An NHC-Stabilized H$_2$GeBH$_2$ Precursor for the Preparation of Cationic Group 13/14/15 Hydride Chains

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Dedicated to Professor Rainer Anwander on the occasion of his 60th birthday

Abstract: The synthesis, characterization and reactivity studies of the NHC-stabilized complex IDipp·GeH$_2$BH$_2$OTf (**1**) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) are reported. Nucleophilic substitution of the triflate (OTf) group in **1** by phosphine or arsine donors provides access to the cationic group 13/14/15 chains [IDipp·GeH$_2$BH$_2$ERR^{1}R^2]$^+$ (**2** E = P; R, R^1 = H; R^2 = ^{t}Bu; **3** E = P; R = H; R^1, R^2 = Ph; **4a** E = P; R, R^1, R^2 = Ph; **4b** E = As; R, R^1, R^2 = Ph). These novel cationic chains were characterized by X-ray crystallography, NMR spectroscopy and mass spectrometry. Moreover, the formation of the parent complexes [IDipp·GeH$_2$BH$_2$PH$_3$][OTf] (**5**) and [IDipp·GeH$_3$][OTf] (**6**) were achieved by reaction of **1** with PH$_3$. Accompanying DFT computations give insight into the stability of the formed chains with respect to their decomposition.

Introduction

The use of N-heterocyclic carbenes (NHCs) in synthesis is a powerful tool for the stabilization of reactive inorganic species. This strategy is widely employed to access main group compounds with low-coordinate (and low-oxidation state) centers, leading to new paradigms in reactivity and catalysis.[1] One prominent example of NHC-stabilization is Robinson's disilene, IDipp·Si=Si·IDipp (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene), with the Si atoms in the formal oxidation state of zero.[2]

For NHC-supported compounds of Ge, investigations started with the isolation of carbene-germylene adducts (type **I**, Chart 1)[3,4] and the first reactivity studies of their Lewis basic character.[4] As a result, *Baines* and coworkers were able to

synthesize germanium(IV) cations by treatment of germylene adducts with alkyl iodides (type **II**, Chart 1).[5] Soon after, related NHC-supported germanium compounds were reported,[6] followed by their lighter silicon congeners,[7] the latter spurred by the development of versatile NHC—Si(II) precursors.[7b,c,v]
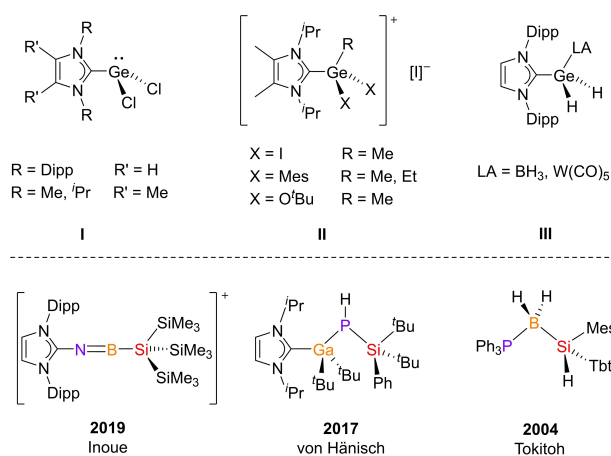

Chart 1. Different types of N-heterocyclic carbene-stabilized germanium complexes (top) and selected examples for mixed group 13/14/15 chain compounds (bottom).

