Supporting Information

Boranyl-Functionalized [Ge₉] Clusters: Providing the Idea of Intramolecular Ge/B Frustrated Lewis Pairs
Christoph Wallach⁺, Felix S. Geitner⁺, Antti J. Karttunen, and Thomas F. Fässler*
Content

1. General information ..............................................................................................................................1
2. Syntheses .............................................................................................................................................2
3. Results and Discussion ........................................................................................................................4
   3.1 Crystallographic data .............................................................................................................4
   3.2 NMR spectra ..........................................................................................................................7
   3.3 ESI MS spectra ....................................................................................................................18
   3.4 Quantum chemical calculations at DFT-PBE0/TZVP level of theory .........................20
4. References .........................................................................................................................................23
1. General information

All manipulations were performed under oxygen-free, dry conditions under argon atmosphere using standard Schlenk or glove box techniques. Glassware was dried prior to use by heating it in vacuo. The solvents used were obtained from an MBraun Grubbs apparatus. All other commercially available chemicals were used without further purification. K$_4$Ge$_9$ was prepared by fusion of stoichiometric amounts of the elements in stainless-steel tubes at 650 °C. The bis-silylated [Ge$_9$] clusters [Ge$_9$(Si(TMS)$_3$)$_2$]$_2$\cite{1}, the chloro-diaza borolidines DABR-Cl (DAB = 2-chloro-1,3,2-diazaborolidine; R = Me,\cite{2} Pr,\cite{2} o-tol,\cite{3} Mes\cite{3}), as well as the imidazolium salt NHC Dipp\_HCl (NHC Dipp = 1,3-di(2,6-diisopropylphenyl)imidazolylidine)\cite{4} and the respective copper NHC complex NHC DippCuCl\cite{5} were prepared according to modified literature procedures.

Single crystal structure determination

The air- and moisture-sensitive crystals of 2a-Cu and 3a-Cu were transferred from the mother liquor into perfluoroalkyl ether oil in an argon filled glove box. For diffraction data collection, the single crystals were fixed on a glass capillary and positioned in a 150 K cold N$_2$ gas stream. Data collection was performed with a STOE StadiVari diffractometer (Mo$_{K\alpha}$ radiation) equipped with a DECTRIS PILATUS 300K detector. Structures were solved by Direct Methods (SHELXS-97)\cite{6} and refined by full-matrix least-squares calculations against $F^2$ (SHELXL-2018).\cite{7} The positions of the hydrogen atoms were calculated and refined using a riding model. Unless stated otherwise, all non-hydrogen atoms were treated with anisotropic displacement parameters. The supplementary crystallographic data for this paper have been deposited with the Cambridge Structural database and are available free of charge via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic data for compounds 2a-Cu and 3a-Cu are summarized in Table S1. In compound 3a-Cu the electron density of disordered co-crystallized toluene molecules was taken care of by the PLATON SQUEEZE function.\cite{8}

NMR spectroscopy

NMR spectra were measured on a Bruker Avance Ultrashield 400 MHz spectrometer. The $^1$H NMR spectra were calibrated using the residual proton signal of the used deuterated solvents. Chemical shifts are reported in parts per million (ppm) relative to TMS, with the solvent peaks serving as internal reference.\cite{9} Abbreviations for signal multiplicities are: singlet (s), doublet (d), triplet (t), heptet (hept), broad signal (brs).

Electrospray ionization mass spectroscopy

ESI MS analyses were performed on a Bruker Daltronic HCT mass spectrometer (injection speed: 240 £L/h), and the data evaluation was carried out using the Bruker Compass Data Analysis 4.0 SP 5 program (Bruker). Spectra were plotted with OriginPro2016G (Origin Lab) and Excel 2016 (Microsoft).

