonded to nitrogen, the isolation and structure determination of stable crystalline germanimines have been of particular interest. Among the dozen stable germanimines reported to date,[3] only three have been characterized by X-ray diffraction. Each was prepared by the reaction between an azide and a germylene: specifically, a bulky azide with either poly(cycloazasilagermylene)[4] or a sterically hindered diazagermylene.[5] In our own search for a convenient and general synthesis of germanimines, we have explored the dehydrohalogenation reaction of halogermyl secondary amines. Although dehydrohalogenation has proved to be an effective route to doubly bonded germanium species such as germaphosphenes and germenes,[6,7] preliminary attempts to obtain a stable germanimine in this way failed because the reactivity of the halogermylamine precursor decreases as internal steric hindrance increases.[8] To overcome this difficulty, we have recently prepared a series of precursors,[9,10] including **1a**, each having a germanium–halogen bond whose reactivity is enhanced by the electron-withdrawing effect of the substituent on the nitrogen and/or by nucleophilic assistance on germanium. We now report the synthesis and physicochemical data characterizing the title dimesitylgermanimines of methyl anthranilate (Mes$_2$Ge=NAE; **2a**) and *N,N*-dimethylanthranilamide (Mes$_2$Ge=NAA; **2b**) and the new precursor **1b**. Preliminary results on the chemical behavior of these new stable germanimines are also included.

Scheme I



1a X=Cl R=OCH$_3$

1b X=F R=N(CH$_3$)$_2$

2a R= O$\overset{8}{C}$H$_3$

2b R= N($\overset{9}{C}$H$_3$)$_2$

Compounds **2a**[11] and **2b**[13] were prepared by treatment of **1a**[10] and **1b**[12] with tBuLi (Scheme I). The lower yield obtained for **2a** compared with **2b** is due to the well-known secondary reactions of tBuLi with the ester carbonyl

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(11) Synthesis of **2a**. With the rigorous exclusion of moisture, to a solution of **1a**[10] (2.400 g, 4.84 × 10^{-3} mol) in THF (8 mL) at −78 °C was added an equimolar amount of *tert*-butyllithium (1.7 M in pentane). After the mixture had been kept between −78 and −20 °C for 3 h and the solvents were replaced by C_6H_6, LiCl was removed by centrifugation, at which stage the solution was deep red; the resulting crystals of **2a** (0.38 g, 17% yield) were yellow, however, once recrystallized from Et_2O at −30 °C: mp 201 °C. IR (Nujol): 1738 (ν(CO)) cm^{-1}. UV (cyclo-C_6H_{12}): 261 (58 860, 282 (34 385), 343 (23 831), 391 (11 715) nm. ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.13 (s, 6H, *p*-Me), 2.29 (s, 12H, *o*-Me), 6.55 (s, 4H, C_6H_2), 3.65 (s, 3 H, OMe), 7.45 (m, 1 H, H_3), 6.68 (s, 2H, H_4, H_5), 6.65 (s, 1 H, H_6). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 134.32 ($C_{1'}$), 142.94 ($C_{2'}$), 128.60 ($C_{3'}$), 137.93 ($C_{4'}$), 23.93 (*o*-Me), 20.91 (*p*-Me), 151.07 (C_1), 126.28 (C_2), 129.24 (C_3), 131.39 (C_5), 120.40 (C_6), 169.03 (C_7), 51.59 (C_8). MS (DCI, CH_4): *m/z* 462 (M + 1, 100). MS (EI, 70 eV): *m/z* 461 (M^+, 30), 446 (M^+ − Me, 17), 430 (M^+ − OMe, 4), 402 (M^+ − COOMe, 1). Anal. Calcd for $C_{26}H_{29}NGeO_2$: C, 67.87; H, 6.35; N, 3.04. Found: C, 67.66; H, 6.59; N, 2.80.