In 2009, the *Rivard* and *Jones* groups simultaneously reported the formation of the germanium dichloride adduct IDipp·GeCl$_2$ by the reaction of IDipp with GeCl$_2$·dioxane.[3] Starting from this Ge(II) complex, *Jones* subsequently achieved the formation of the NHC-stabilized digermanium(0) compound IDipp·Ge=Ge·IDipp,[3a] which represents the heavier homolog of Robinson's disilene. *Rivard* and coworkers then prepared the first donor/acceptor- stabilized parent germanium(II) dihydride complex IDipp·GeH$_2$·BH$_3$ (type **III**, Chart 1) through the reaction of IDipp·GeCl$_2$ with excess of LiBH$_4$.[3b,8] Our group developed the concept of donor/acceptor stabilization for the formation of

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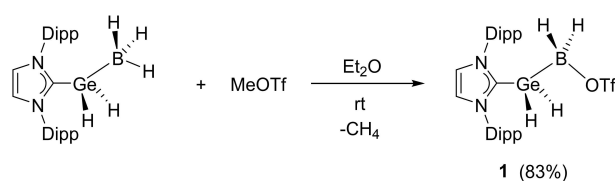European Chemical
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several unsaturated group 13/15 compounds of the type LA·H₂EE'H₂·LB (E = group 15 element, E' = group 13 element, LA = Lewis acid, LB = Lewis base).[9] Later it was even possible to obtain the only LB-stabilized pnictogenyltrieles H₂EE'H₂·LB, which enabled the study of their reactivity in detail, and resulted in the formation of cationic chains of phosphanyl- and arsanylboranes.[10]

Against the backdrop of the above-mentioned prior work, we wondered whether carbene-stabilization would enable the formation of linear, hydride-rich, group 14/13/15 sequences using Rivard's group 14/13 compound IDipp·GeH₂BH₃[3b] as a precursor. Those compounds might be applied as single source precursors for 13-14-15 heteroatomic materials, in contrast to the currently used multisource approaches. Such materials can be used in small band gap optical devices and other applications.[11] In general, only few examples of mixed-element group 13/14/15 compounds are known,[12] especially if only chain compounds are considered (cf. Chart 1 for examples).[13] Notably, borane adducts provide an opportunity for further functionalization, as noted by the *Curran* group in their formation of the NHC-stabilized boryl-triflate IDipp·BH₂OTf by the reaction of IDipp•BH₃ with triflic acid.[14] Hence we reasoned that it may also be possible for the more complex borane adduct IDipp·GeH₂BH₃ to be functionalized in a similar way, with retention of the group 14/13 element sequence. Herein, we report on a novel synthetic strategy to obtain unprecedented cationic group 13/14/15 compounds by substitution reactions involving a NHC-stabilized H₂GeBH₂ precursor as a common building block.

Results and Discussion

Computational studies at B3LYP/def2-TZVP level of theory reveal that the gas phase reaction between IDipp·GeH₂BH₃ and MeOTf with methane evolution and formation of IDipp·GeH₂BH₂OTf (**1**) is highly exothermic (by 196 kJ mol⁻¹) and highly exergonic at room temperature (by 185 kJ mol⁻¹). Indeed, the reaction of IDipp·GeH₂BH₃ with MeOTf in Et₂O at room temperature leads quantitatively to the formation of **1**, which can be crystallized in good yields (83%) from a concentrated Et₂O solution at −30 °C (Scheme 1). Compared to Curran's reaction of IDipp·BH₃ with HOTf in CDCl₃, where the formed triflate IDipp•BH₂OTf cannot be isolated easily, in our case the clean reaction with MeOTf is observed.[14]

While **1** is stable as a solid at ambient temperatures in an inert atmosphere, it slowly decomposes in CH₂Cl₂, thf, as well as in Et₂O. The ¹H NMR spectrum of **1** in thf-d₈ shows a broad signal at $\delta = 2.61$ ppm, which could be assigned to the BH₂ moiety, as confirmed by ¹H{¹¹B} NMR spectroscopy. The second non-carbene signal at $\delta = 3.58$ ppm for the Ge*H₂*-hydrogens shows a triplet pattern due to coupling with the adjacent BH₂ unit. The ¹¹B NMR spectrum of **1** consists of a broad singlet at $\delta = -3.2$ ppm, which is significantly downfield-positioned compared to the starting material IDipp·GeH₂BH₃ ($\delta = -40.0$ ppm).[3b]