Quantum-chemical calculations

Calculations were carried out with the TURBOMOLE program package, using the PBE0 hybrid density functional method and polarized triple-$\zeta$-valence Karlsruhe basis sets (DFT-PBE0/TZVP with def2-TZVP on Ge and Si, def-TZVP on other atoms).\cite{10} Multipole-accelerated resolution-of-the-identity technique was used to speed up the calculations.\cite{11} $m^4$ integration grid was used for the numerical integration of the exchange-correlation functional. As initial structures the crystal structure data of compounds 2a-Cu and 3a-Cu were used. The structures were fully optimized without any symmetry constraints. To simulate the anionic nature of the clusters the [Cu-NHC]$^+$ ligand was deleted and a COSMO solvent field was applied to counter the anionic charge.\cite{12} The molecular orbitals were illustrated using Iboview.\cite{13}
2. Syntheses

**K[Ge_{9}(Si(TMS)_3)_2DABMe] (1a-K):**

In a typical experiment K[Ge_{9}(Si(TMS)_3)_2] (92 mg, 0.075 mmol, 1 equiv.) was weighted in a Schlenk tube in the glove box and a solution of DABMe-Cl (9.9 mg, 0.075 mmol, 1 equiv.) in thf (3 mL) was added, resulting in a deep red solution. After stirring for 3 h at room temperature, the solvent was removed in vacuo yielding a brown solid. The solid was treated with hexane (2·3 mL) which was subsequently removed in vacuo (procedure in order to get rid of residual thf). The obtained brown solid was dissolved in toluene (6 mL), the resulting dark brown solution was filtered, and the solvent of the filtrate was removed to obtain the crude product as a brown oily solid (41 mg, 0.032 mmol, 43% yield).

Further purification to obtain an analytical pure product by recrystallization has not been successful to date.

**1H NMR (400 MHz, 298 K, thf-d8):** \( \delta [ppm] = 3.13 (s, 4H, CH_2(Bb)), 2.78 (s, 6H, Me), 0.25 (s, 54H, MeTMS). \)

**13C NMR (101 MHz, 298 K, thf-d8):** \( \delta [ppm] = 53.46 (s, Me), 38.34 (s, CH_2(Bb)), 3.26 (s, MeTMS). \)

**29Si-INEPT NMR (79 MHz, 298 K, thf-d8):** \( \delta [ppm] = -9.82 (s, Si TMS), -108.11 (s, Si Ge9). \)

**11B NMR (128 MHz, 298 K, thf-d8):** \( \delta [ppm] = 43.41 (brs, B Ge9). \)

**ESI MS (3500 V, 300 °C):** \( m/z = 1246.6 \) [Ge_{9}(Si(TMS)_3)_2DABMe]–.

**K[Ge_{9}(Si(TMS)_3)_2DABIPr] (2a-K):**

In a typical experiment K[Ge_{9}(Si(TMS)_3)_2] (92 mg, 0.075 mmol, 1 equiv.) was weighted in a Schlenk tube in the glove box and a solution of DABIPr-Cl (14.1 mg, 0.075 mmol, 1 equiv.) in dioxane or thf (3 mL) was added, leading to a deep red solution. After stirring for 5 h at room temperature, the solvent was removed in vacuo yielding a brownish solid. Subsequent dissolution in toluene (18 mL) gave a dark red solution, which was filtered to remove remaining solids. Removal of toluene in vacuo and treatment of the obtained oily solid with hexane (2·6 mL; addition and evaporation) yielded the crude product as brown solid (50 mg, 0.037 mmol, 50% yield). Purification to obtain an analytical pure product by recrystallization has not been successful to date.

**1H NMR (400 MHz, 298 K, thf-d8):** \( \delta [ppm] = 4.37 (hept, 3 \times J_{HH} = 6.8 Hz, 2H, CH_IPr), 3.13 (s, 4H, CH_2(Bb)), 1.02 (d, 3 \times J_{HH} = 6.8 Hz, 12H, Me_{IPr}), 0.25 (s, 54H, MeTMS). \)

**13C NMR (101 MHz, 298 K, thf-d8):** \( \delta [ppm] = 48.00 (s, CH_{IPr}), 42.50 (s, CH_2(Bb)), 21.95 (s, Me_{IPr}), 3.28 (s, MeTMS). \)

