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NHC-Stabilized Mixed Group 13/14/15 Element Hydrides

Matthias T. Ackermann,[a] Robert Szlosek,[a] Christoph Riesinger,[a] Michael Seidl,[b]
Alexey Y. Timoshkin,[c] Eric Rivard,[d] and Manfred Scheer*[a]

Dedicated to Professor Felix Tuczek on the occasion of his 65th birthday

The syntheses of novel N-heterocyclic carbene (NHC) adducts of group 13, 14 and 15 element hydrides are reported. Salt metathesis reactions between $NaPH_2$ and $IDipp \cdot GeH_2BH_2OTf$ (**1**) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) led to mixtures of the two isomers $IDipp \cdot GeH_2BH_2PH_2$ (**2a**) and $IDipp \cdot BH_2GeH_2PH_2$ (**2b**); by altering the reaction conditions an almost exclusive formation of **2b** was achieved. Attempts to purify mixtures of **2a** and **2b** by re-crystallization from THF afforded a salt $[IDipp \cdot GeH_2BH_2 \cdot IDipp][PHGeH_2BH_2PH_2BH_2GeH_2]$ (**4**) that contains the novel anionic cyclohexyl-like inorganic heterocycle $[PHGeH_2BH_2PH_2BH_2GeH_2]^-$. In addition, the borane adducts $IDipp \cdot GeH_2BH_2PH_2BH_3$ (**3a**) and $IDipp \cdot BH_2GeH_2PH_2BH_3$ (**3b**) as even longer chain compounds were obtained from reactions of **2a**/**2b** with $H_3B \cdot SMe_2$ and were studied by NMR spectroscopy. Accompanying DFT computations give insight into the mechanism and energetics associated with **2a**/**2b** isomerization as well as their decomposition pathways.

Introduction

Hydrocarbons are an important class of compounds, representing the basis for the large-scale production of fuels as well as bulk and specialized chemicals. Due to the isolobal analogy between $TetH_2$, $E'H_2^-$, EH_2^+ and EH (Tet = Group 14 element; E' = Group 13 element; E = Group 15 element), combinations of such group 13 and group 15 element moieties (or additional group 14-based $TetH_2$ entities) can be considered as isoelectronic analogues of corresponding hydrocarbons. The pioneering work of Stock and Poland on the preparation of borazine $(HBNH)_3$ is just one of many examples for such group 13/15 analogues.[1a–e] Group 13/15 element compounds in general are investigated as valuable starting materials for the deposition of thin films in semiconductor processes and as building blocks for inorganic polymers.[1f–o] Moreover, the study of group 14/15 compounds[2] have only recently shifted to include heavier element homologues.[3] In contrast, heavier homologues of compounds consisting of combinations of group 13, group 14 (Tet ≠ C) and group 15 units remain scarce in the literature.[4]

One possible approach for synthesizing group 13/14/15 chains is via salt-metathesis, as used by Nöth in the synthesis of **I** (Figure 1),[5] and by Inoue to access the *N*-heterocyclic carbene (NHC)-stabilized borasilene **II**.[6] Also, Inoue reported on an alternative synthetic strategy resulting in the formation of **III**, which was obtained by the reaction of $IMe_4 \cdot SiHSitBu_3$ (IMe_4 = 1,3,4,5-tetra(methyl)imidazol-2-ylidene) with $H_3N \cdot BH_3$ by dehydrogenation to H_2NBH_2 and subsequent insertion/rearrangement processes.[7] Furthermore, two very recent examples of heterocycles that include group 13/14/15 element-based building blocks are: **IV**,[8] reported by Kinjo, and the Frustrated Lewis Pair (FLP)-stabilized adducts **V**, synthesized by the Rivard group; notably, compounds **V** can be used as precursors for the low-temperature deposition (< 100 °C) of elemental Si and Ge films from solution.[9] A rare example of a heterocycle that consists exclusively of combinations of group 13, group 14 (Tet ≠ C) and group 15 elements is **VI**, reported by Nöth; however, the characterization of **VI** was limited to NMR spectroscopy.[10] Since most of the abovementioned compounds require some steric stabilization from organic substituents, the idea of an approach to access exclusively H-substituted (parent) compounds came to mind. While very few examples of the parent group 13/14/15 element chain compounds exist, including our recently introduced cationic species $[IDipp \cdot GeH_2BH_2 \cdot PH_3][OTf]$ and $[IDipp \cdot GeH_2BH_2EH_2BH_2 \cdot NMe_3][OTf]$ (E = P, As; IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), to our knowl-

