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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]

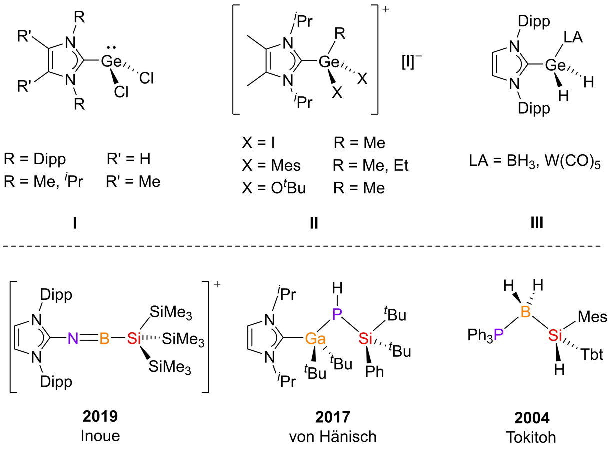

Chart 1. Different types of N-heterocyclic carbene-stabilized germanium complexes (top) and selected examples for mixed group 13/14/15 chain compounds (bottom).

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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several unsaturated group 13/15 compounds of the type $LA \cdot H_2EE'H_2 \cdot LB$ (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 $H_2EE'H_2 \cdot LB$, 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 $IDipp \cdot GeH_2BH_3$[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 $IDipp \cdot BH_2OTf$ by the reaction of $IDipp \bullet BH_3$ with triflic acid.[14] Hence we reasoned that it may also be possible for the more complex borane adduct $IDipp \cdot GeH_2BH_3$ 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 H_2GeBH_2 precursor as a common building block.

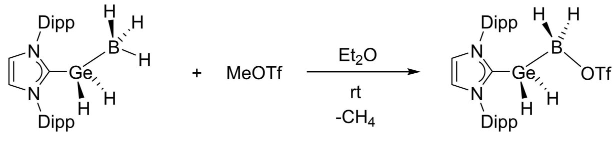
Results and Discussion

Computational studies at B3LYP/def2-TZVP level of theory reveal that the gas phase reaction between $IDipp \cdot GeH_2BH_3$ and MeOTf with methane evolution and formation of $IDipp \cdot GeH_2BH_2OTf$ (**1**) is highly exothermic (by 196 $kJ\,mol^{-1}$) and highly exergonic at room temperature (by 185 $kJ\,mol^{-1}$). Indeed, the reaction of $IDipp \cdot GeH_2BH_3$ with MeOTf in Et_2O at room temperature leads quantitatively to the formation of **1**, which can be crystallized in good yields (83 %) from a concentrated Et_2O solution at −30 °C (Scheme 1). Compared to Curran's reaction of $IDipp \cdot BH_3$ with HOTf in $CDCl_3$, where the formed triflate $IDipp^{\bullet}BH_2OTf$ 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 CH_2Cl_2, thf, as well as in Et_2O. The ^1H NMR spectrum of **1** in thf-d_8 shows a broad signal at $\delta = 2.61$ ppm, which could be assigned to the BH_2 moiety, as confirmed by $^1H\{^{11}B\}$ NMR spectroscopy. The second non-carbene signal at $\delta = 3.58$ ppm for the GeH_2-hydrogens shows a triplet pattern due to coupling with the adjacent BH_2 unit. The ^{11}B NMR spectrum of **1** consists of a broad singlet at $\delta = -3.2$ ppm, which is significantly downfield-positioned compared to the starting material $IDipp \cdot GeH_2BH_3$ ($\delta = -40.0$ 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 $[IDipp \cdot GeH_2BH_2(thf)]^+$. 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 $IDipp \cdot BH_2OTs$ [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 $IDipp \bullet GeH_2BH_3$ [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 $IDipp \cdot GeH_2BH_3$ [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 $^tBuPH_2$, $HPPh_2$ and PPh_3, as well as $AsPh_3$, led to the formation of the unprecedented cationic group 13/14/15 hydride-rich chains $[IDipp \cdot GeH_2BH_2ERR^1R^2]^+$ (**2**: E = P; R, R^1 = H; R^2 = ^tBu; **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). 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