The mass spectrum (ESI-MS), obtained from a thf solution of **1**, shows a peak at 549.3 m/z, which can be assigned to the solvated fragment [IDipp·GeH₂BH₂(thf)]⁺. A single-crystal X-ray structure analysis of **1** (Figure 1) reveals a bond between the boron atom and one oxygen atom of the OTf group with a B–O bond length of 1.564(3) Å, which is slightly longer compared to the boryl-tosylate adduct IDipp·BH₂OTs [B-O = 1.522(7) Å].[14] The Ge1-B1 distance in **1** [2.081(3) Å] is slightly longer than for the borane adduct IDipp•GeH₂BH₃ [Ge-B = 2.053(3) Å], while the coordinative C1-Ge1 bond length in **1** [2.003(2) Å] is shorter than the corresponding bond in IDipp·GeH₂BH₃ [C_IDipp-Ge = 2.011(2) Å].[3b] Compound **1** shows an eclipsed anticlinal conformation with a torsion angle of C1-Ge1-B1-O1 = −114.05(18)°. The C1-Ge1-B1 angle of **1** [109.85(11)°] is smaller compared to the starting material [C_IDipp-Ge-B = 118.82(7)°] due to the added steric demand of the OTf group.

With the potential leaving group, OTf, attached to the boron atom in **1**, the formation of cationic species by substitution reactions with nucleophiles seemed plausible. Therefore, the reactivity of **1** was studied with several pnictogen-based donors varying in nucleophilicity and steric bulk. The reactions of **1** with the phosphines ᵗBuPH₂, HPPh₂ and PPh₃, as well as AsPh₃, led to the formation of the unprecedented cationic group 13/14/15 hydride-rich chains [IDipp·GeH₂BH₂ERR¹R²]⁺ (**2**: E = P; R, R¹ = H; R² = ᵗBu; **3**: E = P; R = H; R¹, R² = Ph; **4a**: E = P; R, R¹, R² = Ph; **4b**: E = As; R, R¹, R² = Ph). After stirring the reaction mixtures overnight, the Ge-B–P chains **2** and **3** can be isolated in good yields of 87 and 84%, respectively (Scheme 2); to obtain comparable yields for
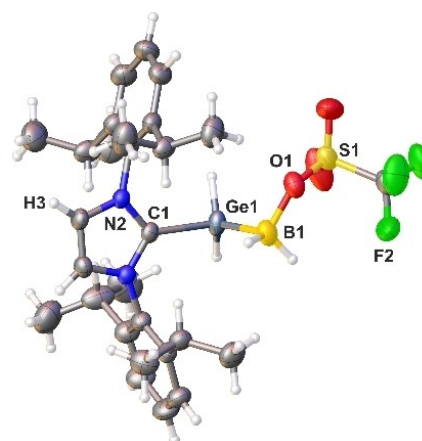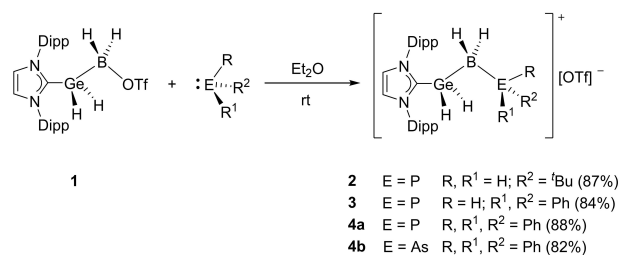

Figure 1. Molecular structure of **1** in the solid state with thermal ellipsoids at a 50% probability level. Selected bond lengths [Å] and angles [°]: C1-Ge1 2.003(2), Ge1-B1 2.081(3), B1-O1 1.564(3), C1-Ge1-B1 109.85(11), Ge1-B1-O1 111.06(17).

Scheme 1. Synthesis of **1**. Yield is given in parentheses.

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Scheme 2. Synthesis of **2**, **3**, **4a**, and **4b**. Yields are given in parentheses.

