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Germylenes and Germyl Cations with the 2,4-Di-*tert*-butyl-6-(*N*,*N*-dimethylaminomethyl)phenyl Ligand

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*Summary: The 2,4-di-tert-butyl-6-(N,N-dimethylaminomethyl)phenyl (Mamx) ligand allows the synthesis of the germylenes MamxGeCl (**1**), Mamx$_2$Ge (**2**), Mamx(Tip)Ge (**3**; Tip = 2,4,6-iPr$_3$C$_6$H$_2$), MamxGeN$_3$ (**4**), MamxGeN(SiMe$_3$)$_2$ (**5**), and MamxGe[Fe(CO)$_2$Cp*] (**6**), which are all stabilized by coordination of the amino side chain. Reactions of **2** and **3** with MeI yield the ionic compounds Mamx(Tip)(Me)Ge$^+$I$^-$ (**7**) and Mamx$_2$(Me)Ge$^+$I$^-$ (**8**), respectively; the X-ray crystal structure of **7** shows a trigonal-planar coordination at the Ge center and a nearly perpendicular Ge−N bond.*

In compounds with low-energy vacant orbitals, substituents with donor groups in the side chain and with suitable geometry lead to intramolecular coordination and consequently to drastic changes in structure and reactivity as compared to the parent species. In the chemistry of germanium, this is documented mainly by some recent examples.[1] The title ligand, abbreviated Mamx (methylaminomethyl-*m*-xylyl), was first synthesized by Yoshifuji et al. and successfully applied in the chemistry of low-coordinated phosphorus.[2] We have tested this ligand in germanium chemistry and present here the first results concerning the synthesis and characterization of monomeric germanium(II) compounds (germylenes) and of ionic germanium(IV) species with novel features of structure and bonding.

Reaction of MamxLi[2] with GeCl$_2$·dioxane in THF in a 1:1 ratio leads nearly quantitatively to MamxGeCl (**1**),[3] which is isolated as a colorless powder with good solubility in THF and in toluene. In Et$_2$O as the solvent, **1** cocrystallizes with 18-crown-6;[4] the molecular structure of **1** is presented in Figure 1.

The first experiments demonstrate that **1** is a suitable substrate for the preparation of the homoleptic, monomeric germylene Mamx$_2$Ge (**2**) and further preparation of heteroleptic germylenes with inorganic, organic, and organometallic substituents. Treatment of GeCl$_2$·dioxane with 2 equiv of MamxLi in THF at −80 °C leads to the formation of pale green **2**.[5] In the solid state, only one of the two amino groups coordinates to the germanium center.[6] As NMR spectra show, the side chains exchange their positions in solution.[7] This process is quite fast at 80 °C;[8] at −80 °C the dynamic behavior of **2** is "frozen" on the NMR time scale.[9] The pale green diarylgermylene Mamx(Tip)Ge (**3**) is prepared analogously by reaction of **1** with 2,4,6-triisopropylphenyllithium.[10] Crystals suitable for an X-ray

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[1] (a) Veith, M.; Hobein, P.; Rösler, R. *Z. Naturforsch.* **1989**, *44b*, 1067. (b) Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1989**, *101*, 1287. (c) Karsch, H. H. *J. Organomet. Chem.* **1988**, *344*, 153. (d) Karsch, H. H. *Russ. Chem. Bull.* **1993**, *42*, 1937 and references cited herein. (e) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1995**, *499*, 7. (f) Barrau, J.; Rima, G.; Amraoui, T. E. *Inorg. Chim. Acta* **1996**, *241*, 9. (g) Foley, S. R.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359. (h) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116. (i) Leung, W.-P.; Kwok, W.-H.; Weng, L.-H.; Law, L. T. C.; Zhou, Z. Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 4301. (j) Drohst, C.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 1141. (k) Karsch, H. H.; Schlüter, P. A.; Reisky, M. *Eur. J. Inorg. Chem.* **1998**, 433.

[2] Yoshifuji, M.; Kamijo, K.; Toyota, K. *Tetrahedron Lett.* **1994**, *35*, 3971.