(12) Synthesis of **1b**. AANHLi (2.15 × 10^{-3} mol) (prepared from $AANH_2$[26] (0.354 g, 2.15 × 10^{-3} mol) and tBuLi (2.15 × 10^{-3} mol)) was added dropwise to a solution of Mes_2GeF_2 (0.75 g, 2.15 × 10^{-3} mol) in C_6H_6 (6 mL). After removal of LiF by centrifugation and evaporation of solvents in vacuo, the residue was dissolved in pentane (at 30 °C) and then evaporated, leaving **1b** as an amorphous white powder (0.949 g, 90% yield): mp 136 °C after reprecipitation from pentane. IR ($CDCl_3$): 1621 (ν(C=O)), 3365 (ν(NH)). ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.27 (s, 6H, *p*-Me), 2.40 (d, 12H, *o*-Me, J_{HF} = 1.3 Hz), 6.84 (s, 4H, C_6H_2), 3.02 (s, 6H, NMe_2), 5.56 (d, 1 H, NH,^{3} J_{HF} = 4.5 Hz), 6.57–7.15 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 130.33 ($C_{1'}$), 143.71 ($C_{2'}$), 129.53 ($C_{3'}$), 140.74 ($C_{4'}$), 22.77 (*o*-Me), 21.14 (*p*-Me), 146.28 (C_1), 121.80 (C_2), 128.21 (C_3), 117.36 (C_4, C_6), 130.74 (C_5), 37 (broad, C_9), 171.45 (C_7). ^{19}F NMR (CF_3COOH, 75 MHz): δ −82.33 (s, ^{1}H decoupled). MS (EI, 70 eV): *m/z* 494 (M^+, 6); 475 (M^+ − F, 3), 450 (M^+ − NMe_2, 6), 375 (M^+ − Mes, 39). Anal. Calcd for $C_{27}H_{33}GeN_2OF$: C, 65.76; H, 6.74; N, 5.68. Found: C, 65.72; H, 6.85; N, 5.64.

(13) Synthesis of **2b**: Experimental conditions were identical with those used to prepare **2a**. **2b** was a white precipitate (2 g, 85% yield) in THF when the reaction mixture (**1b**, 5 × 10^{-3} mol, and tBuLi, 5 × 10^{-3} mol) was brought to room temperature: mp 194–200 °C dec. IR ($CDCl_3$): 1634 cm^{-1} (ν(C=O)). ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.15 (s, 6H, *p*-Me), 2.25 (s, broad, 12H, *o*-Me), 2.67 (s, 3H, NMe), 2.77 (s, 3H, NMe), 6.57 (s, 4H, C_6H_2), 6.69–7.00 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 132.33 ($C_{1'}$), 142.98 ($C_{2'}$), 128.72 ($C_{3'}$), 137.79 ($C_{4'}$), 20.89 (*o*-Me), 24.40 (*p*-Me), 148.88 (C_1), 131.58 (C_2), 127.43 (C_3, C_4), 127.85 (C_5), 120.50 (C_6), 170.53 (C_7), 39.16, 34.34 (C_9); MS (DCI, CH_4): *m/z* 475 (M^+ + 1, 15). MS (EI, 70 eV): *m/z* 459 (M^+ − Me, 3), 430 (M^+ − NMe_2, 1), 355 (M^+ − Mes, 3). Anal. Calcd for $C_{27}H_{32}N_2GeO$: C, 68.54; H, 6.81; N, 5.92. Found: C, 68.55; H, 6.89; N, 5.80.

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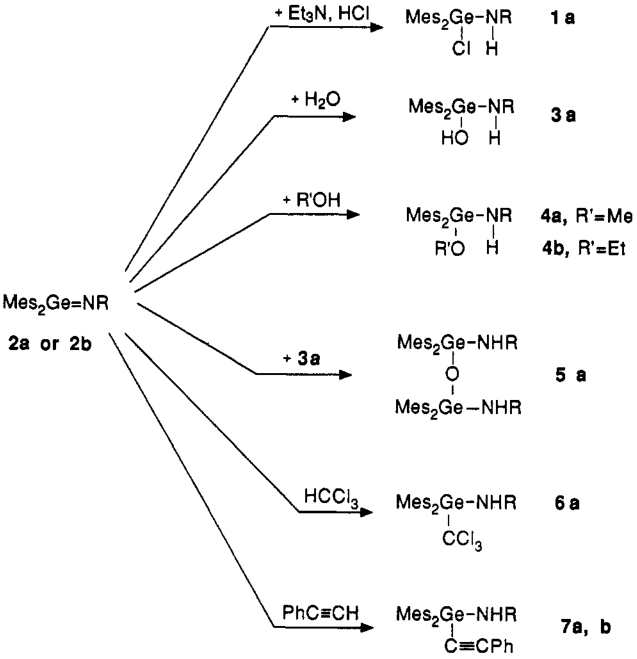
group.[14] Both **2a** and **2b** are very stable thermally (up to 190 °C for **2b**), provided moisture is excluded. The purities of **2a** and **2b** were confirmed by elemental and spectroscopic analyses. Parent molecular ions are present in mass spectra, which also show the absence of polygermylated fragments that would be expected if oligomerization had occurred.