4a and **4b**, the reaction time was increased to 24 h. All reactions were performed in Et_2O, as the cationic complexes precipitate out of the reaction mixture upon formation and can then be isolated as pure white powders.

The reactions of **1** with the phosphines $^tBuPH_2$, $HPPh_2$, and PPh_3 to yield the gas phase ion pairs **2**, **3**, and **4a** are predicted to be slightly exothermic (by 11, 21, and 24 kJ mol^{-1}, respectively). In comparison, the analogous reaction of **1** with $AsPh_3$ is endothermic by 38 kJ mol^{-1}, which is in contrast to the experimentally observed formation of **4b** (see above). In all cases, the crystal lattice energy will favor the formation of the solid compounds, in line with the experimental results. Gas phase dissociation enthalpies of the ion pairs into free ions are in the range between 213 and 260 kJ mol^{-1}. Compounds **2**–**4b** are soluble in more polar solvents like CH_2Cl_2 or thf and are stable in solution and as solids (Figure 2), at ambient temperatures under an inert atmosphere. The ^1H NMR spectra of **2**–**4b** in CD_2Cl_2 afford multiplet resonances in the range of $\delta = 3.37$–3.58 ppm for the GeH_2 moieties, similar to **1** ($\delta = 3.58$ ppm). The ^{31}P NMR spectra for **2**–**4b** yield broad signals in the range of $\delta = -12.3$ to 19.0 ppm with the expected coupling patterns (Figure 3). In addition, the ^{11}B NMR spectra of **2**–**4b** reveal broad signals that are significantly shifted upfield (δ range from -38.1 to -46.2 ppm) compared to the starting material **1** ($\delta = -3.2$ ppm). The expected molecular ion peaks for the cationic chains in **2**–**4b** are detected by ESI-MS spectrometry (cf. Supporting Information for details). Single crystals of **2**–**4b** are obtained by layering a CH_2Cl_2 solution of the products with n-hexane. The structures of **2**–**4b** are shown in Figure 2, and reveal slightly shorter Ge–B bond lengths [2.043(2)–2.063(3) Å] compared to the starting material **1** [2.081(3) Å]. The B–P bond lengths within compounds **2**–**4a** [1.913(2)–1.922(3) Å] and the B–As bond length in **4b** [2.0447(18) Å] are in the expected range for single bonds.[15] Complex **2**, [IDipp·GeH$_2$BH$_2$PH$_2$^{t}Bu][OTf], shows an anticlinal conformation about the Ge–B bond axis with a C1-Ge1-B1-P1 torsion angle of $-104.97(11)°$, while all of the substituents along the B–P axis are arranged in a staggered conformation.

The $HPPh_2$-extended chain in **3** adopts a similar conformation as **2**, with a slightly smaller C1-Ge1-B1-P1 torsion angle of $-101.45(12)°$; the substituents appended to the Ge-B-E chain (E = P, As) in the EPh$_3$-functionalized compounds **4a** and **4b** also adopt a staggered conformation. The intrachain Ge-B–E angle is the smallest in **2** [105.55(12)°], the largest in **3** [112.57(10)°], and has intermediate values in compounds **4a** [110.81(9)°] and **4b** [110.17(9)°]. After the successful formation of the organo-substituted cationic group 14/13/15 chains in **2**–**4b**, we wondered
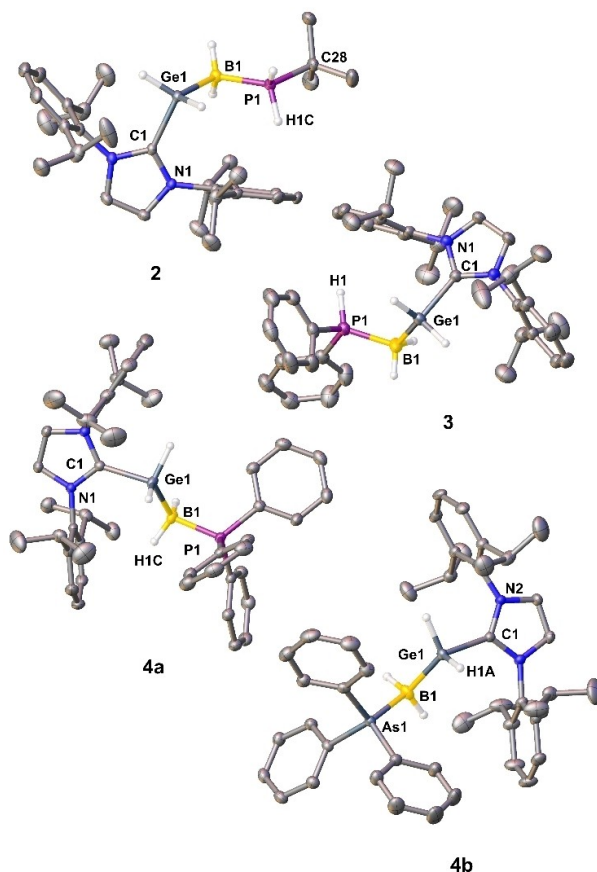