**29Si-INEPT NMR (79 MHz, 298 K, thf-d8):** \( \delta [ppm] = -9.85 (s, Si TMS), -108.28 (s, Si Ge9). \)

**11B NMR (128 MHz, 298 K, thf-d8):** \( \delta [ppm] = 41.90 (brs, B Ge9). \)

**ESI MS (3500 V, 300 °C):** \( m/z = 1302.6 \) [Ge_{9}(Si(TMS)_3)_2DABIPr]–.

**K[Ge_{9}(Si(TMS)_3)_2DABo-tol] (3a-K):**

In a typical experiment equimolar amounts of K[Ge_{9}(Si(TMS)_3)_2] (92 mg, 0.075 mmol, 1 equiv.) and DABo-tol-Cl (21.3 mg, 0.075 mmol, 1 equiv.) were weighted in a Schlenk tube in the glove box and dioxane or thf (3 mL) was added to obtain a deep red solution. After stirring for 5 h at room temperature, the solvent was removed in vacuo yielding a brownish solid. Subsequent dissolution in toluene (18 mL) gave a dark red solution, which was filtered to remove remaining solids. Upon concentration the product precipitated as a microcrystalline ochre solid from the solution. The mother liquor was filtered off, and the solid was dried in vacuo to yield the product as an ochre microcrystalline powder (72 mg, 0.050 mmol, 67% yield).

**1H NMR (400 MHz, 298 K, thf-d8):** \( \delta [ppm] = 7.16-7.11 (m, 2H, CH Ph), 7.08-7.04 (m, 2H, CH Ph), 7.01-6.90 (m, 4H, CH Ph), 3.65 (s, 4H, CH_2(Bb)), 2.35 (s, 6H, Me), 0.18 (s, 54H, MeTMS). \)

**13C NMR (101 MHz, 298 K, thf-d8):** \( \delta [ppm] = 147.03 (s, C Ph(N)), 137.19 (s, C Ph(Me)), 131.38 (s, C Hn), 130.60 (s, C Hn), 127.08 (s, C Hn), 125.66 (s, C Hn), 53.93 (s, CH_2(Bb)), 20.14 (s, Me), 3.28 (s, MeTMS). \)

**29Si-INEPT NMR (79 MHz, 298 K, thf-d8):** \( \delta [ppm] = -9.99 (s, Si TMS), -108.80 (s, Si Ge9). \)

**11B NMR (128 MHz, 298 K, thf-d8):** \( \delta [ppm] = 42.92 (brs, B Ge9). \)

**ESI MS (3500 V, 300 °C):** \( m/z = 1327.8 \) [Ge_{9}(Si(TMS)_3)_2DABo-tol]–.

**Elemental analysis:** anal. calcd. for Ge_{9}Si_{8}BC_{34}H_{72}N_{2}K: C, 28.41; H, 5.05; N, 1.95; found: C, 27.53; H, 4.87; N, 2.02. **ESI MS (3500 V, 300 °C):** \( m/z = 1398.7 \) [Ge_{9}(Si(TMS)_3)_2DABo-tol]–.
NHC\textsuperscript{Dipp}Cu[Ge\textsubscript{9}Si(TMS)\textsubscript{2}]\textsubscript{2}DAB\textsubscript{Pr}\textsuperscript{3 plus} (2a-Cu):

In a typical experiment K\textsubscript{2}[Ge\textsubscript{9}Si(TMS)\textsubscript{2}] (92 mg, 0.075 mmol, 1 equiv.) was weighted into a Schlenk tube in the glove box and a solution of DAB\textsubscript{Pr}-Cl (14.1 mg, 0.075 mmol, 1 equiv.) in dioxane (3 mL) was added, leading to a deep red solution. After stirring for 5 h at room temperature, the solvent was removed in vacuo to leave a brownish solid. The solid was dissolved in 1.5 mL MeCN and an acetonitrile solution of NHC\textsuperscript{Dipp}CuCl (36.5 mg, 0.075 mmol, 1 equiv.) was added dropwise, instantly leading to the precipitation of a reddish solid. After stirring for 15 min at r. t., the slightly red supernatant solution was filtered off, and the solid was washed with MeCN (2 mL) before it was dried in vacuo. Subsequently, the residue was dissolved in toluene (3 mL), and the deep red solution was filtered to remove remaining solids and then was stored in a freezer at -40 °C for crystallization. The product was obtained as red block-shaped crystals (49 mg, 0.028 mmol, 37%).