Scheme II[a]



[a] Legend: **a**, R = C_6H_4COOMe; **b**, R = $C_6H_4CONMe_2$.

The reactivities of **2a** and **2b** were examined in protic dipolar addition reactions, which yielded the expected[14] compounds **1**,[15] **3**,[16] and **4**[17] (Scheme II). New addition reactions across the germanium–nitrogen double bond gave the new adducts **5**,[16] **6**,[18] and **7**,[19] which have interesting

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[15] $Et_3N{\cdot}HCl$ (0.006 g, 0.04 × 10^{-3} mol) dissolved in $CDCl_3$ was slowly added to **2a** (0.020 g, 0.04 × 10^{-3} mol). After 45 min at 40 °C, NMR analysis confirmed the formation of **1a**[10] while the germanimine had completely disappeared.

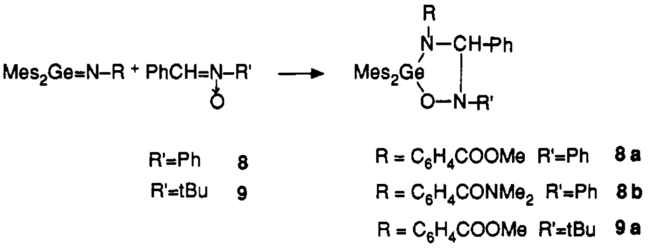
[16] Synthesis of **3a** and **5a**. Aqueous $CDCl_3$ was added gradually to **2a** (0.073 g, 0.16 × 10^{-3} mol) dissolved in 2 mL of $CDCl_3$, and the mixture was heated to 50 °C. After 15 min there were 19% of **3a** and 81% of **2a**. After 90 min, addition of **3a** to **2a** gave **5a** (72%) and 28% of **3a** remained. After 2 h and evaporation of solvents, a residue of pure **5a** remained which was recrystallized from pentane (0.10 g, 67% yield): mp 185 °C. IR ($CDCl_3$): 3357 (ν(NH)), 1689 (ν(C=O)), 789 cm^{-1}. (ν(GeOGe)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.30 (s, 12H, *o*-Me), 2.16 (s, 6H, *p*-Me), 6.59 (s, 4H, C_6H_2), 3.77 (s, 3H, OMe), 8.10 (s, 1H, NH); C_6H_4, 7.37 (ddd, 1 H, H_3), 6.37 (ddd, 1H, H_4), 6.68–6.77 (m, 2H, H_5, H_6) (*J*(3–4) = 8 Hz, *J*(3–6) = 0.5 Hz, *J*(4–6) = 2.3 Hz, *J*(3–5) = 1.4 Hz; *J*(4–5) = 6 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 134.34 ($C_{1'}$), 142.95 ($C_{2'}$), 129.26 ($C_{3'}$), 138.84 ($C_{4'}$), 23.13 (*o*-Me), 20.97 (*p*-Me), 152.07 (C_1), 112.55 (C_2), 130.90 (C_3), 118.64 (C_4), 132.55 (C_5), 115.19 (C_6), 168.64 (C_7), 51.31 (C_8). MS (DCl, CH_4): *m/z* 967 (M^+ + 29, 1), 939 (M^+ + 1, 20), 937 (M^+ −1, 19). MS (EI, 70 eV): *m/z* 788 (M^+ − NHAE, 9). Anal. Calcd for $C_{52}H_{60}Ge_2N_2O_5$: C, 66.57; H, 644; N, 2.98. Found: C, 66.84; H, 6.49; N, 2.87. Compound **3a** was identified by comparison with an authentic sample prepared by hydrolysis of $Mes_2Ge(NMe_2)NHAE$ as follows: to **1a** (0.400 g, 0.8 × 10^{-3} mol) dissolved in benzene (8 mL) was added Et_3GeNMe_2 (0.160 g, 0.80 × 10^{-3} mol), and the mixture was heated for 18 h at 50 °C in a sealed tube. After Et_3GeCl and C_6H_6 were pumped away, pure $Mes_2Ge(NMe_2)NHAE$ remained as a viscous liquid (0.387 g, 96% yield). IR ($CDCl_3$): 3324 (ν(NH)), 1679 (ν(C=O)), 1219 cm^{-} (ν(COC)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.23 (s, 6H, *p*-Me), 2.38 (s, 12H, *o*-Me), 6.80 (s, 4H, C_6H_2), 2.54 (s, 6H, NMe_2), 3.79 (s, 3H, OMe), 7.83 (s, 1H, NH); C_6H_4, 7.86 (ddd, 1H, H_3), 6.51 (ddd, 1 H, H_4), 7.12 (ddd, 1H, H_5), 6.59 (ddd, 1 H, H_6) (*J*(3–4) = 8 Hz, *J*(3–6) = 0.5 Hz, *J*(4–6) = 1.2 Hz, *J*(3–5) = 1.8 Hz, *J*(4–5) = 6.8 Hz, *J*(5–6) = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 133.66 ($C_{1'}$), 143.29 ($C_{2'}$), 129.48 ($C_{3'}$), 138.92 ($C_{4'}$), 22.44 (*o*-Me), 21.01 (*p*-Me), 39.67 (NMe_2), 153.60 (C_1), 112.32 (C_2), 131.38 (C_3), 118.30 (C_4), 133.51 (C_5), 114.88 (C_6), 169.20 (C_7), 51.40 (C_8). MS (EI, 70 eV): *m/z* 507 (M^+ + 1, 1), 491 (M^+ − Me, 67), 355 (M^+ − $AENH_2$, 17). $Mes_2Ge(NMe_2)$ NHAE (0.700 g, 1.38 × 10^{-3} mol) in benzene (5 mL) was exposed to moist air until white needles of **3a** appeared. Evaporation of benzene left **3a**, which was reprecipitated in pentane (0.25 g, 38% yield): mp 82 °C. IR ($CDCl_3$): 3316 (ν(NH)), 3632 (ν(OH)), 1682 cm^{-1} (ν(C=O)). ^1H NMR ($CDCl_3$, 80 MHz: δ 2.43 (s, 12H, *o*-Me), 2.26 (s, 6H, *p*-Me), 6.84 (s, 4H, C_6H_2), 2.61 (s, 1H, OH), 3.81 (s, 3H, OMe), 8.01 (s, 1H, NH), 7.90 (ddd, 1H, H_3), 6.59 (ddd, 1H, H_4), 7.17 (ddd, 1H, H_5), 6.99 (ddd, 1H, H_6) (*J*(3–4) = 8 Hz, *J*(3–6) = 0.6 Hz, *J*(4–6) = 1.7 Hz, *J*(4–5) = 6.5 Hz, *J*(5–6) = 8.4 Hz, *J*(3–5) = 1.7 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 132.71 ($C_{1'}$), 143.34 ($C_{2'}$), 129.63 ($C_{3'}$), 140.01 ($C_{4'}$), 23.08 (*o*-Me), 21.10 (*p*-Me), 152.61 (C_1), 112.75 (C_2), 131.64 (C_3), 117.80 (C_4), 134.15 (C_5), 116.08 (C_6), 169.21 (C_7), 51.51 (C_8). MS (EI, 70 eV): *m/z* 479 (M^+, 9), 462 (M^+ − OH, 4), 447 (M^+ − MeOH, 3), 360 (M^+ − Mes, 7), 329 (M^+ − NHAE, 38). Anal. Calcd for $C_{26}H_{31}NGeO_3$: C, 65.31; H, 6.53; N, 2.93. Found: C, 65.44; H, 6.62; N, 3.03.