Figure 2. Molecular structures of the cations in **2** (top left), **3** (top right), **4a** (bottom left), **4b** (bottom right) in the solid state with thermal ellipsoids at a 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: C1-Ge1 2.001(2), Ge1-B1 2.063(3), B1-P1 1.922(3), C1-Ge1-B1 113.28(10), Ge1-B1-P1 105.55(12). **3**: C1-Ge1 1.9866(15), Ge1-B1 2.043(2), B1-P1 1.913(2), C1-Ge1-B1 115.29(8), Ge1-B1-P1 112.57(10). **4a**: C1-Ge1 1.9968(15), Ge1-B1 2.0570(19), B1-P1 1.9156(18), C1-Ge1-B1 111.06(7), Ge1-B1-P1 110.81(9). **4b**: C1-Ge1 1.9949(14), Ge1-B1 2.0545(19), B1-As1 2.0447(18), C1-Ge1-B1 113.93(7), Ge1-B1-P1 110.17(9).
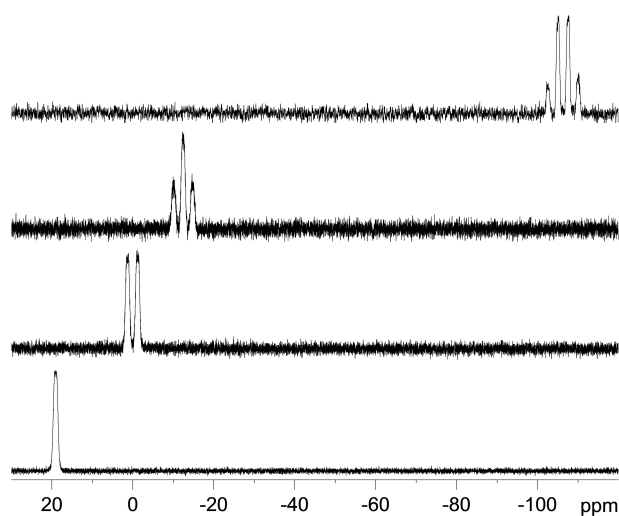

Figure 3. ^{31}P NMR spectra of **4a**, **3**, **2** and **5** (bottom to top) in CD_2Cl_2.

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if the fully hydrogen-substituted derivative [IDipp·GeH₂BH₂PH₃][OTf] (**5**) could be made. However, for this purpose the toxic and difficult to handle gas PH₃ was needed. Therefore, PH₃ was bubbled through a solution of **1** in Et₂O leading to the precipitation of a white powder from the reaction mixture (Scheme 3).