[3] **1**: ^{1}H NMR (C$_6$D$_6$, 500.1 MHz) δ 1.32, 1.60 (2 s, 9 H, *t*Bu), 1.64, 2.25 (2 s, 3 H, NCH$_3$), 2.88, 4.50 (2 d, $^2J_{HH}$ = 14 Hz, 1 H, CH$_2$), 6.96, 7.49 (2 s, 1 H, aryl-H). ^{13}C NMR (C$_6$D$_6$, 125.75 MHz): δ 31.57, 33.75 (C(CH$_3$)$_3$), 34.86, 37.87 (C(CH$_3$)$_3$), 43.37, 45.26 (NCH$_3$), 67.62 (NCH$_2$), 118.49, 121.45 (tert aryl-C), 144.77, 150.98, 156.19, 157.05 (quart aryl-C). MS (CI) [*m*/*z* (I_{rel})]: 355 (57, M$^+$), 320 (100, MamxGe$^+$). Mp: 164 °C. Anal. Calcd for C$_{17}$H$_{28}$NClGe C, 57.59; H, 7.96; N, 3.95. Found: C, 56.44; H, 7.94; N, 3.60.

[4] Colorless crystals of **1** and 18-crown-6 in a ratio of 2:1; no intermolecular coordination to the Ge center is found. Crystallographic data: C$_{23}$H$_{40}$ClGeNO$_3$, monoclinic, space group $P2_1/c$, a = 14.2815(7) Å, b = 9.8468(5) Å, c = 18.9434(10) Å, β = 101.3290(10)°, V = 2612.0(2) Å^3, Z = 4, D_c = 1.237 g cm^{-3}, μ = 1.296 mm^{-1}, T = 183(2) K, 22 940 reflections collected, 5693 unique reflections, *R* indices (all data) R1 = 0.0320, wR2 = 0.0626, GOF = 1.044. Full details of the crystallographic analyses of **1**, **3**, and **7** are described in the Supporting Information.

[5] **2**: MS (CI), [*m*/*z* (I_{rel})]: 567 (30, M$^+$ + H), 320 (100, MamxGe$^+$), 246 (73, Mamx$^+$). Mp: 105 °C. Anal. Calcd for C$_{34}$H$_{56}$N$_2$Ge: C, 72.22; H, 10.02; N, 4.95. Found: C, 72.14; H, 10.15; N, 4.24.

[6] Unpublished results.

[7] **2**: ^{1}H NMR (toluene-d_8, 25 °C) δ 1.38 (s, 18 H, *t*Bu), 1.85 (br, 30 H, *t*Bu + NCH$_3$), 3.05 (br 4 H, CH$_2$), 7.62 (br, 4 H, aryl-H).

[8] **2**: ^{1}H NMR (toluene-d_8, 80 °C) δ 1.35, 1.75 (2 s, 18 H, *t*Bu), 1.81 (s, 12 H, NCH$_3$), 3.12 (d, $^2J_{HH}$ = 14 Hz, 2 H, CH$_2$), 3.65 (br d, 2 H, CH$_2$), 7.21 (br s, 2 H, aryl-H), 7.53 (s, 2 H, aryl-H). ^{13}C NMR (toluene-d_8, 80 °C): δ 31.87, 34.05(C(CH$_3$)$_3$), 34.92, 38.83 (C(CH$_3$)$_3$), 47.70 (NCH$_3$), ∼68 (CH$_2$), 122.30, 149.76 (aryl-C).