[17] Synthesis of **4a**. To **2a** (0.150 g, 0.32 × 10^{-3} mol) dissolved in 2 mL of C_6H_6 was added 1 mL of a solution of CH_3OH (10 g L^{-1}) in C_6H_6 (0.32 mol), and the mixture was agitated for 1 h at 50 °C. After the solvents were evaporated, the viscous residue was identified as **4a** (0.16 g, 99% yield). IR ($CDCl_3$): 3319 (ν(NH)), 1681 (ν(C=O)), 1221 cm^{-1} (ν(COC)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.48 (s, 12H, *o*-Me), 2.25 (s, 6H, *p*-Me), 6.83 (s, 4H, C_6H_2), 3.54 (s, 3H, GeOMe), 3.84 (s, 3H, COOMe), 8.23 (s, 1H, NH), 7.87 (ddd, 1H, H_3), 6.55 (ddd, 1H, H_4), 7.14 (ddd, 1H, H_5), 6.94 (ddd, 1H, H_6) (*J*(3–4) = 8 Hz, *J*(3–6) = 0.5 Hz, *J*(4–6) = 1.7 Hz, *J*(4–5) = 6.5 Hz; *J*(5–6) = 8.5 Hz, *J*(3–5) = 1.7 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 131.77 ($C_{1'}$), 143.49 ($C_{2'}$), 129.57 ($C_{3'}$), 139.76 ($C_{4'}$), 23.15 (*o*-Me), 21.07 (*p*-Me), 51.67 (GeOMe), 153.01 (C_1), 112.59 (C_2), 131.41 (C_3), 115.96 (C_4), 133.96 (C_5), 117.97 (C_6), 169.31 (C_7), 51.50 (C_8). MS (EI, 70 eV): *m/z* 493 (M^+, 10), 374 (M^+ − Mes, 5), 342 (M^+ − $AENH_2$, 64). To **2b** (0.302 g, 0.64 × 10^{-3} mol) was added a solution of ethanol (0.029 g, 0.64 × 10^{-3} mol) in 2 mL of chloroform. After evaporation of the solvents, the residual white powder was washed with pentane, dried, and identified as **4b** (0.29 g, 88% yield): mp 172 °C. IR ($CDCl_3$): 3384 (ν(NH)), 1619 cm^{-1} (ν(C=O)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.46 (s, 12H, *o*-Me), 2.23 (s, 6H, *p*-Me), 6.79 (s, 4H, C_6H_2), 3.73 (q, 2H, CH_2), 1.17 (t, 3H, CH_3, *J*(CH_2CH_3) = 7 Hz), 5.62 (s, 1H, NH), 2.99 (s, 6H, NMe_2), 6.50–7.00 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 132.04 ($C_{1'}$), 143.41 ($C_{2'}$), 129.53 ($C_{3'}$), 139.55 ($C_{4'}$), 21.08 (*p*-Me), 23.21 (*o*-Me), 147.15 (C_1), 122.56 (C_2), 127.75 (C_3), 117.97 (C_4), 130.15 (C_5), 116.64 (C_6), 171.83 (C_7), 19.03 (CH_3), 59.43 (CH_2). MS (EI, 70 eV): *m/z* 520 (M^+, 12), 475 (M^+ − OEt, 25), 357 (M^+ − NHAA, 58). Anal. Calcd for $C_{29}H_{38}GeN_2O_2$: C, 67.08; H, 7.37; N, 5.39. Found: C, 66.87; H, 7.42; N, 5.30.

[18] Synthesis of **6a**. In a sealed tube, **2a** (0.15 g, 0.32 × 10^{-3} mol) was dissolved in 1 mL of $CHCl_3$ and the mixture was heated for 4 h at 50 °C, resulting in **6a** (0.16 g, 90% yield) as a viscous liquid. IR ($CDCl_3$): 3341 (ν(NH)), 1689 (ν(C=O)), 1227 cm^{-1} (ν(COC)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.49 (s, 12H, *o*-Me), 2.25 (s, 6H, *p*-Me), 6.83 (s, 4H, C_6H_2), 8.08 (s, 1H, NH), 3.87 (s, 3H, OCH_3), 7.85 (ddd, 1H, H_3), 6.51 (ddd, 1H, H_4), 6.89 (ddd, 1H, H_5), 6.60 (ddd, 1H, H_6) (*J*(3–4) = 7.6 Hz, *J*(3–6) = 0.8 Hz, *J*(4–6) = 1.6 Hz, *J*(3–5) = 1.8 Hz, *J*(4–5) = 6.7 Hz, *J*(5–6) = 8.5 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 134.07 ($C_{1'}$), 142.90 ($C_{2'}$), 129.98 ($C_{3'}$), 140.01 ($C_{4'}$), 21.00 (*p*-Me), 24.70 (*o*-Me), 77.63 (CCl_3), 154.76 (C_1), 131.40 (C_3), 117.95 (C_4), 133.25 (C_5), 116.35 (C_6), 51.66 (OCH_3), 172.55 (C_7). MS (DCI, CH_4): *m/z* 580 (M^+, 13), 462 (M^+ − CCl_3, 19), 608 (M^+ + 29, 3). MS (EI, 70 eV): *m/z* 497 (M^+ − CCl_2, 7), 461 (M^+ − $CHCl_3$, 5).

