Frustrated Lewis Pairs

Boranyl-Functionalized [Ge₉] Clusters: Providing the Idea of Intramolecular Ge/B Frustrated Lewis Pairs

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 85th Birthday

Abstract: *The unique three-dimensional structure of spherical, homoatomic nine-atom germanium clusters opens various possibilities for the spatial arrangement of functional groups. Ligands comprising lone pairs have recently been introduced in the cluster sphere, and we now report the addition of a boranyl group to the cluster featuring a Ge−B exo-cluster bond. The reaction of the twofold-silylated cluster [Ge₉{Si-(TMS)₃}₂]²⁻ (TMS = trimethylsilyl) with 2-chloro-1,3,2-diaza-borolidines DAB^R-Cl leads to the first boranyl-functionalized [Ge₉] clusters [Ge₉{Si(TMS)₃}₂DAB^R]⁻ (R = methyl (**1a**), iso-propyl (**2a**), ortho-tolyl (**3a**)). The anions **2a** and **3a** were structurally characterized as [NHC^Dipp Cu]⁺ complexes (NHC^Dipp = 1,3-di(2,6-diisopropylphenyl)imidazolylidine) through single crystal X-ray structure determination. Quantum-chemical calculations manifest the frustrated Lewis pair (FLP) character of the boranyl-functionalized cluster [Ge₉-{Si(TMS)₃}₂BCy₂]⁻ (**4a**).*

By fusion of stoichiometric amounts of the elements, the tetrel *Zintl* phase K₄Ge₉ containing soluble [Ge₉]⁴⁻ ions is easily accessible. These clusters have shown great potential to react with main group and transition metal compounds.[1] The silylation of [Ge₉] through a heterogeneous reaction of K₄Ge₉ with chloro-tris(trimethylsilyl)silane in MeCN has proven to be a straightforward way to reduce the fourfold negative cluster charge thereby enhancing the stability and solubility of the clusters. By variation of the stoichiometry of the reaction, either bis-silylated [Ge₉{Si(TMS)₃}₂]²⁻ or tris-silylated [Ge₉-{Si(TMS)₃}₃]⁻ (TMS: trimethylsilyl) species are accessible in high yields.[2] Furthermore, various tris-silylated clusters have been prepared with silyl groups of different bulkiness.[3] In

similar reactions the tris-stannylated cluster [Ge₉(Sn^iPr₃)₃]⁻ can also be obtained.[4] Recently, also ligands with donor functions have been introduced to the sphere of the [Ge₉] clusters allowing for subsequent reactions with Lewis acids, leading to charge-neutral zwitterionic cluster compounds [Ge₉{Si(TMS)₃}₂(^tBu₂P)]*M*(NHC^Dipp) (*M*: Cu, Ag, Au).[5] Up to three ligands with Lewis base groups can be introduced in form of the tris-phosphanyl-functionalized clusters [Ge₉-(PRR¹)₃]⁻ (R: N^iPr₂; R¹: N^iPr₂, ^tBu).[6] These clusters still possess six or seven unsubstituted cluster vertices with low oxidation state,[7] and are thus prone to undergo subsequent reactions.

Owing to the shielding of the [Ge₉] core, reactions of the tris-silylated cluster are limited to the introduction of less bulky main group element ligands, yielding uncharged cluster compounds with Ge−C, Ge−P and Ge−Sn *exo*-cluster bonds such as [Ge₉{Si(TMS)₃}₃R] [R: Et,[8] (CO)^tBu,[9] ^tBu,[9] {(CH₂)ₙCH=CH₂} (*n*: 1, 3)[7c]], [Ge₉{Si(TMS)₃}₃(PRR¹)] (R = R¹: ^iPr, Cy;[5] R: ^tBu, R¹: {(CH₂)₃CH=CH₂}[10]), and [Ge₉{Si-(TMS)₃}₃SnR₃] (R: ^nBu,[8] Ph[11]). Except for the Sn-containing species, which (partially) show multicenter Ge−Sn bonds, all main group element fragments are attached to the [Ge₉] entity via 2-center-2-electron (2c-2e) bonds pointing radially away from the center of the cluster. The Lewis basic property of the [Ge₉] core is manifested in various isolated transition metal decorated clusters such as [Ge₉{Si(TMS)₃}₃TiCp₂-(MeCN)], [Cp₂Ti(η¹-Ge₉{Si(TMS)₃}₂)₂]³⁻,[12] [Ge₉{Si(TMS)₃}₃-Cr(CO)₅]⁻[13] as well as [Zn(η¹-Ge₉{Si(TMS)₃}₂)₄]⁶⁻.[14]