[9] **2**: ^{1}H NMR (toluene-d_8, −80 °C) δ 1.34 (m, 6 H, NCH$_3$), 1.45, 1.49, 1.83 (3 s, 9 H, *t*Bu), 1.96 (s, 6 H, NCH$_3$), 2.09 (s, 9 H, *t*Bu), 2.57, 3.14, 3.27, 3.75 (4 d, $^2J_{HH}$ = 14 Hz, 1 H, CH$_2$), 6.93, 7.56, 7.82, 7.94 (4 s, 1 H, aryl-H). ^{13}C NMR (toluene-d_8, −80 °C): δ 31.52, 31.63, 32.28, 34.60, 34.80, 34.89, 37.55, 39.57 (*t*Bu), 45.33, 46.65, 48.11 (NCH$_3$), 65.25, 69.56 (CH$_2$), 118.28, 121.22, 121.84, 122.27, 141.59, 146.72, 148.86, 149.14, 152.02, 154.66, 158.24, 158.58 (aryl-C).

[10] **3**: ^{1}H NMR (C$_6$D$_6$) δ 1.01, 1.28 (2 m, 6 H, CH(CH_3)$_2$), 1.37 (s, 9 H, *t*Bu), 1.51 (d, $^3J_{HH}$ = 7 Hz, 3 H, CH(CH_3)$_2$), 1.63 (m, 12 H, *t*Bu + CH(CH_3)$_2$), 1.90, 2.02, (2 s, 3 H, NCH$_3$), 2.85 (p-sep, (pseudo-sep), $^3J_{HH}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$), 2.92 (d, $^2J_{HH}$ = 13 Hz, 1 H, CH$_2$), 3.20 (p-sep, $^3J_{HH}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$), 4.04 (d, $^2J_{HH}$ = 13 Hz, 1, H, CH$_2$), 5.13 (p-sep, $^3J_{HH}$ = 7 Hz, 1 H, CH(CH$_3$)$_2$), 7.02, 7.10, 7.29, 7.53 (4 s, 1 H, aryl-H). ^{13}C NMR (C$_6$D$_6$): δ 23.03, 24.33, 25.99, 26.25 27.26 (*i*Pr), 31.69 (C(CH$_3$)$_3$), 32.08 (*i*Pr), 32.80 (C(CH$_3$)$_3$), 33.30, 34.70 (*i*Pr), 38.00 (C(CH$_3$)$_3$), 46.66, 47.75 (NCH$_3$), 70.26 (NCH$_2$), 118.42, 121.27, 121.29, 121.60 (tert aryl-C), 142.35, 147.55, 148.66, 149.25, 155.81, 156.08, 158.33, 158.51 (quart aryl-C). MS (CI), [*m*/*z* (I_{rel})]: 523 (86, M$^+$), 320 (100, MamxGe$^+$). Mp: 107 °C. Anal. Calcd for C$_{32}$H$_{51}$NGe: C, 73.58; H, 9.84; N, 2.68. Found: C, 71.77; H, 10.13; N, 2.49.

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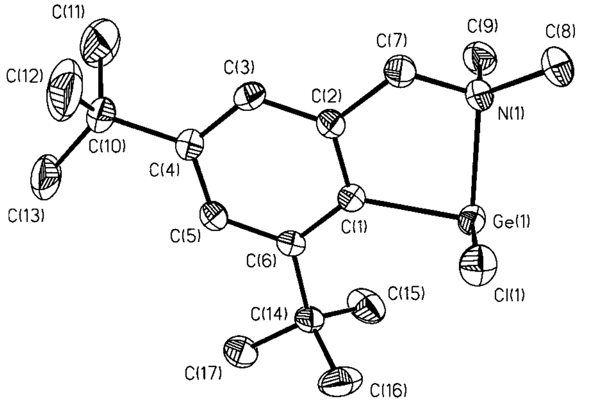

Figure 1. Molecular structure of **1**, ORTEP plot (50% probability). Selected bond lengths (Å) and angles (deg): Ge−C(1), 2.0156(14); Ge−Cl, 2.3283(4); Ge−N, 2.0936(13); C(1)−Ge−Cl, 94.04(4); C(1)−Ge−N, 83.09(5); Cl−Ge−N, 93.12(4).