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[a] Dr. M. T. Ackermann, R. Szlosek, C. Riesinger, Prof. Dr. M. Scheer
Institute of Inorganic Chemistry
University of Regensburg
Universitätsstraße 31, 93053 Regensburg (Germany)
E-mail: manfred.scheer@ur.de
Homepage: http://www.uni-regensburg.de/chemie-pharmazie/anorganische-chemie-scheer/startseite/index.html

[b] Dr. M. Seidl
Institute of General and Theoretical Chemistry
University of Innsbruck
Innrain 80–82, 6020 Innsbruck (Austria)

[c] Prof. Dr. A. Y. Timoshkin
Institute of Chemistry
Saint Petersburg State University
Universitetskaya emb. 7/9, 199034 St Petersburg (Russia)

[d] Prof. Dr. E. Rivard
Department of Chemistry
University of Alberta
11227 Saskatchewan Dr, Edmonton, Alberta, T6G 2G2 (Canada)

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Part of a Special Collection on the p-block elements.

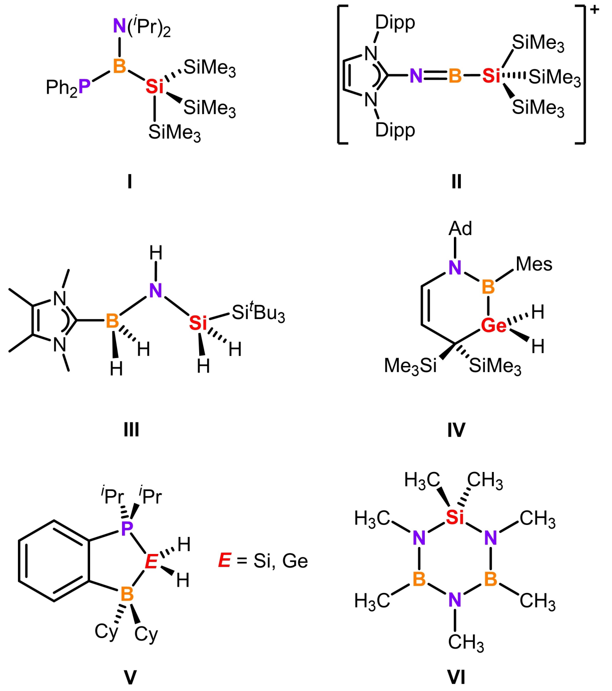


Figure 1. Selected examples of mixed group 13/14/15 chain and cyclic compounds.

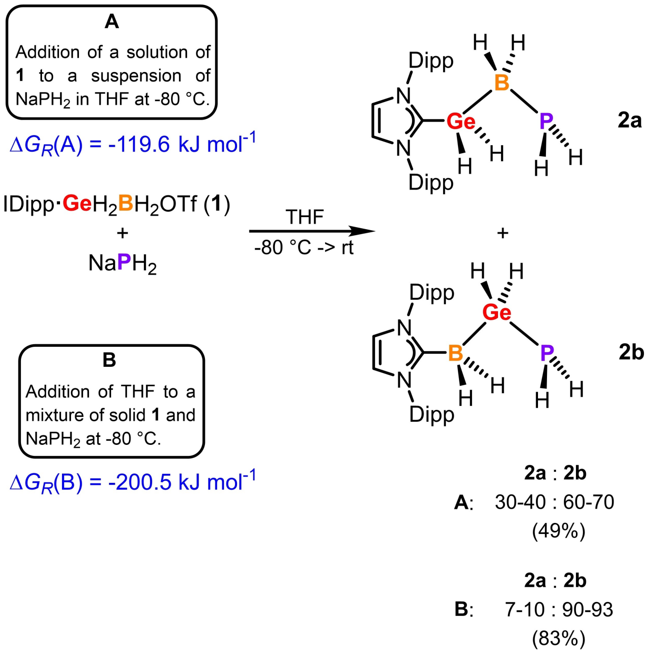
edge, no reports on corresponding parent heterocycles can be found.[11] Specifically, neutral group 13/14/15 element chain compounds bearing hydrogen substituents, which resemble their organic counterparts more closely, impose a synthetic challenge as the stability of such target compounds is reduced compared to their ionic derivatives. Furthermore, neutral mixed group 13/14/15 element hydrides (and their adducts) would be promising single-source precursors to novel ternary optoelectronic materials by MOCVD (Metal-Organic Chemical Vapor Deposition); thus, alternative synthetic strategies and a more versatile element selection for such compounds are desirable.[12] Within the last two decades, our group studied the synthesis and reactivity of only Lewis base (LB)-stabilized parent pnictogenyltrielanes $H_2EE'H_2 \cdot LB$ (E=group 15 element, E'= group 13 element) in detail.[13,14] Since those compounds were mostly obtained through salt-metathesis, we wondered if the previously introduced NHC-stabilized H_2GeBH_2 precursor IDipp$\cdot GeH_2BH_2OTf$ (**1**) might serve as a starting reagent for the synthesis of novel neutral NHC-stabilized parent group 13/14/15 element compounds.