\textsuperscript{1}H NMR (400 MHz, 298 K, C\textsubscript{6}D\textsubscript{6}): \( \delta [ppm] = 7.36-7.30 (m, 2H, CH Ph), 7.27-7.23 (m, 4H, CH Ph), 6.25 (s, 2H, CH Im), 4.40 (hept, \(^3J \text{HH} = 6.8 \text{ Hz}, 2H, CH_{Pr(B)}), 3.20 (s, 4H, CH\textsubscript{2}(Bb)), 2.82 (hept, \(^3J \text{HH} = 7.2 \text{ Hz}, 4H, CH_{Pr}), 1.61 (d, \(^3J \text{HH} = 7.2 \text{ Hz}, 12H, Me_{Pr}), 1.22 (d, \(^3J \text{HH} = 6.8 \text{ Hz}, 12H, Me_{Pr(B)}), 0.41 (s, 54H, MeTMS). \textsuperscript{13}C NMR (101 MHz, 298 K, C\textsubscript{6}D\textsubscript{6}): \( \delta [ppm] = 145.40 (s, C_{Ph(N)-Dipp}), 135.50 (s, C_{Ch(Me)}), 130.63 (s, C_{Ph(Pr)}), 124.88 (s, C_{Ph(Im)}), 122.24 (s, CH_{Im}), 47.82 (s, CH_{Pr(B)}), 42.41 (s, CH_{2(Bb)}), 29.12 (s, CH_{Pr(NHC)}), 24.63 (s, Me_{Pr}), 22.32 (s, Me_{Pr(NHC)}), 3.20 (s, MeTMS). \textsuperscript{29}Si-INEPT NMR (79 MHz, 298 K, C\textsubscript{6}D\textsubscript{6}): \( \delta [ppm] = -9.56 (s, SiTMS), -104.67 (s, SiGe\textsubscript{9}). \textsuperscript{11}B NMR (128 MHz, 298 K, thf-d\textsubscript{8}): \( \delta [ppm] = 23.82 (brs, B_{Ge\beta}). \textsuperscript{Elemental analysis:} anal. calcd. for Ge\textsubscript{9}Si\textsubscript{8}BC\textsubscript{53}H\textsubscript{107}N\textsubscript{4}Cu: C, 36.31; H, 6.15; N, 3.20; found: C, 37.17; H, 6.37; N, 3.24.

**NHCD\textsuperscript{Dipp}Cu[Ge\textsubscript{9}Si(TMS)\textsubscript{2}]\textsubscript{2}DAB\textsubscript{o-tol} (3a-Cu):

In a typical experiment equimolar amounts of K\textsubscript{2}[Ge\textsubscript{9}Si(TMS)\textsubscript{2}] (92 mg, 0.075 mmol, 1 equiv.) and DAB\textsubscript{o-tol}-Cl (21.3 mg, 0.075 mmol, 1 equiv.) were weighted into a Schlenk tube in the glove box, and dioxane (3 mL) was added to obtain a deep red solution. After stirring for 5 h at room temperature, the solvent was removed in vacuo, yielding a yellow-brownish solid. The solid was dissolved in 1.5 mL MeCN, and an acetonitrile solution of NHC\textsuperscript{Dipp}CuCl (36.5 mg, 0.075 mmol, 1 equiv.) was added dropwise, instantly leading to the precipitation of a red solid. The slightly red supernatant solution was filtered off, and the solid was washed with MeCN (2 mL) before it was dried in vacuo. Subsequently the residue was dissolved in toluene (3 mL), and the deep red solution was filtered to remove remaining solids before the solution was stored in a freezer at -40 °C for crystallization. The product was obtained as red block-shaped crystals (56 mg, 0.030 mmol, 40%).