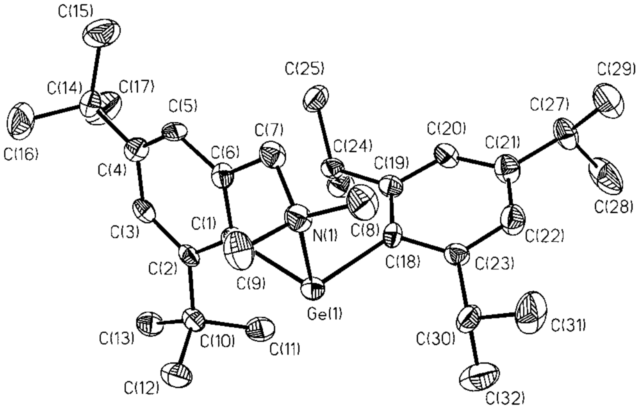

Figure 2. Molecular structure of **3**, ORTEP plot (50% probability). Selected bond lengths (Å) and angles (deg): Ge−C(1), 2.012(6); Ge−C(18), 2.084(6); Ge−N, 2.165(5); C(1)−Ge−C(18), 104.2(2); C(1)−Ge−N, 80.3(2); C(18)−Ge−N, 93.4(2).

crystal structure analysis[11] were obtained from hexane; the molecular structure of **3** is shown in Figure 2.

In the structures of **1** and **3**, the geometry at the germanium atom and the N−Ge bond length is worth mentioning. The angle α (*ipso*-C−Ge−N) is smaller than 90° in both compounds. The angle β (*ipso*-C−Ge−R) is 94° in **1** and 104° in **3**, and the angle γ (N−Ge−R) is comparable (≅93°). The N→Ge donor bond is unexpectedly short in both compounds; the observed distance approaches that in covalent N−Ge(II) bonds ($Me_2Si(NtBu)(NtBuH)GeCl$,[1a] 1.89 Å; $((Me_3Si)_2N)_2Ge$,[12] 1.87 and 1.88 Å).

The heteroleptic germylenes $MamxGeN_3$ (**4**),[13] $MamxGeN(SiMe_3)_2$ (**5**),[14] and MamxGe[Fe(CO)$_2$Cp*] (**6**)[15] are obtained from **1** by reaction with NaN_3 in THF, with $LiN(SiMe_3)_2$ in hexane, and with K[Fe(CO)$_2$Cp*] in hexane, respectively. They are all stable species under ordinary conditions, with the exception of **4** which decomposes slowly in solution. Coordination of the amino group is generally observed, as indicated in the NMR spectra by the existence of diastereotopic CH_2 protons and methyl groups and a low-field shift of the side chain signals.

Reaction of **3** with MeI in THF leads instantanously to the colorless compound **7**,[16] which contains the Mamx(Tip)(Me)Ge$^+$ cation (**7a**) and the counteranion I$^-$. Crystals suitable for an X-ray structure analysis were obtained from THF.[17] The structure of **7a** is shown in Figure 3.

The closest Ge−I distance in the crystal is 5.16 Å, which excludes any bonding interactions. In **7a**, the nearly perfect trigonal-planar arrangement of the GeC_3 unit is of special interest; the angle sum is 352.15°. The GeC_3 plane and the N→Ge bond vector form an angle of 77°. The dihedral angle between the aromatic ring plane of the Mamx ligand and the GeC_3 plane is 72.1°. A nearly perpendicular orientation (92.3°) is observed between the two aromatic ring planes. The structural features of **7a** are novel in the chemistry of germanium cations.[18] In an analogous fashion, the germylene **2** is transferred to the ionic species Mamx$_2$(Me)Ge$^+$I$^-$ (**8**), in which one of the amino groups remains uncoordinated.[19] Interestingly, the methyl cation prefers to attack the germanium and not the nitrogen lone pair in **2**, thus demonstrating the pronounced nucleophilicity of the lone pair at the germanium atom.

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[11] Crystallographic data for **3**: $C_{32}H_{51}GeN$, triclinic, space group $P\bar{1}$, a = 9.86(1) Å, b = 10.04(1) Å, c = 15.66(2) Å, α = 97.42(8)°, β = 96.45(9)°, γ = 93.66(8)°, V = 1524(3) Å^3, Z = 2, D_c = 1.138 g cm^{-3}, μ = 1.024 mm^{-1}, T = 173(2) K, 4270 reflection collected, 3990 unique reflections, R indices (all data) R1 = 0.1055, wR2 = 0.1302, GOF = 1.035.