Herein we report on the syntheses and reactivity of unprecedented neutral parent compounds consisting of elements of the group 13, 14 and 15 stabilized by the N-heterocyclic carbene IDipp.

Results and Discussion

The addition of a cold solution (−80 °C) of IDipp$\cdot GeH_2BH_2OTf$ (**1**) in THF to a suspension of $NaPH_2$ in THF at −80 °C, and subsequent stirring of the reaction mixture at room temperature leads to the formation of a mixture of the initially desired NHC-stabilized parent compound IDipp$\cdot GeH_2BH_2PH_2$ (**2a**) and its unexpected isomer IDipp$\cdot BH_2GeH_2PH_2$ (**2b**), in which the Ge and the B atoms have switched positions (Scheme 1, route **A**). The isomer mixture can be isolated in moderate yield as a white powder with a ratio of **2a**/**2b** between 30–40 : 70–60. **2a**/**2b** mixtures are stable at ambient temperatures in an inert atmosphere. Unfortunately, all attempts to separate both isomers from each other failed due to their very similar solubility and the limited stability of **2a**. As NMR studies indicate no conversion of **2a** to **2b** in solution, altering the reaction conditions was the only possibility to increase the relative amount of one isomer over the other within a product mixture. Indeed, if both solid starting materials (**1** and $NaPH_2$) are combined in the same Schlenk tube and cold THF (−80 °C) is then added, the isolated white powder shows an isomer mixture with up to 93 % of **2b** and only 7 % of **2a** (Scheme 1, route **B**).

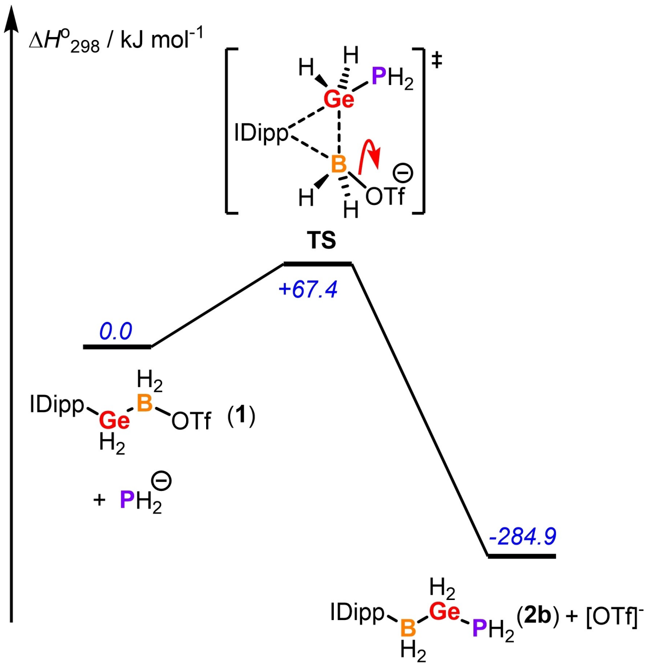
Interestingly, while changing the reaction temperature of route **B** to −60 °C does not affect the obtained **2a**/**2b** isomer ratio, an increased amount of **2a** with a product **2a**/**2b** ratio of 67 : 33 could be observed when employing route **A** at −60 °C (Scheme 1). Subsequently, numerous experiments applying different reaction conditions were carried out to solely obtain one isomer. For instance, an almost exclusive formation of **2b** with an isomer ratio of 97 : 3 was observed from the reaction of **1** with $LiPH_2 \cdot DME$ in DME at −50 °C. However, the additional formation of the inseparable decomposition product IDipp$\cdot GeH_2BH_3$[15] did not lead to an overall improvement compared to route **B** (Scheme 1). Similarly, all other attempts including different solvents (such as Et_2O or DME), alteration of



Scheme 1. Synthesis of the parent compounds **2a** and **2b**. Yields are given in parentheses. Calculated free enthalpy values ΔG_R of routes A and B were calculated at the B3LYP/def2-TZVP level of theory (cf. Supporting Information).

the addition of the starting materials or addition of crown ethers and [2.2.2]cryptand, respectively, did not lead to the selective formation of one isomer over the other. Thus, route **B** was the optimal method to obtain samples enriched in isomer **2b**, while route **A** yields the best results for an increased amount of isomer **2a** (Scheme 1).

