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A convenient route to mixed cationic group 13/14/15 compounds†

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The formation of novel cationic mixed main group compounds is reported revealing a chain composed of different elements of group 13, 14, and 15. Reactions of different pnictogenylboranes $R_2EBH_2\cdot NMe_3$ (E = P, R = Ph, H; E = As, R = Ph, H) with the NHC-stabilized compound $IDipp\cdot GeH_2BH_2OTf$ (**1**) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) were carried out, yielding the novel cationic, mixed group 13/14/15 compounds $[IDipp\cdot GeH_2BH_2ER_2BH_2\cdot NMe_3]^+$ (**2a** E = P; R = Ph; **2b** E = As; R = Ph; **3a** E = P; R = H; **3b** E = As; R = H) by the nucleophilic substitution of the triflate (OTf) group. The products were analysed by NMR spectroscopy and mass spectrometry and for **2a** and **2b** also by X-ray structure analysis. Further reactions of **1** with $H_2EBH_2\cdot IDipp$ (E = P, As) resulted in the unprecedented parent complexes $[IDipp\cdot GeH_2BH_2EH_2BH_2\cdot IDipp][OTf]$ (**5a** E = P; **5b** E = As), which were studied by X-ray structure analysis, NMR spectroscopy and mass spectrometry. Accompanying DFT computations give insight into the stability of the formed products with respect to their decomposition.

Introduction

Carbon- and main group element-containing catena compounds based on C–El (*e.g.*, El = B, Si, P) building blocks have been known for a long time and are used for various applications.[1a–f] For instance, 1,3-disilabutane, $H_3SiCH_2SiH_2$-CH_3, serves as a precursor for SiC thin film deposition in several CVD (Chemical Vapor Deposition) processes.[2] Similarly, inorganic chain compounds that consist of two different main group elements are well known in the literature, especially in the case of group 13/15 [3] and 14/15 [4] compounds, respectively. However, comparable compounds that are assembled by three different elements of group 13, 14 and 15 are very limited, in particular, if heavier homologues are considered.[5] For example, in 2004 Tokitoh and coworkers reported the neutral silylboranephosphine **I**, which was synthesised by reaction of a sterically crowded silylene with $BH_3\cdot PPh_3$ (Chart 1).[6] Alternatively, the anionic phosphineboranestannate **II** was synthesized by Wright and coworkers through the reaction of $LiSn(NMe_2)_3$ with the phosphine-borane $^tBu_2PH\cdot BH_3$.[7] Examples for chain-like group 13/14/15 compounds which are stabilized by β-diketiminate ligands are the very recently reported compound **III** by Schulz[8] and compound **IV** by von Hänisch and

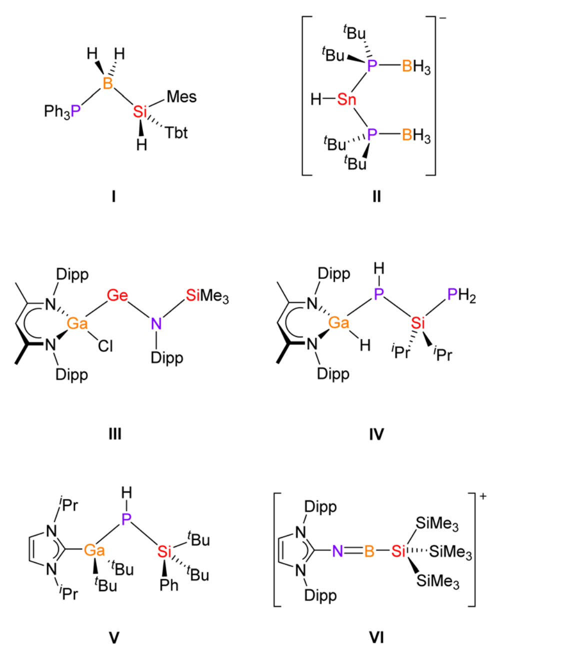

Chart 1 Selected examples for mixed group 13/14/15 chain compounds.