\textsuperscript{1}H NMR (400 MHz, 298 K, C\textsubscript{6}D\textsubscript{6}): \( \delta [ppm] = 7.49-7.46 (m, 2H, CH Ph), 7.38-7.34 (m, 2H, CH Ph), 7.22-7.19 (m, 2H, CH Ph), 7.14-7.11 (m, 4H, CH Ph), 6.24 (s, 2H, CH Im), 3.89 (s, 4H, CH\textsubscript{2}(Bb)), 2.82 (hept, \(^3J \text{HH} = 6.9 \text{ Hz}, 4H, CH_{Pr}), 2.48 (s, 6H, Me-o-tol), 1.64 (d, \(^3J \text{HH} = 6.9 \text{ Hz}, 12H, Me_{Pr}), 1.13 (d, \(^3J \text{HH} = 6.9 \text{ Hz}, 12H, Me_{Pr}), 0.38 (s, 54H, MeTMS). \textsuperscript{13}C NMR (101 MHz, 298 K, C\textsubscript{6}D\textsubscript{6}): \( \delta [ppm] = 145.45 (s, C_{Ph(N)-o-tol}), 145.18 (s, C_{Ph(N)-Dipp}), 136.08 (s, C_{Ph(Pr)}), 135.52 (s, C_{Ph(Pr)}), 131.32 (s, C_{Ph(Im)}), 130.77 (s, C_{Ph(Im)}), 130.71 (s, CH_{Im}), 126.77 (s, CH_{Im}), 126.20 (s, CH_{Im}), 124.82 (s, CH_{Pr}), 122.21 (s, CH_{Im}), 53.12 (s, CH_{2(Bb)}), 29.10 (s, CH_{Pr}), 25.78 (s, Me_{Pr}), 24.65 (s, Me_{Pr}), 19.68 (s, Me-o-tol), 3.27 (s, MeTMS). \textsuperscript{29}Si-INEPT NMR (79 MHz, 298 K, C\textsubscript{6}D\textsubscript{6}): \( \delta [ppm] = -9.72 (s, SiTMS), -104.67 (s, SiGe\beta). \textsuperscript{11}B NMR (128 MHz, 298 K, thf-d\textsubscript{8}): \( \delta [ppm] = 23.36 (brs, B_{Ge\beta}). \textsuperscript{Elemental analysis:} anal. calcd. for Ge\textsubscript{9}Si\textsubscript{8}BC\textsubscript{61}H\textsubscript{109}N\textsubscript{4}Cu \cdot 0.33 o-tol: C, 40.42; H, 5.98; N, 2.98; found: C, 40.53; H, 5.95, N, 2.89 (toluene content was calculated according to NMR spectrum of the respective sample, Figure S19).
3. Results and Discussion

3.1 Crystallographic data

Table S1. Crystallographic data for compounds 2a-Cu and 3a-Cu.

|          | 2a-Cu                          | 3a-Cu                          |
|----------|--------------------------------|--------------------------------|
| formula  | Ge₉Si₆BC₃₉H₁₀₈N₄Cu · 1 tol     | Ge₉Si₆BC₆₁H₁₀₈N₄Cu · 1.5 tol   |
| fw [g·mol⁻¹] | 1845.94                       | 1988.10                        |
| space group | P₂₁/n                         | I₂/a                           |
| a [Å]    | 20.5298(9)                    | 26.8283(8)                     |
| b [Å]    | 20.9024(7)                    | 25.2020(5)                     |
| c [Å]    | 20.5938(8)                    | 26.9602(7)                     |
| α [deg]  | 90                            | 90                             |
| β [deg]  | 102.548(3)                    | 90.959(2)                      |
| γ [deg]  | 90                            | 90                             |
| V [Å³]   | 8626.2(6)                     | 18226.0(8)                     |
| Z        | 4                             | 8                              |
| T [K]    | 150                           | 150                            |
| λ [Å]    | Mo Kα                         | Mo Kα                          |
| ρ calc [g·cm⁻³] | 1.421                          | 1.348                          |
| μ [mm⁻¹] | 3.474                         | 3.289                          |
| collected reflections | 188759                        | 222615                         |
| independent reflections | 16949                         | 17896                          |
| Rint / Rf | 0.0756/0.0529                 | 0.1076/0.0705                  |
| parameters / restraints | 779/24                        | 785/0                          |
| R₁ [I > 2 σ(I) / all data] | 0.0366/0.0740                 | 0.0394/0.0843                  |
| wR₂ [I > 2 σ(I) / all data] | 0.0701/0.0804                 | 0.0672/0.0778                  |
| goodness of fit | 0.978                         | 0.917                          |
| max./min. diff. el. density [e / Å³] | 0.95/-0.67                   | 0.67/-0.43                     |
| CCDC     | 1993869                       | 1993870                        |