Computational studies reveal that the formation of both isomers **2a** and **2b** is exothermic and exergonic in the gas phase at room temperature (see Supporting Information for details). Since the formation of isomer **2b** is more exergonic by 80 kJ mol^{-1} (cf. Scheme 1), it represents the thermodynamically favored product, while isomer **2a** is feasible probably due to kinetic reasons. Furthermore, the experimental observation of significant amounts of **2a** (10–67%) indicates that a rearrangement process from **2a** to **2b** seems to be kinetically hindered.



Scheme 2. Proposed reaction pathway for the formation of **2b**. Standard enthalpy values are given at the B3LYP/def2-TZVP level of theory.

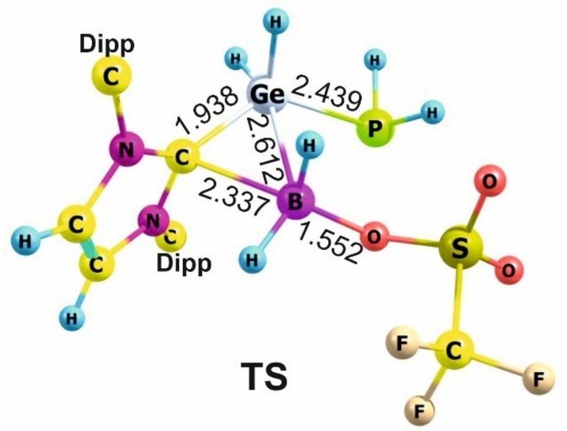


Figure 2. Optimized geometry of the transition state (Scheme 2, B3LYP/def2-TZVP). For clarity, only one carbon atom of each Dipp substituent is shown.

According to the ^{31}P NMR spectrum of a mixture of **2a**/**2b** in THF, no significant change of the ratio of **2a**:**2b** is observed over time, even after one week at room temperature. A possible reaction pathway in this case involves the nucleophilic attack of $[PH_2]^-$ at the germanium atom, resulting in the transition state **TS**, which then rearranges by a concerted mechanism to **2b** under elimination of the triflate group, $[OTf]^-$ (Scheme 2, Figure 2). This reaction pathway might also be favored at low temperatures since the resulting less labile B–O bond in **1** should lead to a higher probability of $[PH_2]^-$ to attack at the Ge atom and thus result in the formation of the thermodynamically more stable product **2b**, which confirms the experimentally found isomer ratios. Also, our quantum chemical calculations were able to locate a corresponding transition state **TS** for the formation of **2b** (Scheme 2, Figure 2; cf. Supporting Information). This transition state features a bridging NHC that links both the Ge and B atoms, and the energy of this **TS** lies only 70 kJ mol^{-1} higher than the total energy of isolated **1** and $[PH_2]^-$, which helps explain the formation of **2b** even at low temperatures.

While only the decomposition by-product [IDipp-H]$^+$ of **2a** and **2b** could be detected by LIFDI-MS spectrometry, both isomers were successfully characterized by NMR spectroscopy and single-crystal X-ray structure analysis. The ^{1}H NMR spectra of **2a** and **2b** in C_6D_6 show a multiplet resonance for the GeH$_2$-moiety at $\delta = 3.85$ ppm (**2a**) and a doublet of pseudo-quintets at $\delta = 3.46$ ppm (**2b**; $^{2}J_{H,P} = 17.5$ Hz, $^{3}J_{H,H} = 4.3$ Hz). The ^{31}P{^{1}H} NMR spectrum of **2a** ($\delta = -202.3$ ppm) reveals a broad multiplet due to the coupling with the neighboring boron atom, a sharp singlet is found for **2b** ($\delta = -244.0$ ppm). Both signals show further splitting in the corresponding ^{31}P NMR spectra into a broad triplet (**2a**, $^{1}J_{H,P} = 180$ Hz) and a triplet of triplets (**2b**; $^{1}J_{H,P} = 176$ Hz, $^{2}J_{H,P} = 17.5$ Hz). Similarly, the ^{11}B NMR spectra reveal broad triplets at $\delta = -37.9$ ppm (**2a**, $^{1}J_{H,B} = 104$ Hz) and $\delta = -34.7$ ppm (**2b**, $^{1}J_{H,B} = 97$ Hz) that both collapse into a broad multiplet (**2a**) and a singlet (**2b**) within the respective ^{11}B{^{1}H} NMR spectra. Slow solvent evaporation of Et_2O solutions of mixtures of **2a** and **2b** afforded colorless single crystals with different ratios of the co-crystallized isomers (Figure 3).