[19] Synthesis of **7a**. In a sealed tube, **2a** (0.120 g, 0.26 × 10^{-3} mol) and $PhC{\equiv}CH$ (0.026 g, 0.26 × 10^{-3} mol) dissolved in 1 mL of C_6D_6 were heated for 14 h at 100 C, after which an amorphous white powder of **7a** was recovered (0.09 g, 61% yield): mp 65 °C. IR ($CDCl_3$): 3316 (ν(NH)), 1679 (ν(C=O)), 1221 (ν(COC)), 2160 cm^{-1} (ν($C{\equiv}C$)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.53 (s, 12H, *o*-Me), 2.29 (s, 6H, *p*-Me), 6.88 (s, 4H, C_6H_2), 7.79 (s, 1H, NH), 3.82 (s, 3H, OCH_3), 7.93 (ddd, 1H, H_3), 6.60 (ddd, 1H, H_4), 6.90–7.50 (m, 7H, C_6H_5, H_5, H_6) (*J*(3–4) = 8 Hz, *J*(3–6) = 0.7 Hz, *J*(4–6) = 2 Hz, *J*(3–5) = 1.6 Hz, *J*(4–5) = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 132.64 ($C_{1'}$), 143.98 ($C_{2'}$), 129.90 ($C_{3'}$), 139.79 ($C_{4'}$), 21.21 (*p*-Me), 23.57 (*o*-Me), 153.22 (C_1), 112.90 (C_2), 131.73 (C_3), 118.50 (C_4), 133.76 (C_5), 115.65 (C_6), 169.46 (C_7), 51.51 (C_8); PhCC, 123.49 ($C_{1''}$), 131.55 ($C_{2''}$), 128.34 ($C_{3''}$), 128.62 ($C_{4''}$); 93.87 (CPh), 106.57 (CGe). MS (EI, 70 eV): *m/z* 563 (M^+, 4), 444 (M^+ − Mes, 7), 462 (M^+ − $PhC{\equiv}C$, 12), 412 (M^+ − NHAE, 73). Anal. Calcd for $C_{34}H_{35}GeNO_2$: C, 72.63; H, 6.27; N, 2.49. Found: C, 72.83; H, 6.31; N, 2.41. **7a** (0.41 g, 64%) was also obtained from **1a** (0.566 g, 1.14 × 10^{-3} mol) by addition at −10 °C of $PhC{\equiv}CLi$ (1.14 × 10^{-3} mol) dissolved in a mixture of benzene (3 mL) and pentane (1 mL). Synthesis of **7b**. A mixture of **2b** (0.255 g, 0.54 × 10^{-3} mol) and $PhC{\equiv}CH$ (0.055 g, 0.54 × 10^{-3} mol) in 3 mL of C_6H_6 was heated for 14 h at 100 °C in a sealed tube. After evaporation of the solvent, the residual white powder (0.28 g, 90% yield) was identified as **7b**: mp 52 °C. IR ($CDCl_3$): 3383 (ν(NH)), 1620 (ν(CO)), 2160 (ν($C{\equiv}C$)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.50 (s, 12H, *o*-Me), 2.27 (s, 6H, *p*-Me), 6.85 (s, 4H, C_6H_2), 6.50–7.50 (m, 9H, C_6H_5, C_6H_4), 4.86 (s, 1H, NH), 2.99 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 131.87 ($C_{1'}$), 143.85 ($C_{2'}$), 129.72 ($C_{3'}$), 139.62 ($C_{4'}$), 21.09 (*p*-Me), 23.37 (*o*-Me), 146.95 (C_1), 122.50 (C_2), 127.88 (C_3), 117.74 (C_4), 129.98 (C_5), 116.16 (C_6), 171.73 (C_7); $PhC{\equiv}C$, 123.46 ($C_{1''}$), 131.59 ($C_{2''}$), 128.21 ($C_{3''}$), 128.44 ($C_{4''}$); 106.22 (GeC), 93.97 (CPh). MS (EI, 70 eV): *m/z* 576 (M^+, 3), 532 (M^+ − NMe, 4), 457 (M^+ − Mes, 8), 475 (M^+ − $PhC{\equiv}C$, 7), 413 (M^+ − NHAA, 53). Anal. Calcd for $C_{35}H_{38}GeN_2O$: C, 73.08; H, 6.65; N, 4.87. Found: C, 73.16; H, 6.68; N, 4.89. **7b** (0.46 g, 80% yield) was also prepared from **1b** (0.53 g, 1 × 10^{-3} mol) and $PhC{\equiv}CLi$ (1 × 10^{-3} mol).