Figure S1. Structures of compounds 2a-Cu (a) and 3a-Cu (b). For clarity reasons, protons and co-crystallized toluene molecules are omitted, and all carbon atoms are depicted as black wire sticks. Different views on compounds 2a-Cu and 3a-Cu can be found in the manuscript (Figure 2).
Table S2. Selected bond lengths in compound 2a-Cu.

| bond       | distance [Å] |
|------------|--------------|
| Ge1-Ge2    | 2.8957(6)    |
| Ge1-Ge3    | 2.8266(6)    |
| Ge1-Ge4    | 2.5071(6)    |
| Ge1-Ge5    | 2.5164(6)    |
| Ge2-Ge5    | 2.5363(6)    |
| Ge2-Ge6    | 2.4978(6)    |
| Ge3-Ge4    | 2.5171(6)    |
| Ge3-Ge6    | 2.4943(6)    |
| Ge4-Ge7    | 2.5598(6)    |
| Ge4-Ge9    | 2.5804(6)    |
| Ge5-Ge7    | 2.5673(6)    |
| Ge5-Ge8    | 2.5430(6)    |
| Ge6-Ge8    | 2.5306(6)    |
| Ge6-Ge9    | 2.5638(6)    |
| Ge7-Ge8    | 2.6536(7)    |
| Ge7-Ge9    | 2.5977(7)    |
| Ge8-Ge9    | 2.6739(6)    |
| Ge1-Cu1    | 2.4628(6)    |
| Ge2-Cu1    | 2.5716(6)    |
| Ge3-Cu1    | 2.4914(6)    |
| Ge4-Si1    | 2.384(1)     |
| Ge5-Si5    | 2.385 (1)    |
| Ge6-B1     | 2.063(5)     |
| Ge1-Ge7    | 3.584(1)     |
| Ge2-Ge8    | 3.164(1)     |
| Ge3-Ge9    | 3.283(2)     |
Table S3. Selected bond lengths in compound 3a-Cu.

| bond       | distance [Å] |
|------------|--------------|
| Ge1-Ge2    | 2.8220(6)    |
| Ge1-Ge3    | 2.8534(6)    |
| Ge1-Ge4    | 2.5139(6)    |
| Ge1-Ge5    | 2.5199(7)    |
| Ge2-Ge5    | 2.5229(6)    |
| Ge2-Ge6    | 2.4921(6)    |
| Ge3-Ge4    | 2.5138(6)    |
| Ge3-Ge6    | 2.4968(7)    |
| Ge4-Ge7    | 2.5552(7)    |
| Ge4-Ge9    | 2.5690(7)    |
| Ge5-Ge7    | 2.5632(7)    |
| Ge5-Ge8    | 2.5547(6)    |
| Ge6-Ge8    | 2.5417(7)    |
| Ge6-Ge9    | 2.5413(7)    |
| Ge7-Ge8    | 2.6124(7)    |
| Ge7-Ge9    | 2.6187(7)    |
| Ge8-Ge9    | 2.7396(7)    |
| Ge1-Cu1    | 2.4716(6)    |
| Ge2-Cu1    | 2.5586(7)    |
| Ge3-Cu1    | 2.5405(7)    |
| Ge4-Si1    | 2.377(1)     |
| Ge5-Si5    | 2.385(1)     |
| Ge6-B1     | 2.055(5)     |
| Ge1-Ge7    | 3.682(1)     |
| Ge2-Ge8    | 3.166(1)     |
| Ge3-Ge9    | 3.147(1)     |
3.2 NMR spectra

Figure S2. $^1$H NMR spectrum of 1a-K acquired in thf-$d_8$.