Interestingly, crystals that contain a higher amount of **2a** ($\geq$ 63%) crystallize in the monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit, while crystals containing a higher amount of **2b** ($\geq$90%) crystallize in the orthorhombic space group *Pccn*, although co-crystallization of both isomers is observed in every case. For **2b** the H_2GePH_2 moiety shows slight disorder (see Supporting Information for details). In the solid state, the C–Ge distances [1.962(6)–2.007(7) Å] as well as the Ge–B [2.031(15)–2.076(19) Å] and B–P distances [1.93(2)–2.07(2) Å] of **2a** are all in the expected range of single bonds. Analogously, the C–B [1.572(4) Å], B–Ge [2.047(4) Å] and Ge–P [2.320(3) Å] bond lengths within isomer **2b** are in the expected range of single bonds. The C–Ge–B–P torsion angles of **2a** in the asymmetric unit adopt values up to 169.9(5)°, while the C–B–Ge–P torsion angle of **2b** is 157.2(3)°.[16]

As the lone pair at the phosphorus atoms within the isomers **2a** and **2b** should provide the opportunity for follow-

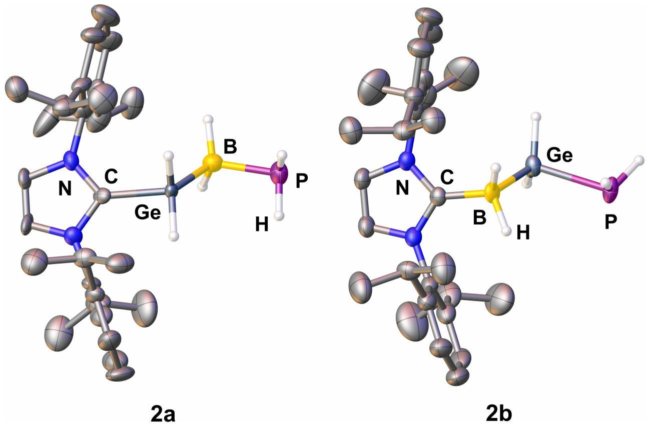
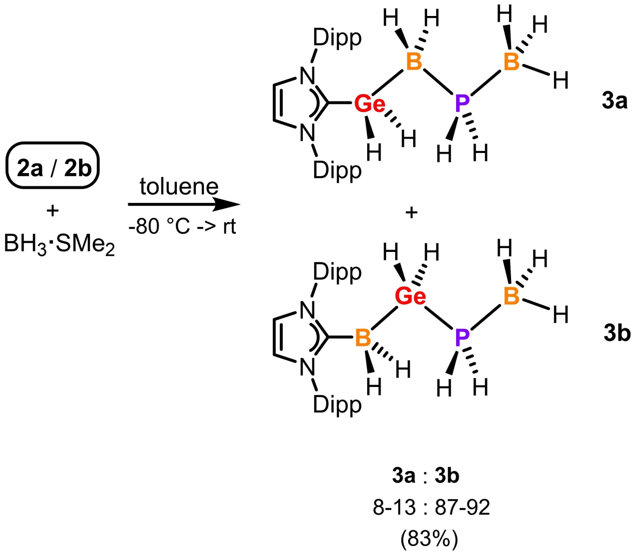


Figure 3. Molecular structure of one molecule of **2a** from a mixture containing largely **2a** (left) in the asymmetric unit with thermal ellipsoids at a 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°] with metrical parameters for the second molecule listed in parentheses: C–Ge 1.962(6) [2.007(7)], Ge–B 2.076(19) [2.031(15)], B–P 1.93(2) [2.07(2)]; C–Ge–B 119.1(6) [115.3(6)], Ge–B–P 107.3(9) [103.7(9)]. Molecular structure of **2b** from a mixture containing mostly **2b** (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 [°]: C–B 1.572(4), B–Ge 2.047(4), Ge–P 2.320(3); C–B–Ge 113.3(1), B–Ge–P 106.47(13).