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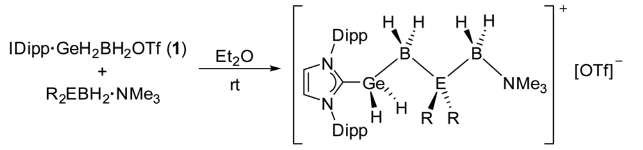
coworkers.[9] Furthermore, the von Hänisch group reported unexpected reactivity of a four-membered Ga/P heterocycle towards bulky *N*-heterocyclic carbene (NHC) ligands, leading to the silylphosphinogallane **V**.[10] In addition, Inoue and coworkers prepared the structurally related silylaminoborane $IMe_4 \cdot BH_2$-$NHSiH_2Si^tBu_3$ (IMe_4 = 1,3,4,5-tetra(methyl)imidazole-2-ylidene)[11] and the NHC-stabilized compound **VI** from a salt-metathesis reaction.[12]

The few existing examples of linear group 13/14/15 compounds are usually short (3-membered) chains and possess organic groups to stabilize them. Thus, the only examples of parent group 13/14/15 chains containing only hydrogen substituents, including the triple mixed hydrides $H_3TetPH_2BH_3$ (Tet = Si, Ge) and our recently reported compound [IDipp·$GeH_2BH_2PH_3$][OTf] (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene), could not be isolated or show very limited stability, which prevented their full characterization.[13] Thus, it is still very desirable to develop efficient synthetic routes for longer parent chain compounds, as they might represent suitable single-source precursors to bulk and nanodimensional ternary solids of tuneable composition and function, which can serve as small bandgap semiconductors for optoelectronics.[14]

Our group has a special interest in hydride-substituted (parent) group 13/15 compounds, and donor/acceptor stabilization is an elegant method for the development of several group 13/15 parent compounds of the type LA·$H_2EE'H_2$·LB (E = group 15 element, E' = group 13 element, LA = Lewis acid, LB = Lewis base).[15] This concept was successfully refined to the LB-only stabilization of pnictogenyltriels $H_2EE'H_2$·LB.[16] Besides neutral compounds, the NMe_3-stabilized pnictogenylboranes $H_2EBH_2 \cdot NMe_3$ (E = P, As) could also be applied to build up cationic chain complexes.[3c,d] Hence, we wondered if it is possible to obtain long mixed group 13/14/15 chain compounds (group 14 element ≠ C) by the reaction of LB-stabilized pnictogenylboranes with the mixed group 13/14 starting material IDipp·GeH_2BH_2OTf (**1**) and if so, this approach could enable access to the longest cationic group 13/14/15 chains bearing only hydrogen substituents.

Results and discussion

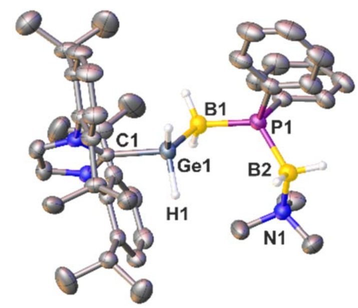
Reactions of IDipp·GeH_2BH_2OTf (**1**) with the LB-stabilized diphenyl substituted pnictogenylboranes $Ph_2EBH_2 \cdot NMe_3$ (E = P, As) led to the formation of the unprecedented mixed cationic group 13/14/15 chains as OTf^- salts of [IDipp·$GeH_2BH_2EPh_2$-$BH_2 \cdot NMe_3$]$^+$ (**2a** E = P; **2b** E = As) (Scheme 1) and represent, to our knowledge, the longest cationic, mixed element 13/14/15 (group 14 element ≠ C) chain compounds so far. After stirring the reaction mixture overnight, the Ge–B–E–B–N chains **2a** and **2b** could be isolated in high yields of 94 and 93%, respectively. The reactions were performed in Et_2O solutions, as the cationic complexes precipitate out of the reaction mixture upon formation and can then be isolated as pure white powders. Compounds **2a** and **2b** are well soluble in more polar solvents like CH_2Cl_2 or THF and are stable in solution and as solids, at ambient temperatures under an inert atmosphere. After the



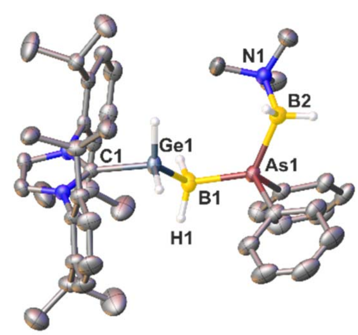
2a	E = P	R = Ph (94%)
2b	E = As	R = Ph (93%)
3a	E = P	R = H (68%)
3b	E = As	R = H (74%)

Scheme 1 Synthesis of the group 13/14/15 chain compounds **2a**, **2b**, **3a** and **3b**. Yields are given in parentheses.