Scheme III



functional groups attached to germanium.

These reactions confirm beyond doubt that compounds **2a** and **2b** are Ge=N doubly bonded molecules and cannot be dimeric as in cyclodigermazanes; otherwise they would not form[20,21] the observed compounds **3**–**7**. Unfortunately, molecular weights of **2a** and **2b** could not be determined because they are not soluble enough in suitable cryoscopic solvents.

Further evidence of the high reactivity of **2a** and **2b** is provided by their (2 + 3) cycloaddition reactions with nitrones **8** and **9** (Scheme III). The resulting adducts **8a**,[22] **8b**,[23] and **9a**[24] are the first thermally stable 1-oxa-2,4-diaza-5-germolane rings (unstable when R = Me, Ph, Mes[7,25]). Apparently, the anthranilamide and anthranilate groups of **2b** and **2a**, respectively, stabilize the heterocyclic ring, perhaps by their electron-withdrawing effects. The possibility of intramolecular $O\rightarrow Ge$ bonding between the oxygen of the carbonyl group and the germanium atom of **2a** or **2b** is suggested by decreases in ν(CO) on formation of the adducts in Scheme II. Single-crystal X-ray diffraction data are necessary to test this suggestion.

To summarize, the novel germanimines **2a** and **2b** are not only stable compounds but are also very reactive toward protic reagents and cycloaddition reactions with nitrones. The dehydrohalogenation reaction is shown to be a very effective way of preparing germanimines, provided the precursor has a reactive germanium–halogen bond. We continue to explore this reaction in order to obtain a wider range of N-substituted germanimines.

OM920813Z

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(22) Synthesis of **8a**. In a sealed tube, **2a** (0.142 g, 0.3×10^{-3} mol) and **8** (0.061 g, 0.3×10^{-3} mol) in benzene (3 mL) were heated for 3 days at 100 °C. After evaporation of solvents and extraction of the residue with pentane, a yellow powder of **8a** (0.19 g, 95% yield) was obtained: mp 210 °C. IR ($CDCl_3$): 1656 (ν(C=O)), 1240 cm^{-1} (ν(COC)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.60 (s, 6H, *o*-Me), 2.29 (s, 3H, *p*-Me), 6.86 (s, 2H, C_6H_2), 2.46 (s, 6H, *o*-Me), 2.20 (s, 3H, *p*-Me), 6.73 (s, 2H, C_6H_2), 5.45 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 7.71 (ddd, 1H, H_3), 6.52 (ddd, 1H, H_4), 6.78–7.47 (m, 12H, C_6H_5, H_5, H_6) (J(3–4) = 8 Hz, J(3–6) = 0.5 Hz, J(4–6) = 1.3 Hz, J(3–5) = 1.8 Hz, J(4–5) = 6.7 Hz). ^{13}C NMR ($CDCl_3$), 50.3 MHz): δ 153.02 (C_1), 110.90 (C_2), 131.99 (C_3), 118.51 (C_4), 135.25 (C_5), 116.08 (C_6), 171.09 (C_7), 52.75 (C_8), 134.88 ($C_{1'}$), 143.61, 142.79 ($C_{2'}$), 129.44, 129.38 ($C_{3'}$), 138.57, 137.77 ($C_{4'}$), 21.13, 20.97 (*p*-Me), 24.51, 23.47 (*o*-Me); CHPh, 139.26 ($C_{1''}$), 128.15 ($C_{2''}$), 130.34 ($C_{3''}$), 127.59 ($C_{4''}$); 85.58 (CH); NPh, 150.34 ($C_{1'''}$), 122.77 ($C_{2'''}$), 127.81 ($C_{3'''}$), 124.14 ($C_{4'''}$). MS (EI, 70 eV): *m/z* 658 (M^+, 3), 419 (M^+ – PhCHNAE, 52). Anal. Calcd for $C_{39}H_{40}GeN_2O_3$: C, 71.26; H, 6.13; N, 4.26. Found: C, 70.93; H, 6.12; N, 4.10.

