An NHC-Stabilized $\text{H}_2\text{GeBH}_2$ 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 $\text{IDipp} \cdot \text{GeH}_2\text{BH}_2\text{OTf}$ (1) ($\text{IDipp} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolin-2-ylidene}$) 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 BH$_2$EtR]$^+$) (2 E = P, R, R" = H; R" = "Bu; 3 E = P; R, R" = Ph; 4 a E = P; R, R', R" = Ph; 4 b E = As; R, R', R" = Ph). These novel cationic compounds with low-coordinate (and low-oxidation state) were characterized by X-ray crystallography, NMR spectroscopy and mass spectrometry. Moreover, the formation of the parent complexes $\text{[IDipp-GeH}_2\text{BH}_2\text{PH}_3\text{]OTf}$ (5) and $\text{[IDipp-GeH}_2\text{]OTf}$ (6) were achieved by reaction of 1 with $\text{PH}_3$. 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, $\text{IDipp} \cdot \text{Si-Si} \cdot \text{IDipp}$ ($\text{IDipp} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolin-2-ylidene}$), 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) and the first reactivity studies of their Lewis basic character.[3] 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). Soon after, related NHC-supported germanium compounds were reported,[4] followed by their lighter silicon congeners,[5] the latter spurred by the development of versatile NHC-Si(III) precursors.[6]

In 2009, the Rivard and Jones groups simultaneously reported the formation of the germanium dichloride adduct $\text{IDipp-GeCl}_3$ by the reaction of $\text{IDipp}$ with $\text{GeCl}_2$-dioxane.[5] Starting from this Ge(II) complex, Jones subsequently achieved the formation of the NHC-stabilized digermanium(0) compound $\text{IDipp-Ge-Ge} \cdot \text{IDipp}$,[5] which represents the heavier homolog of Robinson’s disilene. Rivard and coworkers then prepared the first donor/acceptor-stabilized parent germanium(II) dihydride complex $\text{IDipp-GeH}_2\text{BH}_2$ (type III, Chart 1) through the reaction of $\text{IDipp-GeCl}_3$ with excess of $\text{LiBH}_4$.[6] Our group developed the concept of donor/acceptor stabilization for the formation of...
several unsaturated group 13/15 compounds of the type LA-H_{2}E_{3}EEH_{2}·LB (E = group 15 element, E' = group 13 element, LA = Lewis acid, LB = Lewis base). Later it was even possible to obtain the only LB-stabilized pnictogenyltrienes H_{2}E_{3}EEH_{2}·LB, which enabled the study of their reactivity in detail, and resulted in the formation of cationic chains of phosphanyl- and arsanylboranes.\(^\text{[16]}\)

Against the backdrop of the above-mentioned prior work, we wondered whether carbene-stabilization would enable the formation of linear, hydride-rich, group 13/15 sequences using Rovir’s group 14/13 compound IDipp-GeH_{3}BH_{3}\(^\text{[16]}\) 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.\(^\text{[11]}\) In general, only few examples of mixed-element group 13/14/15 compounds are known,\(^\text{[12]}\) especially if only chain compounds are considered (cf. Chart 1 for examples).\(^\text{[13]}\)

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-GeH_{3}·OTf by the reaction of IDipp·BH_{3} with triflic acid.\(^\text{[14]}\) Hence we reasoned that it may also be possible for the more complex borane adduct IDipp·GeH_{3}BH_{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_{2}GeH_{3} 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·GeH_{3}BH_{3} and MeOTf with methane evolution and formation of IDipp·GeH_{3}BH_{3}·OTf (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·GeH_{3}BH_{3} with MeOTf in Et_{2}O at room temperature leads quantitatively to the formation of 1, which can be crystallized in good yields (83\%) from a concentrated Et_{2}O solution at \(-30^\circ\text{C}\) (Scheme 1). Compared to Curran’s reaction of IDipp·BH_{3} with HOTf in CDCl\(_3\), where the formed triflate IDippBH_{3}·OTf cannot be isolated easily, in our case the clean reaction with MeOTf is observed.\(^\text{[14]}\)

While 1 is stable as a solid at ambient temperatures in an inert atmosphere, it slowly decomposes in CH\(_2\)Cl\(_2\), thf, as well as in Et\(_2\)O. The \(^1\)H NMR spectrum of 1 in thf-d\(_8\) shows a broad signal at \(\delta = 2.61\) ppm, which could be assigned to the BH\(_3\) moiety, as confirmed by \(^{11}\)B \((\text{H}^{11})\) 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\(_3\) unit. The \(^{19}\)F NMR spectrum of 1 consists of a broad singlet at \(\delta = \approx 3.2\) ppm, which is significantly downfield-located positioned compared to the starting material IDipp·GeH_{3}BH_{3} (\(\delta = \approx -40.0\) ppm).\(^\text{[15]}\)

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·GeH_{3}BH_{3}·(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 boryltosylate adduct IDipp·BH_{3}·OTs (B–O = 1.522(7) Å).\(^\text{[14]}\) The Ge1–B1 distance in 1 (2.081(3) Å) is slightly longer than for the borane adduct IDipp·GeH_{3}BH_{3} (Ge–B = 2.053(3) Å), while the coordinative bond in IDipp·GeH_{3}BH_{3} [C\(_{\text{IDipp}}\)-Ge = 2.011(2) Å].\(^\text{[16]}\)