up chemistry, we wondered if it would be possible to extended the group 13/14/15 moieties by combination with a main-group Lewis acid. In fact, the addition of $H_3B\cdot SMe_2$ to a toluene solution of mixtures of **2a** and **2b** at −80°C and subsequent stirring of the reaction mixture for 1.5 hours at room temperature affords the two borane adducts $IDipp\cdot GeH_2BH_2PH_2BH_3$ (**3a**) and $IDipp\cdot BH_2GeH_2PH_2BH_3$ (**3b**) (Scheme 3), which feature an extended hydrogen-substituted 13/14/15/13 element chain. Mixtures of **3a** and **3b** can be isolated as white powders in high yields, however, these isomers cannot be separated due to their similar solubilities. Both **3a** and **3b** are stable as solids at room temperature under an inert atmosphere but slowly decompose in solution with release of PH_3. While neither characterization of **3a** and **3b** by LIFDI-MS, nor crystallization of both isomers was successful (due to their very limited stability in solution), these isomers could be characterized by NMR spectroscopy.



Scheme 3. Synthesis of the parent compounds **3a** and **3b**. Yields are given in parentheses.

The ^1H NMR spectra of **3a**/**3b** mixtures in C_6D_6 show two multiplet resonances for the respective GeH_2-moieties at $\delta = 3.84$ ppm (**3a**) and $\delta = 3.45$ ppm (**3b**), respectively. The ^{31}P NMR data assigned to **3a** shows a distinct triplet at $\delta = -104.2$ ppm ($^1J_{H,P} = 311$ Hz) and for **3b** a broad triplet at $\delta = -131.3$ ppm ($^1J_{H,P} = 326$ Hz) is observed; both resonances are significantly downfield-shifted in comparison to the signals from the starting materials (**2a**: $\delta = -202.3$ ppm, **2b**: $\delta = -244.0$ ppm; Figure 4). In addition, the ^{11}B NMR spectral data of **3b** yields a triplet for the BH_2 moiety at $\delta = -36.1$ ppm ($^1J_{H,B} = 99$ Hz) and a broad quartet for the terminal BH_3 moiety at $\delta = -38.7$ ppm ($^1J_{H,B} = 100$ Hz). The ^{11}B NMR signals for **3a** are superimposed by those of **3b** but can still be located as a broadened quartet at −39.5 ppm (BH_3) and a singlet at −40.4 ppm (BH_2, $^1J_{BH}$ coupling not resolved due to significant signal broadening). Furthermore, quantum chemical computations reveal that the formation of **3a** and **3b** are both exothermic and exergonic, which is in line with the experimental observations of the constant ratio between the isomers with respect to the isomer ratio of the starting mixture of **2a**/**2b** (cf. Supporting Information). According to the computational studies, **3b** is more stable than **3a** by $-58.3\ kJ\,mol^{-1}$ and can thus be considered as the thermodynamic product.

Coming back to the initially introduced compounds **2a** and **2b**, which can be successfully crystallized either by slow evaporation of Et_2O or by cooling concentrated toluene/*n*-hexane solutions, to our surprise, the crystallization attempts by solvent diffusion of *n*-hexane into a THF solution of a mixture of **2a**/**2b** (4°C, 9:91 ratio, Scheme 4) yielded a few colorless crystals of $[IDipp\cdot GeH_2BH_2\cdot IDipp][PHGeH_2BH_2PH_2BH_2GeH_2]$ (**4**). **4** represents the first inorganic example of a heterocycle that exclusively consists of combinations of hydrogen-substituted

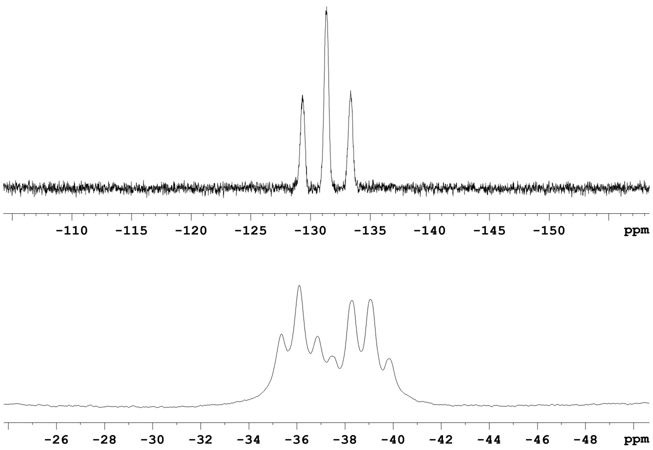
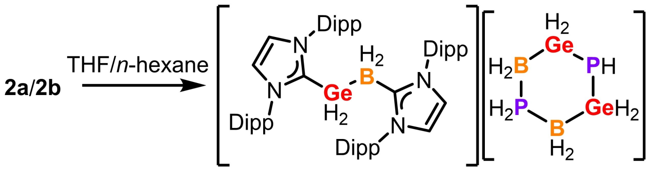


Figure 4. ^{31}P (top) and ^{11}B (bottom) NMR spectra of **3b** in C_6D_6 as sections of the overall spectra at 298 K.