Because of the decreased shielding of the [Ge₉] cluster core, the di-anion [Ge₉{Si(TMS)₃}₂]²⁻ is an attractive candidate for subsequent reactions. Upon addition of further halo-silanes, mixed-substituted [Ge₉] clusters of the general composition [Ge₉{Si(TMS)₃}₂R]⁻ [R: Si(TMS)₂SiPh₃,[2a] Si-(TMS)₂Si(^iPr)₃,[3b] SiPh₂{(CH₂)ₙCH=CH₂}[16] (*n* = 1, 3)] are formed. Using a rigid bis-halo-silane, a connection of two clusters to the anion [{Si(SiMe₃)₃}₂Ge₉-SiMe₂-(C₆H₄)-SiMe₂-Ge₉{Si(SiMe₃)₃}₂]²⁻ is achieved.[17] Comparable to the reactions reported for the tris-silylated species, alkyl-, germanyl- or phosphanyl-decorated anions [Ge₉{Si(TMS)₃}Et]²⁻ (one Si(TMS)₃ group is cleaved upon crystallization),[18] [Ge₉{Si-(TMS)₃}₂Ge(TMS)₃]⁻[19] or [Ge₉{Si(TMS)₃}₂(PRR¹)]⁻ (R, R¹: alkyl, aryl, aminoalkyl)[5,10,20] can be synthesized, revealing the prosperous chemistry of [Ge₉{Si(TMS)₃}₂]²⁻ with halo-main group element compounds.

We have shown that ligands with free electron lone pairs such as phosphanyl groups (Scheme 1, **A**) allow for the attachment of Lewis acidic organometallic fragments,[5,10,20] and now focused on the introduction of electron acceptor

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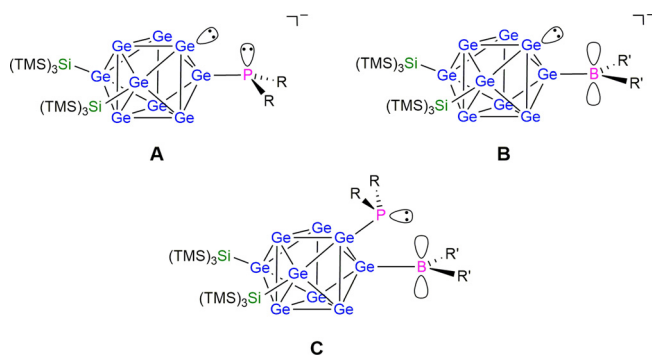
Scheme 1. Different Lewis basic sites at [Ge₉] occurring in reported **A**[5,10,20] and boranyl-functionalized [Ge₉] cluster **B** with FLP character according to quantum-chemical calculations. The lone pair of only one Ge atom is shown. **C** shows a potential mixed-functionalized [Ge₉] core featuring both Lewis acidic and basic moieties.