1 (83%)

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

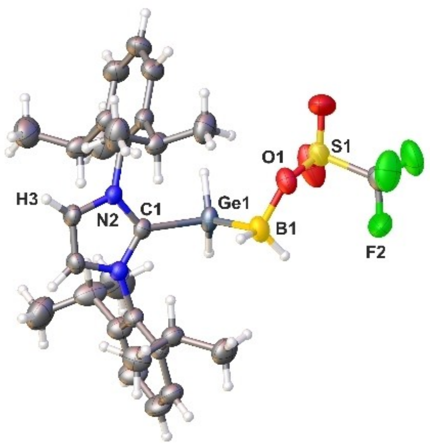
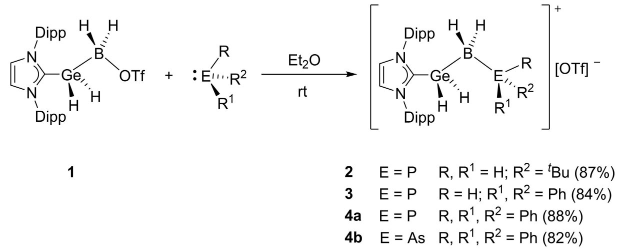


Figure 1. Molecular structure of **1** in the solid state with thermal ellipsoids at a 50 % probability level. Selected bond lengths [Å] and angles [°]: C1-Ge1 2.003(2), Ge1-B1 2.081(3), B1-O1 1.564(3), C1-Ge1-B1 109.85(11), Ge1-B1-O1 111.06(17).



Scheme 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$_2$O, 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 ^{t}BuPH$_2$, 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$_2$Cl$_2$ or thf and are stable in solution and as solids (Figure 2), at ambient temperatures under an inert atmosphere. The ^{1}H NMR spectra of **2**–**4b** in CD$_2$Cl$_2$ 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$_2$Cl$_2$ 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$\cdot$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

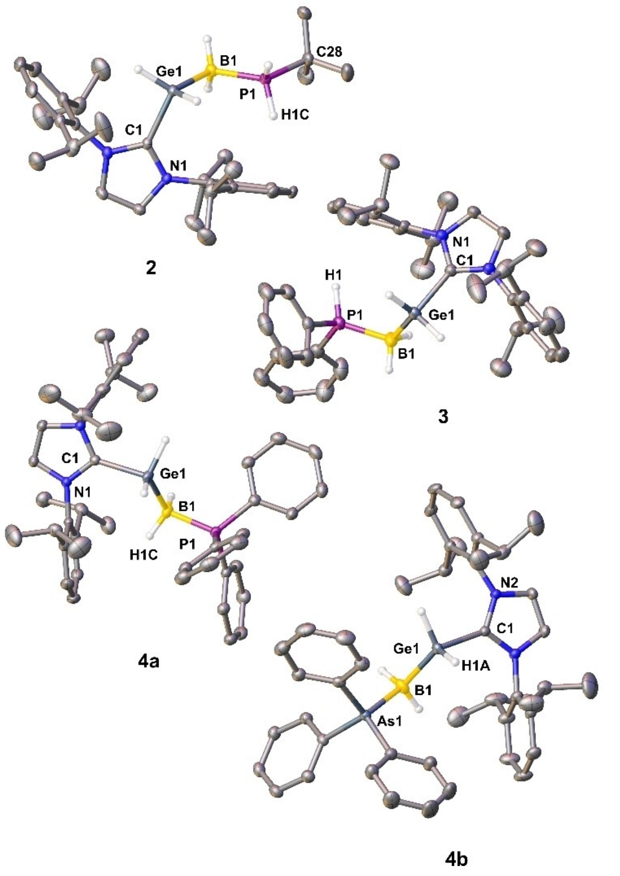


Figure 2. Molecular structures of the cations in **2** (top left), **3** (top right), **4a** (bottom left), **4b** (bottom right) in the solid state with thermal ellipsoids at a 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: 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).