Figure S3. $^{13}$C NMR spectrum of 1a-K acquired in thf-$d_8$. 
Figure S4. $^{11}$B NMR spectrum of 1a-K acquired in thf-$d_8$. *excessive reactant; **unknown side product.

Figure S5. $^{29}$Si-INEPT NMR of 1a-K spectrum acquired in thf-$d_8$. 
Figure S6. $^1$H NMR spectrum of 2a-K acquired in thf-$d_8$.

Figure S7. $^{13}$C NMR spectrum of 2a-K acquired in thf-$d_8$. 
Figure S8. $^{11}$B NMR spectrum of 2a-K acquired in thf-$d_8$. Unassigned impurity.

Figure S9. $^{29}$Si-INEPT NMR spectrum of 2a-K acquired in thf-$d_8$. 

10
Figure S10. $^1$H NMR spectrum of 3a-K acquired in thf-$d_8$.

Figure S11. $^{13}$C NMR spectrum of 3a-K acquired in thf-$d_8$. 
Figure S12. $^{11}$B NMR spectrum of 3a-K acquired in thf-$d_8$.

Figure S13. $^{29}$Si-INEPT NMR spectrum of 3a-K acquired in thf-$d_8$. 
Figure S14. $^1$H NMR spectrum of 2a-Cu acquired in C$_6$D$_6$.

Figure S15. $^{13}$C NMR spectrum of 2a-Cu acquired in C$_6$D$_6$. 
Figure S16. $^{11}$B NMR spectrum of 2a-Cu acquired in thf-$d_8$. *: unknown side product.

Figure S17. $^{29}$Si-INEPT NMR spectrum of 2a-Cu acquired in C$_6$D$_6$. 
Figure S18. $^1$H NMR spectrum of 3a-Cu acquired in C$_6$D$_6$. 
Figure S19. $^1$H NMR spectrum of the elemental analysis sample of 3a-Cu acquired in C$_6$D$_6$. For signal assignment see Figure S18.

Figure S20. $^{13}$C NMR spectrum of 3a-Cu acquired in C$_6$D$_6$.
Figure S21. $^{11}$B NMR spectrum of 3a-Cu acquired in thf-$d_8$.

Figure S22. $^{29}$Si-INEPT NMR spectrum of 3a-Cu acquired in C$_6$D$_6$. 
3.3 ESI MS spectra

Figure S23. ESI MS spectrum (negative-ion mode, 3500 V, 300 °C) obtained upon examination of a thf solution of \([\text{Ge}_9\{\text{Si(TMS)}_3\}_3\text{DABMe}]^- 1\text{a}\) in thf. Besides the signal at \(m/z\) 1246.6 (1\text{a}), two further signals at \(m/z\) 1396 \([\text{Ge}_9\{\text{Si(TMS)}_3\}_3]\) and \(m/z\) 1322 (unidentified species) are observed as side products. A detailed view of the signal of anion 1\text{a} is provided in the manuscript (Figure 1).