functions to the sphere of the [Ge₉] cluster (Scheme 1, **B**). Scheschkewitz and *co*-workers recently reported on the grafting of silicoinoids of general composition Si_6R_6 with $[BH_3]^-$ fragments,[21] as well as p-doping such clusters by a formal exchange of one Si vertex by a boranyl group.[22] These clusters exhibit unsubstituted vertices and thus are conceptually related to *Zintl* ions.[21b] For several reasons we particularly suspected halo-boranes, 1,3,2-diazaborolidines (DABs), as promising candidates for this venture. Due to the straightforward preparation of 2-halo-DABs from BX_3 (X: Cl, Br) and diamines, the wingtip substituents can easily be tuned concerning their bulkiness. Furthermore, the electron deficiency of the boron center is compensated by π-donation of the lone pairs of adjacent N atoms into the boron p_z orbital, thereby enhancing the stability of the compounds. These species have been established as ligands in complex chemistry reported for the shell-structured ion $[In_{68}\{DAB^{Dipp}\}_{12}]^-$[23] or in lanthanide boryl compounds.[24] Furthermore, diazaboroles act as σ-donor ligands and have recently been used to prepare new types of low-valent group 14 element (Si,[25] Ge,[25,26] Sn,[25,26c,27] Pb[28]) compounds. Such species are prone to activate small molecules via oxidative addition (e.g. H₂ or further nonpolar E−H bonds; E: B, Si, N, O), and also insertion reactions into the Ge−B bond (e.g. phenylacetylene and diphenylacetylene) have been reported.[26c,e,27a] Within this work we investigated reactions of the negatively charged germanide cluster $[Ge_9\{Si(TMS)_3\}_2]^{2-}$ towards DABs, focusing on the generation of a hitherto

unreported boranyl-functionalized cluster species revealing unprotected Ge atoms in negative oxidation states.

Treatment of solid $K_2[Ge_9\{Si(TMS)_3\}_2]$ with THF or 1,4-dioxane solutions of DAB^R-Cl (R: Me, ^{i}Pr, *o*-tol, Mes = 2,4,6-trimethylbenzene) yielded deep red reaction mixtures, which were stirred for 3–5 h at room temperature. Subsequently, the mixtures were filtered, and the solvent was removed in vacuo. The remaining oily solids were treated with hexane, which was then removed in vacuo to eliminate traces of remaining solvents (this procedure was repeated twice). The brown (R: Me, Mes) or ochre (R: ^{i}Pr, *o*-tol) residues were investigated by NMR spectroscopy.

¹H NMR examinations indicated the formation of $[Ge_9\{Si(TMS)_3\}_2DAB^R]^-$ [R: Me (**1a**), ^{i}Pr (**2a**) and *o*-tol (**3a**)] by the downfield shift of the cluster's silyl group protons and the 1:2 ratio of signals assigned to the boranyl moiety and the cluster's silyl protons. The formation of **1a**–**3a** (Scheme 2a) was confirmed by further NMR experiments (¹¹B, ¹³C and ²⁹Si). In the ¹¹B NMR spectra a significant downfield shift of the product signal from approx. 27 ppm (thf-d_8) (DAB^R-Cl; R: Me, ^{i}Pr, *o*-tol) to 43.31 ppm (**1a**), 41.90 ppm (**2a**) and 42.92 ppm (**3a**) was observed. Moreover, anions **1a**–**3a** were detected in ESI MS experiments at *m/z* 1246.6 (**1a**), *m/z* 1302.6 (**2a**) and *m/z* 1398.7 (**3a**) in the negative-ion mode (Figure 1).
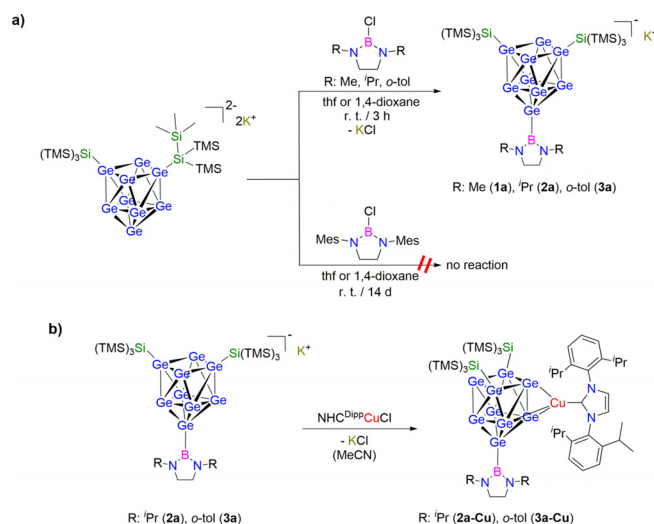
Scheme 2. a) Overview on the reactivity of $K_2[Ge_9\{Si(TMS)_3\}_2]$ towards DAB^R-Cl (R: Me, ^{i}Pr, *o*-tol, Mes); b) formation of **2a-Cu** and **3a-Cu** upon addition of NHC^{Dipp}CuCl to **2a** and **3a**, respectively.
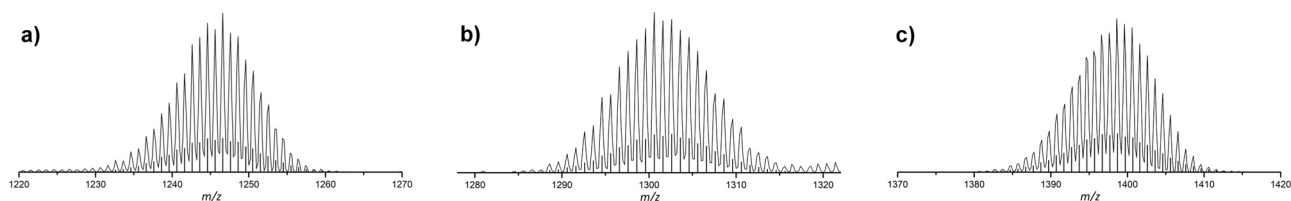