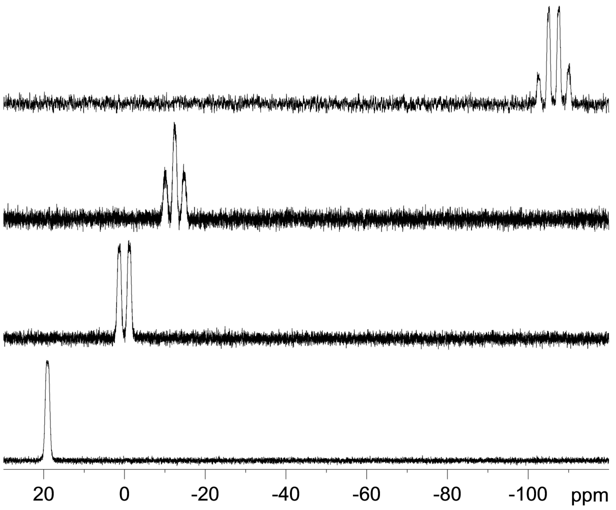


Figure 3. ^{31}P NMR spectra of **4a**, **3**, **2** and **5** (bottom to top) in CD$_2$Cl$_2$.

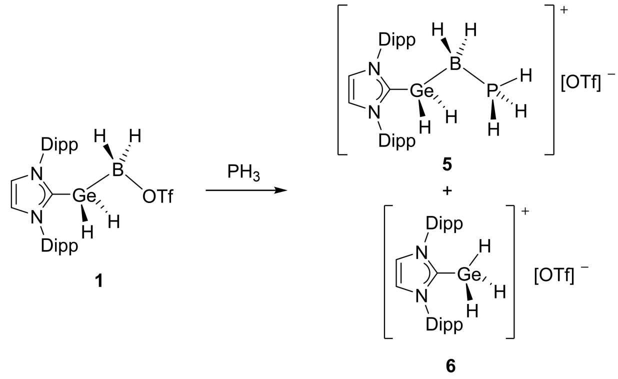
if the fully hydrogen-substituted derivative $[\mathrm{IDipp{\cdot}GeH_2BH_2PH_3}][\mathrm{OTf}]$ (**5**) could be made. However, for this purpose the toxic and difficult to handle gas $\mathrm{PH_3}$ was needed. Therefore, $\mathrm{PH_3}$ was bubbled through a solution of **1** in $\mathrm{Et_2O}$ leading to the precipitation of a white powder from the reaction mixture (Scheme 3).

According to DFT computations, the gas phase reactions of the $[\mathrm{IDipp{\cdot}GeH_2BH_2}]^+$ cation with all considered Lewis bases, to form $[\mathrm{IDipp{\cdot}GeH_2BH_2{\cdot}LB}]^+$ cations, are highly exothermic: exothermicity decreases in order $\mathrm{PPh_3} > \mathrm{HPPh_2} > {}^t\mathrm{BuPH_2} > \mathrm{AsPh_3} > \mathrm{PH_3} > \mathrm{OEt_2}$ (cf. Supporting Information for details). The ^{1}H NMR spectrum of the precipitate formed from the reaction of **1** with $\mathrm{PH_3}$ 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 $\mathrm{IDipp{\cdot}GeH_2BH_2OTf}$ (**1**). The major IDipp-containing product in this mixture showed the expected ^{1}H NMR signals for the target parent hydride $[\mathrm{IDipp{\cdot}GeH_2BH_2PH_3}][\mathrm{OTf}]$ (**5**). Specifically, the ^{1}H{^{11}B} NMR spectrum shows a broad multiplet at $\delta = 0.52$ ppm for the $\mathrm{BH_2}$-group in **5**, which splits into a broad quartet in the boron-coupled ^{1}H NMR spectrum.