[12] Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Power, P. P.; Olmstead, M. M. *Inorg. Chim. Acta* **1992**, *198−200*, 203.

[13] **4**: Colorless solid.^{1}H NMR (C_6D_6): δ 1.31, 1.56 (2 s, 9 H, *t*Bu), 1.57, 2.05(2 s, 3 H, NCH_3), 2.83, 4.07 (2 d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 6.93, 7.48 (2 s, 1 H, aryl-H). ^{13}C NMR (C_6D_6): δ 31.60, 33.63 (C(CH$_3$)$_3$), 34.89, 37.59 (C(CH$_3$)$_3$), 43.73, 45.54 (NCH_3), 68.20 (CH_2), 118.58, 121.16 (tert aryl-C), 145.03, 151.43, 152.43, 157.24 (quart aryl-C). IR (Nujol): 2072 cm^{-1}. Mp: 106 °C. Due to the instability in solution, crystalline **4** could not yet be obtained. Therefore, satisfactory analytical data are not available.

[14] **5**: Colorless oil. ^{1}H NMR (C_6D_6): δ −0.01, 0.56 (2 s, 9 H, $SiCH_3$), 1.34. 1.63 (2 s, 9 H, *t*Bu), 1.82, 2.18 (2 s, 3 H, NCH_3), 2.97, 4.06 (2 d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 6.91, 7.45 (2 s, 1 H, aryl-H). ^{13}C NMR (C_6D_6): δ 5.80, 6.55 ($SiCH_3$), 31.66, 33.39 (C(CH$_3$)$_3$), 34.75, 38.08 (C(CH$_3$)$_3$), 45.35, 45.93 (NCH_3), 69.07 (CH_2), 118.63, 121.82 (tert aryl-C), 143.75, 150.59, 156.29, 156.67 (quart aryl-C). MS (CI), [m/z (I_{rel})]: 480 (1.3, M$^+$), 465 (1.2, M$^+$ − CH_3), 320 (100, MamxGe$^+$). Anal. Calcd for $C_{23}H_{46}N_2GeSi_2$: C, 57.61; H, 9.67; N, 5.84. Found: C, 57.87; H, 9.95; N, 5.61.

[15] **6**: ^{1}H NMR (C_6D_6) δ 1.32, 1.65 (2 s, 9 H, *t*Bu), 1.68 (s, 15 H, Cp*), 2.16, 2.37 (2 s, 3 H, NCH_3), 3.22, 4.78 (2 d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 7.01, 7.54 (2 s, 1 H, aryl-H). ^{13}C NMR (C_6D_6): δ 9.75 (C_5(CH$_3$)$_5$), 31.66, 32.56 (C(CH$_3$)$_3$), 34.58, 38.52 (C(CH$_3$)$_3$), 45.80, 48.72 (NCH_3), 69.60 (CH_2), 94.53 (C_5(CH$_3$)$_5$), 117.95, 121.89 (tert aryl-C), 142.65, 148.69, 156.11, 163.47 (quart aryl-C), 219.72, 223.92 (CO). IR (Nujol, cm^{-1}): 1952, 1939, 1888, 1877. MS (CI), [m/z (I_{rel})]: 509 (8.9, M$^+$ − C_4H_{10}), 320 (74.6, MamxGe$^+$), 246 (24.5, Mamx$^+$), 203 (42.0, $C_{15}H_{23}{}^+$), 136 (100, Cp*H$^+$). UV−Vis (hexane, nm): λ_{max} 224 (ϵ = 24 000), 255 (ϵ = 16 000), 303 (ϵ = 9200). Mp: 148 °C. Anal. Calcd for $C_{29}H_{43}NO_2FeGe$: C, 61.52; H, 7.65; N, 2.47. Found: C, 61.48; 7.68, 2.47.