Figure S24. ESI MS spectrum (negative-ion mode, 3500 V, 300 °C) obtained upon examination of a thf solution of \([\text{Ge}_9\{\text{Si(TMS)}_3\}_2\text{DABiPr}]^- 2\text{a}\) in thf (\(m/z\) 1302.6). A detailed view of the signal of anion 2\text{a} is provided in the manuscript (Figure 1).
Figure S25. ESI MS spectrum (negative-ion mode, 3500 V, 300 °C) obtained upon examination of a thf solution of $\text{[Ge}_9\text{Si(TMS)}_3\text{]_2}DAB^{\text{a,b,c}}$ 3a in thf ($m/z$ 1398.7). A detailed view of the signal of anion 3a is provided in the manuscript (Figure 1).
3.4 Quantum chemical calculations at DFT-PBE0/TZVP level of theory

Table S4. Molecular orbital energies of anion 1a.

| Orbital            | Energy [eV] (position) |
|--------------------|------------------------|
| HOMO-LUMO gap      | 3.8                    |
| LUMO+4             | -0.160 (DAB)           |
| LUMO+3             | -0.493 ([Ge9])        |
| LUMO+2             | -0.638 ([Ge9])        |
| LUMO+1             | -0.689 ([Ge9])        |
| LUMO                | -0.810 ([Ge9])       |
| HOMO                | -4.610 ([Ge9])       |

Figure S26. Molecular orbitals at anion 2a. Orbital figures are drawn in such way that 50% of the density is enclosed within the isosurface, corresponding to approximately 0.04 a.u. isovalue.

Table S5. Molecular orbital energies of anion 2a.

| Orbital            | Energy [eV] (position) |
|--------------------|------------------------|
| HOMO-LUMO gap      | 3.8                    |
| LUMO+4             | -0.098 (DAB)           |
| LUMO+3             | -0.456 ([Ge9])        |
| LUMO+2             | -0.618 ([Ge9])        |
| LUMO+1             | -0.640 ([Ge9])        |
| LUMO                | -0.778 ([Ge9])       |
| HOMO                | -4.577 ([Ge9])       |
Figure S27. Molecular orbitals at anion 3a. Orbital figures are drawn in such way that 50% of the density is enclosed within the isosurface, corresponding to approximately 0.04 a.u. isovalue.

Table S6. Molecular orbital energies of anion 3a.

| Orbital        | Energy [eV] (position) |
|----------------|------------------------|
| HOMO-LUMO gap  | 3.8                    |
| LUMO+5         | -0.113 (DAB)           |
| LUMO+4         | -0.202 (DAB)           |
| LUMO+3         | -0.476 ([Ge9])         |
| LUMO+2         | -0.489 ([Ge9])         |
| LUMO+1         | -0.656 ([Ge9])         |
| LUMO           | -0.742 ([Ge9])         |
| HOMO           | -4.516 ([Ge9])         |
Figure S28. Molecular orbitals at the theoretical anion 4a. Orbital figures are drawn in such way that 50% of the density is enclosed within the isosurface, corresponding to approximately 0.04 a.u. isovalue.

Table S7. Molecular orbital energies of the theoretical anion 4a.

| Orbital     | Energy [eV] (position) |
|-------------|------------------------|
| HOMO-LUMO gap | 3.4                    |
| LUMO+2      | -0.693 ([Ge=])         |
| LUMO+1      | -0.706 ([Ge=])         |
| LUMO        | -1.197 (B)             |
| HOMO        | -4.567 ([Ge=])         |
| HOMO-1      | -4.873 ([Ge=])         |
| HOMO-2      | -5.042 ([Ge=])         |
4. References

1. O. Kysliak, A. Schnepf, *Dalton Trans.* **2016**, *45*, 2404-2408.
2. C. Kleeberg, *Dalton Trans.* **2013**, *42*, 8276-8287.
3. Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069-16079.
4. L. Hintermann, *Beilstein J. Org. Chem.* **2007**, *3*, 22.
5. O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.* **2013**, *49*, 10483-10485.
6. G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, Göttingen, 1997.
7. G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8.
8. A. Spek, *Acta Crystallogr., Sect. D: Struct. Biol.* **2009**, *65*, 148-155.
9. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.
10. a) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305; d) TURBOMOLE V7.3 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from www.turbomole.com.
11. a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283-290; b) M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136-9148; c) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.
12. A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, *5*, 799-805.
13. G. Knizia, J. E. Klein, *Angew. Chem. Int. Ed.* **2015**, *54*, 5518-5522; *Angew. Chem.* **2015**, *127*, 5609-5613.