Figure 1. Selected areas of ESI MS spectra of anions **1a-3a**. Spectra were recorded from diluted THF solutions of the samples in the negative-ion mode (3500 V, 300°C). Calculated isotope patterns are represented as black bars. a) molecule peak of **1a** $[Ge_9\{Si(TMS)_3\}_2DAB^{Me}]^-$ at *m/z* 1246.6; b) molecule peak of **2a** $[Ge_9\{Si(TMS)_3\}_2DAB^{iPr}]^-$ at *m/z* 1302.6; c) molecule peak of **3a** $[Ge_9\{Si(TMS)_3\}_2DAB^{o-tol}]^-$ at *m/z* 1398.7. The respective overview spectra can be found in the Supporting Information.

For crystallization, the crude solids **1a-K** to **3a-K** containing the K⁺-salt of **1a** to **3a** were dissolved in toluene and filtered. Unfortunately, the purification of **1a-K** and **2a-K** has not been successful to date, but [Ge₉{Si(TMS)₃}₂DAB^{o-tol}]K (**3a-K**) was obtained as an ochre, polycrystalline powder from concentrated toluene solutions. In analogous reactions of K₂[Ge₉{Si(TMS)₃}₂] with DAB^{Mes}-Cl no conversion of the reactants was observed (14 d at room temperature and at elevated temperature; Scheme 2a). Since the DAB^{Mes} ligand has a higher steric demand, we assume that there is a steric limitation for the introduction of boranyl moieties at [Ge₉].