According to DFT computations, the gas phase reactions of the [IDipp·GeH₂BH₂]⁺ cation with all considered Lewis bases, to form [IDipp·GeH₂BH₂·LB]⁺ cations, are highly exothermic: exothermicity decreases in order PPh₃ > HPPh₂ > ᵗBuPH₂ > AsPh₃ > PH₃ > OEt₂ (cf. Supporting Information for details). The ¹H NMR spectrum of the precipitate formed from the reaction of **1** with PH₃ shows three different sets of signals for the IDipp groups with an integration ratio of 1.0:1.3:0.8. The IDipp group with the ratio of 1.0 could be identified as the starting material IDipp·GeH₂BH₂OTf (**1**). The major IDipp-containing product in this mixture showed the expected ¹H NMR signals for the target parent hydride [IDipp·GeH₂BH₂PH₃][OTf] (**5**). Specifically, the ¹H{¹¹B} NMR spectrum shows a broad multiplet at $\delta = 0.52$ ppm for the BH₂-group in **5**, which splits into a broad quartet in the boron-coupled ¹H NMR spectrum.

The PH₃ moiety in **5** appears as a doublet of triplets ($\delta = 4.26$ ppm, $^1J_{H,P} = 403$ Hz) and collapses into a triplet resonance in the ¹H{³¹P} NMR spectrum. The GeH₂-group in **5** yields a broad doublet of triplets ¹H NMR resonance ($\delta = 3.62$ ppm, $^3J_{H,P} = 11.2$ Hz, $^3J_{H,H} = 4.5$ Hz), which becomes sharper (better resolved) in the ¹H{¹¹B} NMR spectrum, as no broadening due to the boron atom occurs. Upon recording a ¹H{³¹P} NMR spectrum, the signal belonging to the GeH₂ unit in **5** merges into a triplet ($^3J_{H,H} = 4.5$ Hz). The ¹H NMR spectrum of the precipitate, from the reaction of **1** with PH₃, afforded only one non-carbene signal that did not belong to compounds **1** or **5**. This sharp singlet at $\delta = 4.03$ ppm lies within the range for germanium-bound hydrides[3b,8] and integration of this resonance with respect to the remaining IDipp resonances is consistent with a GeH₃ group being present in the product. The ³¹P{¹H} NMR spectrum of the precipitate only shows one broad multiplet instead of an ideal 1:1:1:1 quartet (see Supporting Information for details) at $\delta = -105.7$ ppm originating from compound **5**, which splits into a quartet ($^1J_{P,H} = 403$ Hz) in the proton-coupled ³¹P NMR spectrum (Figure 3). Furthermore, the ¹¹B{¹H} NMR spectrum of the isolated precipitate only gave

resonances for **1** and **5**, with the latter compound displaying a doublet at $\delta = -46.4$ ppm ($^1J_{B,P} = 47$ Hz), which further splits into a triplet of doublets in the ¹¹B NMR spectrum ($^1J_{B,H} = 106$ Hz). Thus, the new IDipp and -GeH₃ containing product does not have P or B present. The ESI-MS spectrum of the precipitate shows two main peaks: a molecular ion peak for the cationic [IDipp·GeH₂BH₂PH₃]⁺ unit in **5** (at 511.3 m/z) and a peak corresponding to the germylium cation [IDipp·GeH₃]⁺ (**6**) (at 465.2 m/z). By layering a CH₂Cl₂ solution of the precipitate with *n*-hexane colorless crystals of the triflato salt [IDipp·GeH₃][OTf] (**6**) could be obtained that were of suitable quality for single-crystal X-ray diffraction (Figure 4); all attempts to grow suitable single crystals of **5** failed. Notably, the refined structure of **6** agrees with the ESI-MS and NMR data described above.