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Scheme 4. Partial conversion of **2a**/**2b** to [IDipp·GeH_2BH_2·IDipp][$PHGeH_2BH_2PH_2BH_2GeH_2$] (**4**) by layering in THF/*n*-hexane.

(parent) group 13,14 and 15 moieties. In contrast, analogous layering/crystallization attempts where THF is substituted by CH_2Cl_2 only led to decomposition, as **2a**/**2b** show limited stability in CH_2Cl_2.

While **4** is stable as a solid at ambient temperatures in an inert atmosphere, it slowly decomposes in solution with the release of PH_3. In the mass spectra (ESI-MS) of a freshly prepared CH_2Cl_2 solution of **4**, the molecular ion peaks for the anionic heterocycle (negative mode) and the cation [IDipp·GeH_2BH_2·IDipp]$^+$ (positive mode) are detected (cf. Supporting Information for details). The ^{1}H NMR spectrum of **4** in CD_2Cl_2 shows two signals for the GeH_2-moieties of the anionic heterocycle due to the existence of axial and equatorial protons, which is comparable to the ^{1}H NMR spectrum of cyclohexane at low temperatures (see Supporting Information for details).[17] In the ^{31}P{^{1}H} NMR spectrum a broad multiplet is detected at $\delta = -98.1$ ppm ($^1J_{P,B} = 64$ Hz) and an additional sharp singlet is located at $\delta = -270.5$ ppm. While the signal at $\delta = -98.1$ ppm shows further splitting into a broad triplet (PH_2; $^1J_{H,P} = 320$ Hz) in the ^{31}P NMR spectrum, the signal at $\delta = -270.5$ ppm splits into a doublet (PH; $^1J_{H,P} = 163$ Hz). In addition, the ^{11}B NMR spectrum reveals a doublet of triplets for the BH_2 moieties of the anionic heterocycle at $\delta = -40.3$ ppm ($^1J_{P,B} = 64$ Hz, $^1J_{H,B} = 102$ Hz) and a triplet resonance from the counter-ion at $\delta = -37.7$ ppm ($^1J_{H,B} = 100$ Hz).

The solid-state structure of **4** shows a cation featuring a $[H_2BGeH_2]^+$ unit that is stabilized by two capping IDipp donors. The Ge–B bond length of 2.089(12) Å is in range of a slightly elongated single bond, which is consistent with computed Wiberg bond index of 0.927. The anion represents a cyclohexyl-like unit, which consists of two GeH_2 moieties, that enclose one PH entity, two BH_2 moieties and one PH_2 component (Figure 5). As a side note, a minor part (17%) of the inorganic heterocycle in **4** crystallized with an envelope conformation (cf. Supporting Information); the $B_2Ge_2P_2$ heterocycle is also distorted between several positions (see Supporting Information for details). The P–Ge distances [2.3264(15)–2.4284(18) Å], the Ge–B bond lengths [1.952(6)–2.047(9)Å] and the B–P distances [1.911(9)–1.965(5) Å] of the heterocycle are all in the expected range of single bonds.[16] Corresponding Wiberg bond indices are in range 0.91–1.0, which is consistent with single bonds. Furthermore, the computational results indicate, that the negative charge in the anion is distributed between PH (−0.39 ē), two BH_2 groups (−0.21 ē each) and two GeH_2 groups (−0.08 ē each). The most negative charge of −0.41 ē possesses the P atom of the PH group, while the negative charge of BH_2 groups is predominantly located on H atoms (−0.1 ē each).

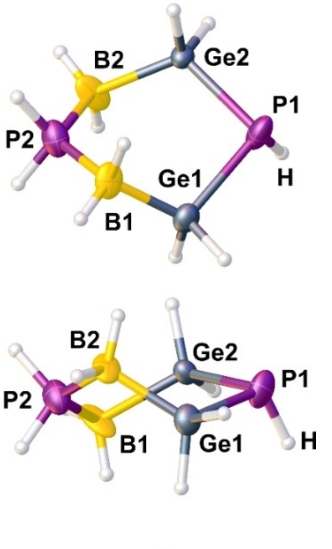

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Figure 5. Top view (top) and side view (bottom) of the major part of the molecular structure of the anion in **4** in the solid state with thermal ellipsoids at a 50% probability level. Selected bond lengths [Å] and angles [°]: P–Ge 2.3264(15)–2.4284(18), Ge–B 1.952(6)–2.047(9), B–P 1.911(9)–1.965(5); Ge–P–Ge 99.42(6), B–P–B 122.8(4), B–Ge–P 110.8(2)–116.4(4), P–B–Ge 108.2(3)–109.6(4).