[16] **7**: ^{1}H NMR (C_6D_6) δ 0.66, 0.85 (2 d, $^3J_{HH}$ = 7 Hz, 3 H, CH(CH_3)$_2$), 1.10, 1.20 (2 m, 12 H, *t*Bu + CH(CH_3)$_2$), 1.57, 1.75 (2 d, $^3J_{HH}$ = 6 Hz, 3 H, CH(CH_3)$_2$), 1.96 (s, 3 H, $GeCH_3$), 2.63, 2.92 (2 p-sep, 1 H, CH(CH$_3$)$_2$), 3.40 (s, 3 H, NCH_3), 3.65 (p-sep, 1 H, CH(CH$_3$)$_2$), 3.83 (s, 3 H, NCH_3), 4.03, 5.95 (2 d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 6.98, 7.21, 7.50, 7.61 (4 s, 1 H, aryl-H). ^{13}C NMR (C_6D_6): δ 12.08 ($GeCH_3$), 23.67, 23.93, 25.71, 27.06, 27.17 (*i*Pr), 31.15 (C(CH$_3$)$_3$), 31.70 (*i*Pr), 32.25 (C(CH$_3$)$_3$), 34.33 (*i*Pr), 35.06 (C(CH$_3$)$_3$), 35.48 (*i*Pr), 36.61 (C(CH$_3$)$_3$), 47.33, 47.70 (NCH_3), 67.31 (CH_2), 122.24, 123.32, 124.32 (tert aryl-C), 124.78 (quart aryl-C), 125.64 (tert aryl-C), 131.80, 140.73, 153.32, 154.72, 154.83, 156.81, 158.18 (quart aryl-C). MS (CI, M$^+$ = Mamx(Tip)(CH$_3$)Ge$^+$), [m/z (I_{rel})]: 522 (55, M$^+$ − CH_4), 507 (100, M$^+$ − C_2H_7), 320 (20, MamxGe$^+$). Anal. Calcd for $C_{33}H_{54}NGeI$: C, 60.11; H, 7.49; N, 2.12. Found: C, 59.61; H, 8.42; N, 1.69.

[17] Colorless crystals of **7**, containing 1 equiv of THF, which is not coordinated to the Ge center. Crystallographic data: $C_{37}H_{62}GeINO$, triclinic, space group $P\bar{1}$, a = 12.6238(6) Å, b = 12.6753(6) Å, c = 13.2373/7) Å, α = 81.066(1)°, β = 68.145(1)°, γ = 77.837(1)°, V = 1914.8(2) Å^3, Z = 2, D_c = 1.277 g cm^{-3}, μ = 1.632 mm^{-1}, T = 183(2) K, 18 255 reflections collected, 8124 reflections unique, R indices (all data) R1 = 0.0829, wR2 = 0.1056, GOF = 1.075.

[18] Belzner, J. *Angew. Chem.* **1997**, *109*, 1331.

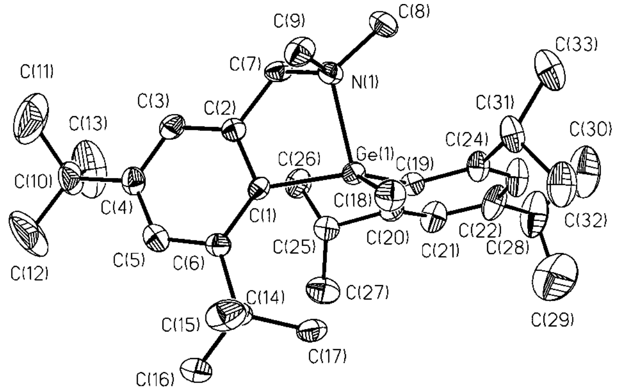

Figure 3. Structure of **7a**, ORTEP plot (50% probability). Selected bond lengths (Å) and angles (deg): Ge−C(1), 1.961(4); Ge−C(18), 1.942(4); Ge−C(19), 1.975(4); Ge−N, 2.034(3); C(1)−Ge−C(18), 117.27(18); C(1)−Ge−C(19), 117.36(17); C(18)−Ge−C(19), 117.52(19); C(1)−Ge−N, 86.44(15); C(18)−Ge−N, 104.65(17); C(19)−Ge−N, 106.65(16).