(23) Synthesis of **8b**. Similarly, **8b** (0.31 g, 94% yield) was obtained from **2b** (0.227 g, 0.48×10^{-3} mol) and **8** (0.095 g, 0.48×10^{-3} mol) at 100 °C for 18 h: mp 125 °C. IR ($CDCl_3$): 1607 cm^{-1} (ν(C=O)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.52 (s, 6H, *o*-Me), 2.28 (s, 3H, *p*-Me), 6.83 (s, 2H, C_6H_2), 2.42 (s, 6H, *o*-Me), 2.17 (s, 3H, *p*-Me), 6.68 (s, 2H, C_6H_2), 2.83 (s, 6H, NMe_2), 5.82 (s, 1H, CH), 6.80–7.15 (m, 14H, C_6H_5, C_6H_4). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 136.47 ($C_{1'}$), 122.87, 143.31 ($C_{2'}$), 130.01, 129.26 ($C_{3'}$), 138.20, 138.30 ($C_{4'}$), 20.99, 21.13 (*p*-Me), 23.46, 23.89 (*o*-Me), 150.33 (C_1), 119.68 (C_2), 129.37 (C_3), 120.82 (C_4), 131.47 (C_5), 117.22 (C_6), 172.64 (C_7), 34.18 (C_9); CHPh, 138.59 ($C_{1''}$), 127.60 ($C_{2''}$), 127.69 ($C_{3''}$), 127.77 ($C_{4''}$); 83.49 (CH); NPh, 149.71 ($C_{1'''}$), 120.52 ($C_{2'''}$), 128.98 ($C_{3'''}$), 122.58 ($C_{4'''}$). MS (EI, 70 eV): *m/z* 671 (M^+, 45), 419 (M^+ – PhCHNAA, 83). Anal. Calcd for $C_{40}H_{43}GeN_3O_2$: C, 71.66; H, 6.46; N, 6.26. Found: C, 71.04; H, 6.68; N, 5.92.

(24) Synthesis of **9a**. **9a** (0.18 g, 95% yield) was prepared by heating for 3 days at 100 °C a mixture of **2a** (0.14 g, 0.3×10^{-3} mol) and **9** (0.054 g, 0.3×10^{-3} mol) and benzene (2 mL) in a sealed tube. IR ($CDCl_3$): 1660 (ν(C=O)), 1240 cm^{-1} (ν(COC)). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.60 (s, 6H, *o*-Me), 2.32 (s, 3H, *p*-Me), 6.88 (s, 2H, C_6H_2), 2.39 (s, 6H, *o*-Me), 2.16 (s, 3H, *p*-Me), 6.67 (s, 2H, C_6H_2), 0.74 (s, 9H, tBu), 5.39 (s, 1H, CH), 3.66 (s, 3H, OCH_3), 6.43 (ddd, 1H, H_4) (J(3–4) = 8.2 Hz, J(4–6) = 2.4 Hz, J(4–5) = 5.6 Hz), 7.14–7.76 (m, 8H, C_6H_5, H_3, H_5, H_6). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 153.16 (C_1), 110.70 (C_2), 131.87 (C_3), 115.45 (C_4), 134.64 (C_5), 118.45 (C_6), 170.65 (C_7), 52.46 (C_8), 133.96 ($C_{1'}$), 142.60, 140.86 ($C_{2'}$), 129.30, 129.10 ($C_{3'}$), 138.28, 137.39 ($C_{4'}$), 21.19, 20.95 (*p*-Me), 24.34, 23.35 (*o*-Me); CHPh, 140.21 ($C_{1''}$), 127.93 ($C_{2''}$), 131.04 ($C_{3''}$), 127.51 ($C_{4''}$); 80.04 (CH); NtBu, 58.35 (CH_3), 27.26 (C). MS (EI, 70 eV): *m/z* 638 (M^+, 15), 399 (M^+ – PhCHNAE, 84). Anal. Calcd for $C_{37}H_{44}GeN_2O_3$: C, 69.72; H, 6.95; N, 4.39. Found: C, 69.37; H, 6.90; N, 4.26.

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