The $\mathrm{PH_3}$ moiety in **5** appears as a doublet of triplets ($\delta = 4.26$ ppm, $^1J_{\mathrm{H,P}} = 403$ Hz) and collapses into a triplet resonance in the ^{1}H{^{31}P} NMR spectrum. The $\mathrm{GeH_2}$-group in **5** yields a broad doublet of triplets ^{1}H NMR resonance ($\delta = 3.62$ ppm, $^3J_{\mathrm{H,P}} = 11.2$ Hz, $^3J_{\mathrm{H,H}} = 4.5$ Hz), which becomes sharper (better resolved) in the ^{1}H {^{11}B} NMR spectrum, as no broadening due to the boron atom occurs. Upon recording a ^{1}H{^{31}P} NMR spectrum, the signal belonging to the $\mathrm{GeH_2}$ unit in **5** merges into a triplet ($^3J_{\mathrm{H,H}} = 4.5$ Hz). The ^{1}H NMR spectrum of the precipitate, from the reaction of **1** with $\mathrm{PH_3}$, 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 $\mathrm{GeH_3}$ group being present in the product. The ^{31}P{^{1}H} 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 ($^1J_{\mathrm{P,H}} = 403$ Hz) in the proton-coupled ^{31}P NMR spectrum (Figure 3). Furthermore, the ^{11}B{^{1}H} 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 ($^1J_{\mathrm{B,P}} = 47$ Hz), which further splits into a triplet of doublets in the ^{11}B NMR spectrum ($^1J_{\mathrm{B,H}} = 106$ Hz). Thus, the new IDipp and $-\mathrm{GeH_3}$ 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 $[\mathrm{IDipp{\cdot}GeH_2BH_2PH_3}]^+$ unit in **5** (at 511.3 m/z) and a peak corresponding to the germylium cation $[\mathrm{IDipp{\cdot}GeH_3}]^+$ (**6**) (at 465.2 m/z). By layering a $\mathrm{CH_2Cl_2}$ solution of the precipitate with *n*-hexane colorless crystals of the triflato salt $[\mathrm{IDipp{\cdot}GeH_3}][\mathrm{OTf}]$ (**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 $\mathrm{IDipp{\cdot}GeH_2}$ 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 $\mathrm{PH_3}$ 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 $\mathrm{PH_3}$ may be accompanied by the formation of the insoluble phosphinoborane polymer $(\mathrm{BH_2PH_2})_n$. As was shown before, the formation of such polymers may be modelled computationally by the cyclic trimer $(\mathrm{BH_2PH_2})_3$.[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.

$$\mathbf{1} + \mathrm{PH_3} \rightleftharpoons \mathbf{6} + {}^1/_3\ (\mathrm{BH_2PH_2})_3 \qquad (1)$$



Scheme 3. Synthesis of the element hydride complexes **5** and **6**.

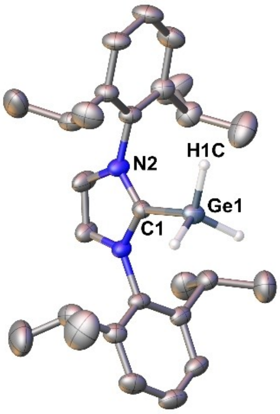


Figure 4. Molecular structure of the cation in **6** in the solid state, with thermal ellipsoids at a 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond length [Å]: C1-Ge1 1.998(3).

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

Another possibility for the formation of **6** is the reaction of **1** with the solvent (Et_2O). 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 $[IDipp\cdot GeH_2BH_2\cdot LB]^+$, 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_2O) 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 $GeH_2BH_2EPh_3{}^+$ 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_2O) 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 $BH_2PH_3{}^+$.[17]

Conclusion

In summary, we have shown that the donor/acceptor-stabilized parent germylene $IDipp\cdot GeH_2BH_3$ can be readily functionalized with the good leaving group, OTf, through the reaction with MeOTf. Subsequently, the resulting product $IDipp\cdot GeH_2BH_2OTf$ (**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 $[IDipp\cdot GeH_2BH_2PH_3][OTf]$ (**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 $[IDipp\cdot GeH_3][OTf]$ (**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.

Table 1. Gas phase standard enthalpies $\Delta_{diss}H^{\circ}_{298}$, kJ mol^{-1} for the dissociation of $IDipp\cdot GeH_2BH_2\cdot LB^+$, 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
$PH_2{}^tBu$	316	344	163
$PHPh_2$	301	308	179
PPh_3	275	276	185
$AsPh_3$	276	289	146
Et_2O	305	234	94

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.

Deposition Numbers 2115643 (**1**), 2115644 (**2**), 2115645 (**3**), 2115646 (**4a**), 2115647 (**4b**) and 2115648 (**6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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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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