Quantum mechanical calculations[20] at a density functional level (b3lyp/6−31g*) on various model compounds (a) parent **7a** (without alkyl substitution at the phenyl ring and the germanium and nitrogen atom) and the donor−acceptor adducts of (b) NH_3 with GeH_3^+ and (c) $N(CH_3)_3$ with $Ge(CH_3)_3^+$ show that in cations of this type a total charge of ca. 0.3 electrons is transferred from N to Ge, creating a dative bond which is one-half as strong as a single bond. The equilibrium bond lengths are 2.01, 2.02, and 2.04 Å (for cases a, b, and c), in close agreement with the experimentally found value for **7a**. Therefore, **7a** has to be considered as a base-stabilized germyl cation or a "germylium ion" and not as a germyl-substituted ammonium ion. Calculations further verify that there is no significant interaction between the Ge center and a methyl group in the axial position, so the stabilizing effect of the *ortho*-*tert*-butyl group has to be attributed merely to steric factors.

In germanium chemistry, the Mamx ligand combines the steric properties of the Mes* (2,4,6-tri-*tert*-butylphenyl) ligand[21] and the donor function of the 2-dimethylaminomethylphenyl ligand.[22] This behavior allows the synthesis of so far unknown compounds with new variants in structure and reactivity. Further investigations are in progress.

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Supporting Information Available: Tables of crystal data and structure refinement, measurement and program parameters, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1**, **3**, and **7** and experimental procedures for the synthesis of **1**−**8** (21 pages). Ordering information is given on any current masthead page.

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(19) (a) **8**: ^1H NMR (C_6D_6) δ 1.09, 1.19, 1.30 (3 s, 9 H, *t*Bu), 1.36 (s, 3 H, $GeCH_3$), 1.41 (s, 9 H, *t*Bu), 1.42 (s, 6 H, NCH_3), 2.67 (d, $^2J_{HH} = 12$ Hz, 1 H, CH_2), 2.93, 3.58 (2 s, 3 H, NCH_3), 3.70 (d, $^2J_{HH} = 12$ Hz, 1 H, CH_2), 4.99, 6.02 (2 d, $^2J_{HH} = 15$ Hz, 1 H, CH_2), 7.15, 7.49, 7.65, 7.86 (4 s, 1 H, aryl-H). ^{13}C NMR (C_6D_6): δ 17.66 ($GeCH_3$), 30.91, 31.35, 32.36, 34.52 ($C(CH_3)_3$), 34.80, 35.12, 36.91, 37.54 ($C(CH_3)_3$), 44.08 (NCH_3), 50.74, 53.45 (NCH_3), 65.93, 70.41 (CH_2), 122.60, 124.66, 125.94, 129.72 (tert aryl-C), 132.68, 140.38, 146.06, 152.43, 153.67, 154.33, 158.25 (quart aryl-C). MS (CI, $M^+ = Mamx_2(CH_3)Ge^+$), [m/z (I_{rel})]: 579 (6.6, $M^+ - H_2$), 565 (21, $M^+ - CH_4$), 335 (25, $MamxGeCH_3+$), 320 (45, $MamxGe^+$), 246 (100, $Mamx^+$). Crystals containing **8** and 2 equiv of THF could be isolated in traces. The structure of **8** was also confirmed by an X-ray crystal analysis. Due to the poor quality of the crystals, details of the structure will not be discussed in this paper.

(20) (a) All calculations were performed with the Gaussian set of programs. *Gaussian 94, Revision B.3*: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995. (b) For a general discussion on donor−acceptor formation at silylene, germylene, and stannylene, see: Schoeller, W. W.; Schneider, R. *Chem. Ber.* **1997**, *130*, 1013.

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