Moreover, computations for a possible isomer of the anionic heterocycle in **4** with the PH group placed in between two BH_2 moieties predict much longer Ge–P, Ge–B and B–P bond distances and a higher relative energy (145 kJ mol^{-1}) compared to the experimentally found isomer, proving support for the atom connectivity assigned via crystallography.[18]

Conclusions

In summary, we have shown that reactions of IDipp·GeH_2BH_2OTf (**1**) with $NaPH_2$ result in mixtures of the isomers IDipp·$GeH_2BH_2PH_2$ (**2a**) and IDipp·$BH_2GeH_2PH_2$ (**2b**), revealing unprecedented neutral NHC-stabilized parent group 13/14/15 compounds. The formation of **2b** was rather unexpected, however, tuning the reaction conditions enabled formation of **2b** with an isomer amount of over 90%. Both isomers were characterized by single-crystal X-ray diffraction and NMR spectroscopy. Furthermore, the corresponding isomer mixtures of the parent adducts IDipp·$GeH_2BH_2PH_2BH_3$ (**3a**) and IDipp·$BH_2GeH_2PH_2BH_3$ (**3b**) could be obtained from reactions of **2a** and **2b** with H_3B·SMe_2 and feature novel, even longer group 13/14/15 element chains with only hydrogen atom substituents. Computational results indicate that the isomers with a group 14 element occupying the central position of a chain are more energetically favorable and appear to be prospective synthetic targets. In addition, attempts to crystallize a mixture of **2a** and **2b** from THF solutions surprisingly afforded the anionic cyclohexyl-like ring $[PHGeH_2BH_2PH_2BH_2GeH_2]^-$ within the final product **4**, which represents the first example of an only hydrogen-substituted inorganic heterocycle consisting of group 13, 14 and 15 elements. Further investigations will be focused on the synthesis of comparable 13/14/15 element units with alternate congeners.

Supporting Information

The authors have cited additional references within the Supporting Information.[19]

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical calculations and X-ray crystallographic details are summarized in the Supporting Information. The authors have cited additional references within the Supporting Information (Ref. [19]).

Deposition Numbers 2301528 (**2a**), 2301529 (**2b**), and 2301530 (**4**) 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.

Computational details: The geometries of the compounds have been fully optimized with gradient-corrected density functional theory (DFT) in form of Becke's three-parameter hybrid method B3LYP[19g,h] with def2-TZVP all electron basis set.[19i] The Gaussian 09 program package[19j] was used throughout. All structures correspond to minima on their respective potential energy surfaces as verified by computation of second derivatives. Basis sets were obtained from the EMSL basis set exchange database.[19k,l]

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Conflict of Interests

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.

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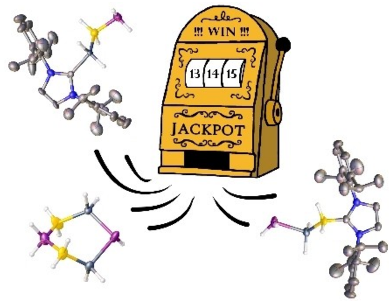
RESEARCH ARTICLE

Reactions of the NHC-stabilized compound IDipp$\cdot$$GeH_2BH_2OTf$ with $NaPH_2$ were carried out. Hereby, mixtures of isomers of the unprecedented parent hydride adducts IDipp$\cdot$$GeH_2BH_2PH_2$ and IDipp$\cdot$$BH_2GeH_2PH_2$ were isolated in different ratios in favour of the latter isomer, depending on the reaction conditions. Subsequent reactions of these isomers yielded the borane adducts IDipp$\cdot$$GeH_2BH_2PH_2BH_3$ and IDipp$\cdot$$BH_2GeH_2PH_2BH_3$ as well as the cyclohexyl-like anion $[PHGeH_2BH_2PH_2BH_2GeH_2]^-$.



*Dr. M. T. Ackermann, R. Szlosek, C. Riesinger, Dr. M. Seidl, Prof. Dr. A. Y. Timoshkin, Prof. Dr. E. Rivard, Prof. Dr. M. Scheer**

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NHC-Stabilized Mixed Group 13/14/15 Element Hydrides