In previous studies we found that neutral species with a [NHC^{Dipp}Cu]⁺ moiety as the fourth substituent crystallized much more easily than the respective anionic species.[6,20] Since the isolation of single-crystalline material suitable for structure determination was not possible from the isolated solids, we carried out subsequent reactions of **1a-K** to **3a-K** with NHC^{Dipp}CuCl (Scheme 2b). **1a-K** to **3a-K** were dissolved in MeCN and the resulting dark red solutions were treated dropwise with MeCN solutions of the Cu-NHC complex, immediately resulting in the precipitation of brown (**1a-Cu**) or reddish (**2a-Cu**, **3a-Cu**) solids. In order to assure complete conversion, the mixtures were stirred at room temperature for further 30 min, before the supernatant red solutions were filtered, and the residues were washed with MeCN. ¹H NMR examinations of the solids indicated the addition of [NHC^{Dipp}Cu]⁺ to **2a** and **3a** under formation of NHC^{Dipp}Cu[Ge₉{Si(TMS)₃}₂DAB^R] [R: ^iPr (**2a-Cu**) and *o*-tol (**3a-Cu**)]. By contrast, the product resulting from the reaction of **1a** with NHC^{Dipp}CuCl was identified as the previously published species (NHC^{Dipp}Cu)₂[Ge₉{Si(TMS)₃}₂] comprising two [NHC^{Dipp}Cu]⁺ moieties.[29] The Ge–B bond cleavage upon the reaction with the Cu-NHC complex hints for an increased lability of DAB moieties with smaller wingtip substituents. Crude materials of **2a-Cu** and **3a-Cu** were dissolved in toluene and filtered to remove remaining solids. The samples were stored in a freezer at −40 °C for crystallization yielding red block-shaped single crystals of **2a-Cu** and **3a-Cu** suitable for single crystal X-ray diffraction. The isolated materials were further characterized by elemental analysis and NMR spectroscopy (¹H, ¹¹B, ¹³C and ²⁹Si). Compounds **2a-Cu** and **3a-Cu** crystallize in the monoclinic space groups P2₁/n and I2/a, respectively, and show functionalized clusters and [NHC^{Dipp}Cu]⁺ moieties in a 1:1 ratio. The shapes of the [Ge₉] cluster cores are best described as slightly distorted, tricapped trigonal prisms (their heights are emphasized by fragmented thick lines between the eclipsed triangles Ge1 to Ge3 and Ge7 to Ge9, Figure 2), with one prism height [d(Ge1-Ge7) = 3.584(1) Å (**2a-Cu**) and d(Ge1-Ge7) = 3.682-(1) Å (**3a-Cu**)] being significantly longer compared to the others [3.164(2) Å (Ge2-Ge8) and 3.283(1) Å (Ge3-Ge9) in **2a-Cu** and 3.147(1) Å (Ge3-Ge9) and 3.166(1) Å (Ge2-Ge8) in **3a-Cu**], resulting in C₂ᵥ-symmetry. The three substituents (two silyl groups and the DAB moiety) bind to three capping Ge atoms (Ge4, Ge5 and Ge6; Figure 2). All Ge-Ge and Ge-Si distances are in the typical range of known functionalized [Ge₉] cluster species.[2,30] The DAB ligands in **2a-Cu** and **3a-Cu** bind to the [Ge₉] cluster through *exo*-cluster single bonds between one cluster vertex atom and the B atom, with Ge–B
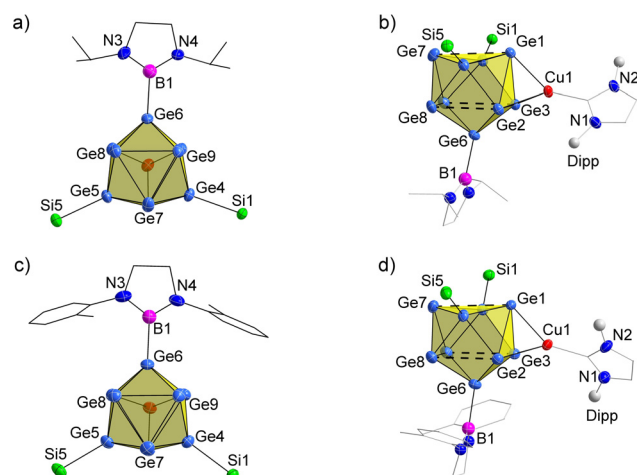

Figure 2. Molecular structures of compounds **2a-Cu** (a,b) and **3a-Cu** (c,d). Ellipsoids are shown at a 50% probability level. a) Front view on compound **2a-Cu** with the two silyl groups and the DAB ligand bonding to the capping Ge atoms of the tricapped trigonal prism. b) Side view on **2a-Cu** showing C₂ᵥ symmetric shape of [Ge₉] core (prism heights are indicated by thick fragmented lines) and coordination of [NHC^{Dipp}Cu]⁺ moiety via one of the trigonal prism bases. c) and d) analogue pictures for compound **3a-Cu**. In all pictures protons as well as toluene solvent molecules are omitted. Moreover, TMS groups of silyl substituents (a–d) as well as the NHC^{Dipp} (a,c) ligand are omitted and carbon atoms of DAB ligands are shown as black (a,c) or grey (b,d) wire sticks for clarity. For the same reason the Dipp wingtips in b) and d) are indicated as grey spheres.

distances of 2.063(5) Å and 2.055(5) Å, respectively. The bond lengths are in the range of previously reported Ge–B bonds in germaborates,[31] germacarboranes[32] or germylenes.[25,26b,c,e,33] The [NHC^{Dipp}Cu]⁺ fragment coordinates one of the trigonal bases of the prism in an η³-fashion with Ge-Cu distances known for analogous complexes.[6,20,29,34]