Compound 1 shows an eclipsed anticalcinal 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\(_{\text{IDipp}}\)-Ge = 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 BuPH\(_3\), HPPH\(_3\), and PPH\(_3\) as well as AsPH\(_3\), led to the formation of the unprecedented cationic group 13/14/15 hydride-rich chains [IDipp·GeH_{3}BH_{3}·ERR'\(_2\)·R']\(^+\) (2; E = P; R, R' = H; R\(_2\) = Bu; 3: E = P; R = H; R\(_1\) = R\(_2\) = Ph; 4a: E = P; R, R' = Ph; 4b: E = As; R, R' = 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

![Diagram](Image)

**Scheme 1.** Synthesis of 1. Yield is given in parentheses.
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4a and 4b, the reaction time was increased to 24 h. All reactions were performed in EtO, 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 ‘BuPH, HPPh2, and PPh3 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 AsPh3 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 CH2Cl2 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 CD2Cl2 afford multiplet resonances in the range of δ = 3.37–3.58 ppm for the GeH2 moieties, similar to 1 (δ = 3.58 ppm). The 31P NMR spectra for 2–4b yield broad signals in the range of δ = −12.3 to 19.0 ppm with the expected coupling patterns (Figure 3). In addition, the 11B 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 (δ = −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 CH2Cl2 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.[16] Complex 2, [Dipp-GeH2BH2P4Bu][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 HPPh2-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 EPh2-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...
if the fully hydrogen-substituted derivative [IDipp-GeH₂BH₂PH₂][OTf] (5) could be made. However, for this purpose the toxic and difficult to handle gas PH₂ was needed. Therefore, PH₂ 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-GeH₂BH₃]⁺ cation with all considered Lewis bases, to form [IDipp-GeH₂BH₃-L⁺] cations, are highly exothermic: exothermicity decreases in order PPh₃ > HPPh₃ > BuPH₃ > AsPH₃ > PH₃ > OEt₃ (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-GeH₂BH₃PH₂][OTf] (5). Specifically, the ¹H[¹B] NMR spectrum shows a broad multiplet at δ = 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 (δ = 4.26 ppm, ¹J₃P = 403 Hz) and collapses into a triplet resonance in the ¹H[¹P] NMR spectrum. The GeH₂ group in 5 yields a broad doublet of triplets ¹H NMR resonance (δ = 3.62 ppm, ¹J₃H = 11.2 Hz, ¹J₃H = 4.5 Hz), which becomes sharper (better resolved) in the ¹H[¹B] NMR spectrum, as no broadening due to the boron atom occurs. Upon recording a ¹H[¹P] NMR spectrum, the signal belonging to the GeH₃ unit in 5 merges into a triplet (¹J₃H = 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 δ = 4.03 ppm lies within the range for germanium-bound hydrides 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 δ = −105.7 ppm originating from compound 5, which splits into a quartet (¹J₃H = 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 δ = −46.4 ppm (¹J₃P = 47 Hz), which further splits into a triplet of doublets in the ¹³C NMR spectrum (¹J₃C = 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-GeH₂BH₂PH₂]⁺ unit in 5 (at 511.3 m/z) and a peak corresponding to the germymication [IDipp-GeH₁][OTf] (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] 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 germainiun (IV) cations [1.994(9)–2.014(5) Å] synthesized by Baines and coworkers (type II, Chart 1).¹⁵ The oxidation state of the germainiun atom in 6 cannot be unequivocal defined, because 6 might also be regarded as the parent germene compound IDipp-GeH₄ 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 (BH₃PH₃)ₙ. As was shown before, the formation of such polymers may be modelled computationally by the cyclic trimer (BH₃PH₃)₃. 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.

1 + PH₃ ⇌ 6 + 1/3 (BH₃PH₃)₃  

(1)
Another possibility for the formation of 6 is the reaction of 1 with the solvent (Et₂O). 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 [Dipp·GeH₃BH₃-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 Δdiss[H₂₉₈] values ranging from 94 (LB = Et₂O) to 185 (LB = P(PH₃)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 EPh₃-bound derivatives are caused by additional (stabilizing) Ge-Ph interactions in the resulting GeH₃BH₃EPh₃⁺ cations (E = P, As). The Ge-B bond dissociation enthalpies depend strongly on the nature of the Lewis base, with Δdiss[H₂₉₈] values ranging from 234 (Et₂O) to 386 (PH₃) kJ mol⁻¹. These large dissociation energies are due to the lower stability of the small cations, such as BH₃(OEt)⁺ and BH₃PH₃⁺.[17]

Conclusion

In summary, we have shown that the donor/acceptor-stabilized parent germylene [Dipp·GeH₃BH₃] can be readily functionalized with the good leaving group, OTf, through the reaction with MeOTf. Subsequently, the resulting product [Dipp·GeH₃BH₃·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 PH₃ led to the formation of [Dipp·GeH₃(BH₃PH₃)]·OTf (5), which represents the first example of an inorganic group 13/14/15 chain with only hydrogen substituents; moreover, the NHC-stabilized parent germyleum salt [Dipp·GeH₃]·OTf (6) was obtained as a side product, which is an interesting all-hydrogen-extension of the halide-substituted germanium(V) 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[11,12] 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.

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

Table 1. Gas phase standard enthalpies Δdiss[H₂₉₈] kJ mol⁻¹ for the dissociation of [Dipp·GeH₃BH₃-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  | -    |
| PH₃      | 337  | 386  | 120  |
| PH₃Bu    | 316  | 344  | 163  |
| PPH₃     | 301  | 308  | 179  |
| PPH₃     | 275  | 276  | 185  |
| AsPH₃    | 276  | 289  | 146  |
| Et₂O     | 305  | 234  | 94   |

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