Compound **6** shows a similar C–Ge distance [C1-Ge1 = 1.998(3) Å] in the solid state when compared to the germanium (IV) cations [1.994(9)–2.014(5) Å] synthesized by Baines and coworkers (type **II**, Chart 1).[5] The oxidation state of the germanium atom in **6** cannot be unequivocal defined, because **6** might also be regarded as the parent germylene compound IDipp·GeH₂ stabilized by a proton acting as a Lewis acid. All further attempts to separate compound **5** from **6** failed due to their similar solubility and the limited stability of **5** in solution. DFT computations indicate that the reaction of **1** with the parent phosphine PH₃ leading to the ion pair **5** in the gas phase is endothermic by 6 kJ mol⁻¹, but will be favored to give solid **5**, due to the crystallization energy. Loss of boron and formation of the ion pair **6** upon reaction of **1** with PH₃ may be accompanied by the formation of the insoluble phosphinoborane polymer (BH₂PH₂)ₙ. As was shown before, the formation of such polymers may be modelled computationally by the cyclic trimer (BH₂PH₂)₃.[16] This overall reaction (Equation (1)) is predicted to be endothermic by 6 kJ mol⁻¹ in the gas phase. However, the formation of solid **6** is thermodynamically favored if the crystal lattice energy of **6** is taken into account.

$$\mathbf{1} + PH_3 \rightleftharpoons \mathbf{6} + \tfrac{1}{3}\,(BH_2PH_2)_3 \qquad (1)$$
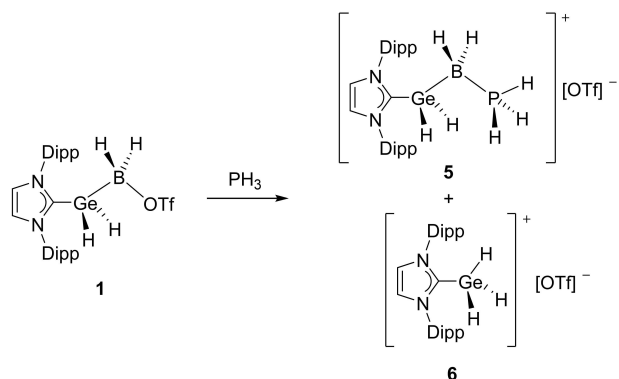
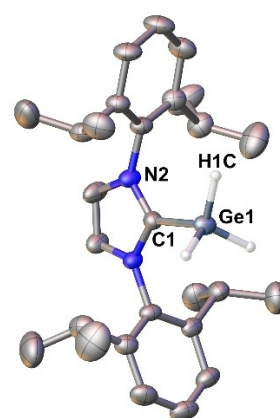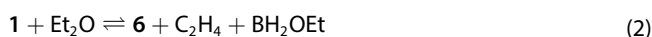**Scheme 3.** Synthesis of the element hydride complexes **5** and **6**.

Figure 4. Molecular structure of the cation in **6** in the solid state, with thermal ellipsoids at a 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond length [Å]: C1-Ge1 1.998(3).

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$$1 + Et_2O \rightleftharpoons 6 + C_2H_4 + BH_2OEt \qquad (2)$$

Another possibility for the formation of **6** is the reaction of **1** with the solvent (Et$_2$O). The model gas phase process (Equation (2)) is endothermic by 44 kJ mol^{-1}, but exergonic by 14 kJ mol^{-1} when entropy is considered. In light of possible further reactivity of the Lewis base-stabilized cations [IDipp·GeH$_2$BH$_2$·LB]$^+$, it is also of interest to compare the C—Ge, Ge—B and B—P(As) binding energies in these species. To this end, the dissociation enthalpies associated with bond breaking and formation of the corresponding closed shell fragments were computed (Table 1). The B-LB bonds are the weakest within the C—Ge-B-LB chains, with $\Delta_{diss}H^{\circ}_{298}$ values ranging from 94 (LB=Et$_2$O) to 185 (LB=PPh$_3$) kJ mol^{-1}. The dissociation of C—Ge bond generally requires more than 300 kJ mol^{-1} and does not depend much on the nature of the capping LB; the smaller C—Ge dissociation enthalpies in the EPh$_3$-bound derivatives are caused by additional (stabilizing) Ge⋯Ph interactions in the resulting GeH$_2$BH$_2$EPh$_3$$^+$ cations (E=P, As). The Ge—B bond dissociation enthalpies depend strongly on the nature of the Lewis base, with $\Delta_{diss}H^{\circ}_{298}$ values ranging from 234 (Et$_2$O) to 386 (PH$_3$) kJ mol^{-1}. These large dissociation energies are due to the lower stability of the small cations, such as BH$_2$(OEt$_2$)$^+$ and BH$_2$PH$_3$$^+$.[17]