The anions **1a**–**3a** and compounds **2a-Cu** and **3a-Cu** are the first examples of boranyl-functionalized [Ge₉] clusters. In general, group 13 element decoration of silylated [Ge₉] species is rather rare if compared to the plethora of examples for group 14 (C-, Si-, Ge-, Sn-based) and group 15 (P) element substituted [Ge₉] clusters. [Ge₉{Si(TMS)₃}₃Tl] is the only known example of a triel derivative, however, the Tl atom is included as an additional cluster vertex.[8]

The most interesting aspect about the anions **1a**–**3a** is the targeted introduction of boranyl groups to the [Ge₉] core, which is an important step on the way to the possible formation of intramolecular frustrated Lewis acid base pairs (FLPs). The FLP is formed by the combination of an electron-deficient electrophilic boranyl ligand and the [Ge₉] cluster core comprising electron lone pairs at each ligand-free Ge vertex atom with Lewis base properties (Scheme 1, **B**).

In order to obtain a deeper understanding of the electronic situation we carried out quantum-chemical calculations at the DFT-PBE0/TZVP level of theory[35] using the TURBOMOLE program package.[36] As an initial structure model for the [Ge₉] cluster the single crystal data of compounds **2a-Cu** and **3a-Cu** were used, the [NHC-Cu]⁺ fragments were deleted, and a COSMO solvent field was applied to counter the anionic charge.[37] As depicted in

Figure 3 the HOMO and LUMO of **2a** are located at the [Ge$_9$] cluster, and it is not until LUMO + 4 that the LUMO becomes boron-centered (for more MO diagrams see Supporting Information). Similar findings were obtained for anion **3a**. The calculated HOMO–LUMO gaps are 3.8 eV for anions **1a**–**3a**, which is in a similar range as reported for 1,3,2,5-diazadiborinines (up to 3.7 eV), which are capable of activating small molecules like CO_2, ketones and alkenes.[38] In order to investigate the impact of the ligand design on the localization of the HOMO and LUMO, further theoretical studies were carried out, in which the diazaborolidine ligand is substituted by a -BCy$_2$ group ([Ge$_9${Si(TMS)$_3$}$_2$BCy$_2$]$^-$, **4a**). Indeed, we observed a shift in the localization of the LUMO, which as for a FLP required becomes boron-based, and the HOMO–LUMO gap decreases to 3.4 eV. This arrangement of orbitals could be favorable to facilitate interactions with small molecules in a frustrated Lewis acid–base type manner, with the cluster acting as the Lewis base (HOMO) and the boranyl ligand as the Lewis acid (LUMO). Interestingly, also the
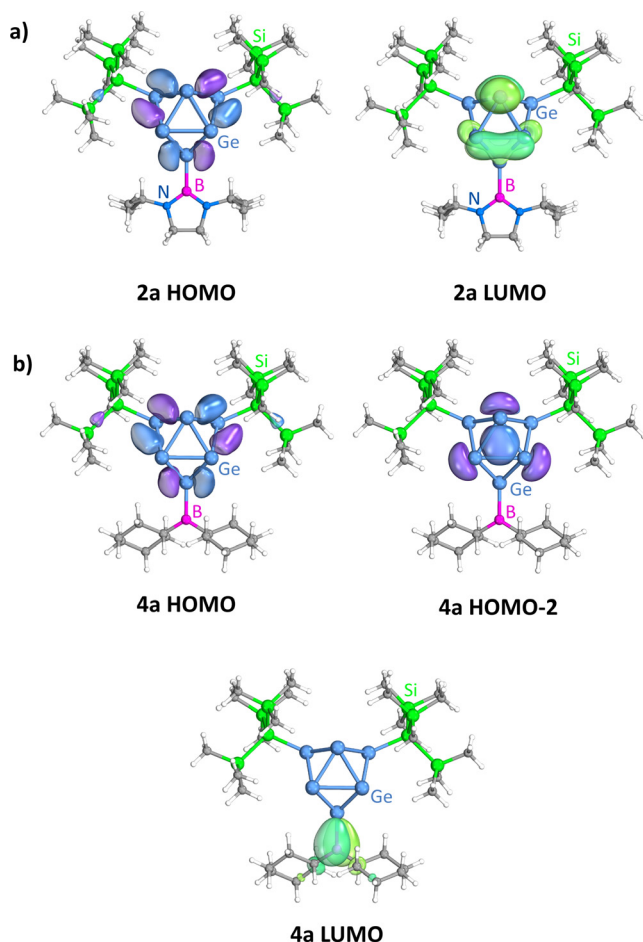
HOMO-2 of **4a**, which is energetically only 0.5 eV lower in energy than the HOMO, allows for another spatial orientation to interact with a Lewis acid. Investigations on the targeted synthesis of **4a** and other derivatives are ongoing. We found for example that the sterically more demanding arylborane Mes$_2$BBr remained unreactive in dioxane solution.