Conclusion

In summary, we have shown that the donor/acceptor-stabilized parent germylene IDipp·GeH$_2$BH$_3$ can be readily functionalized with the good leaving group, OTf, through the reaction with MeOTf. Subsequently, the resulting product IDipp·GeH$_2$BH$_2$OTf (**1**) can be used as a novel building block for the formation of hydride-rich cationic group 14/13/15 chain-like compounds upon addition of phosphines or arsines. All products are obtained in good yields and were fully characterized. In addition, the reaction of **1** with PH$_3$ led to the formation of [IDipp·GeH$_2$BH$_2$PH$_3$][OTf] (**5**), which represents the first example of an inorganic group 13/14/15 chain with only hydrogen substituents; moreover, the NHC-stabilized parent germylium salt [IDipp·GeH$_3$][OTf] (**6**) was obtained as a side product, which is an interesting all-hydrogen-extension of the halide-substituted germanium(IV) cations reported by the *Baines* group. Further investigations will be aimed at the synthesis of longer group 13/14/15 units using the general synthetic methodology presented here, and the use of these compounds as possible precursors to

bulk and nanodimensional ternary solids[11,12j] of tunable composition and function.

Experimental Section

General experimental procedures for the synthesis of all compounds, characterization, quantum chemical calculations and X-ray crystallography are described in the Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: boron · cations · carbenes · germanium · hydrides · main group elements · phosphorus

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Table 1. Gas phase standard enthalpies $\Delta_{diss}H^{\circ}_{298}$, kJ mol^{-1} for the dissociation of IDipp·GeH$_2$BH$_2$·LB$^+$, with breaking Ge—C, Ge—B, and B-LB bonds, and formation of closed shell fragments. B3LYP/def2-TZVP level of theory.

| LB	C-Ge	Ge-B	B-LB
none	419	567	–
PH$_3$	337	386	120
PH$_2$^{t}Bu	316	344	163
PHPh$_2$	301	308	179
PPh$_3$	275	276	185
AsPh$_3$	276	289	146
Et$_2$O	305	234	94

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[17] For related computational studies on the dissociation enthalpies in IDipp·GeH₂BH₃, see: J. Sinclair, G. Dai, R. McDonald, M. J. Ferguson, A. Brown, E. Rivard, *Inorg. Chem.* **2020**, *59*, 10996–11008.

RESEARCH ARTICLE
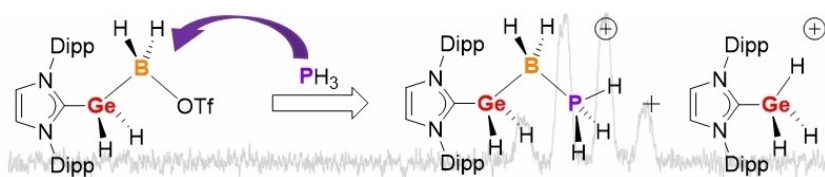
The NHC-stabilized compound IDipp·GeH₂BH₂OTf was synthesized. Reactivity studies on this novel building block with different phosphines and AsPh₃ showed its potential to serve as an ideal precursor for un-precedented cationic group 13/14/15 chain compounds. In addition, a reaction with PH₃ leads to the formation of the parent hydrides [IDipp·GeH₂BH₂PH₃][OTf] and [IDipp·GeH₃][OTf].

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An NHC-Stabilized H₂GeBH₂ Precursor for the Preparation of Cationic Group 13/14/15 Hydride Chains