At this point it has to be mentioned that Roesky et al. previously reported an intramolecular Ge/B Lewis pair which, however, showed Ge–B interactions in the ground state (no FLP).[33b] Due to their unique reactivity, FLPs have recently gained a lot of attention with respect to the activation of small molecules (CO_2, H_2), and have also been applied as metal-free hydrogenation catalysts for imines or enamines.[39] Furthermore, phosphine-borane based FLPs have been reported to insert sterically demanding azides.[40] These reports hold promise for further investigations at the here presented systems. The unique three-dimensional structure of the [Ge$_9$] core opens further possibilities for the spatial arrangement of Lewis-acid Lewis-base pairs. In this context we are currently investigating the addition of a phosphanyl group adjacent to a boranyl group (Scheme 1, **C**).

In summary we report on the synthesis of the first boranyl functionalized [Ge$_9$] clusters [Ge$_9${Si(TMS)$_3$}$_2$DAB^R]$^-$ [R: Me (**1a**), ^{i}Pr (**2a**), *o*-tol (**3a**)]. The addition of a DAB ligand to the [Ge$_9$] core is limited by steric factors (no reaction of bulky DAB^{Mes}-Cl). Subsequent reactions with NHC^{Dipp}CuCl led to the formation of NHC^{Dipp}Cu[Ge$_9${Si(TMS)$_3$}$_2$DAB^R] [R: ^{i}Pr (**2a-Cu**) and *o*-tol (**3a-Cu**)]. The structural characterization is in accordance with the spectroscopic data and confirms the presence of a localized Ge–B *exo*-cluster bond. Moreover, Ge–B bond cleavage during the analogous reaction with **1a** reveals an increased lability for DAB ligands with small wingtips (cleavage of DAB^{Me}). Molecular orbital analyses for the anions **1a**–**3a** using DFT calculations show [Ge$_9$] based HOMOs and LUMOs. The isolation of the anions **1a**–**3a** clearly accounts for the possibility of introducing boranyl moieties to the cluster core. Moreover, quantum-chemical calculations reveal the possibility of altering the position of the LUMO by changing the boranyl group to -BCy$_2$ (**4a**), which might open the way to [Ge$_9$] cluster-based FLP systems. Cyclic-ether ring opening and FLP-type nitrile activation of halo-borane nonagermanide-cluster Lewis acid-base-pairs will be reported in a forthcoming paper.[41]

a)

2a HOMO   **2a LUMO**

b)

4a HOMO   **4a HOMO-2**

4a LUMO

Figure 3. Selected molecular orbitals of a) the anion [Ge$_9${Si-(TMS)$_3$}$_2$DAB^{iPr}]$^-$ (**2a**) and b) the theoretical anion [Ge$_9${Si-(TMS)$_3$}$_2$BCy$_2$]$^-$ (**4a**). The calculations were carried out on the DFT-PBE0/TZVP level of theory, using the single crystal structure data of **2a-Cu** and **3a-Cu** with deleted [NHC-Cu]$^+$ fragments as a starting point. Orbital figures are drawn so that 50% of the density is enclosed within the isosurface, corresponding to approximately 0.04 a.u. isovalue.

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Conflict of interest

The authors declare no conflict of interest.

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