successful formation of the organo-substituted cationic group 13/14/15 chains in **2a** and **2b**, we wondered if the all hydrogen-substituted Ge-B-E-B chains [IDipp·$GeH_2BH_2EH_2BH_2 \cdot NMe_3$] [OTf] (**3a** E = P; **3b** E = As) could be synthesized analogously. Reactions were performed under the same conditions as for **2a** and **2b** by using IDipp·GeH_2BH_2OTf (**1**) and the parent pnictogenylboranes $H_2EBH_2 \cdot NMe_3$ (E = P, As) as starting materials. Similar to the diphenyl-substituted compounds, the formed ionic products **3a** and **3b** precipitate out of the reaction mixture and could be isolated as white powders, however, in slightly lower yields of 68 and 74%, respectively (Scheme 1). While both



2a



2b

Fig. 1 Molecular structures of the cations in **2a** (top) and **2b** (bottom) in the solid state with thermal ellipsoids at a 50% probability level. Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2a**: C1–Ge1 2.009(2), Ge1–B2 2.051(3), B1–P1 1.937(3), P1–B2 1.969(3), B2–N1 1.609(3); C1–Ge1–B1 111.86(10), Ge1–B1–P1 112.17(14), P1–B2–N1 116.50(18). **2b**: C1–Ge1 2.0075(18), Ge1–B1 2.054(2), B1–As1 2.047(2), As1–B2 2.072(2), B2–N1 1.599(3); C1–Ge1–B1 112.01(8), Ge1–B1–As1 111.19(10), As1–B2–N1 114.43(13).

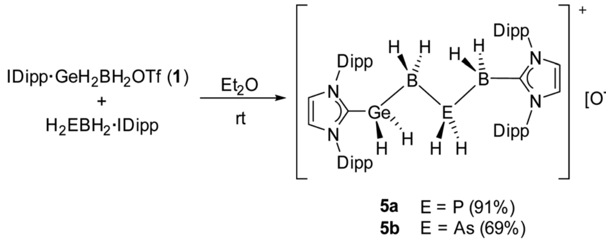
products are stable as solids at ambient temperatures in an inert atmosphere, they slowly decompose within several days in solutions of CH_2Cl_2 or THF.

While single crystals of the diphenyl-substituted compounds **2a** and **2b** were successfully obtained (Fig. 1) by layering a THF solution of the corresponding compounds with *n*-hexane, numerous attempts to crystalize the parent compounds **3a** and **3b** failed due to their rather fast decomposition in solution, leading only to the crystallization of [IDippH][OTf].

In order to perform X-ray structure analysis on salts of the parent chains **3a/b**, attempts to exchange the $[OTf]^-$ anions with the larger weakly coordinating anions (WCAs) $[BArF_{20}]^-$ ($BArF_{20}$ = $[B(C_6F_5)_4]$) and $[TEF]^-$ (TEF = $[Al\{OC(CF_3)_3\}_4]$) were carried out, as the bigger anions might promote a more favorable packing of the ion pairs within the solid state. However, those attempts failed to yield crystals. Thus, experiments to exchange the rather small LB NMe_3 with the sterically more demanding NHCs were performed. Out of the NHCs used IMe_4, IMes (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene) and IDipp, only the latter was suitable for the crystallization of the desired products (*vide infra*). Whereas only decomposition was observed for the reaction of **1** and $H_2PBH_2\cdot IMe_4$, the parent compound $[IDipp\cdot GeH_2BH_2PH_2BH_2\cdot IMes][OTf]$ (**4**) could be isolated as white powder in 68% yield from the reaction of **1** and $H_2PBH_2\cdot IMes$. While **4** was verified by NMR spectroscopy, all crystallization attempts failed and only decomposition was observed. Similarly to $H_2PBH_2\cdot IMes$, reactions of **1** with $H_2EBH_2\cdot IDipp$ (E = P, As) in Et_2O result in the formation of the desired parent complexes $[IDipp\cdot GeH_2BH_2PH_2BH_2\cdot IDipp][OTf]$ (**5a** E = P; **5b** E = As) in high yields for **5a** (91%) and good yields for **5b** (69%) (Scheme 2).

The ^1H NMR spectra in CD_2Cl_2 of all isolated group 13/14/15 chain compounds show signals for the GeH_2-moieties in the expected range of $\delta = 3.20–3.57$ ppm. Furthermore, the ^{31}P NMR spectrum of **2a** contains a broad singlet at $\delta = -24.9$ ppm due to the coupling with the ^{11}B nuclei and shows a downfield shift compared to the starting material $Ph_2PBH_2\cdot NMe_3$ ($\delta = -39.5$ ppm).[17] Analogously, the hydrogen-substituted compounds **3a**, **4** and **5a** each display a broad ^{31}P NMR triplet resonance with almost identical chemical shifts for the PH_2 moieties ($\delta = -112.1$ to -116.6 ppm; $^1J_{P,H} = 334–340$ Hz). The ^{11}B NMR spectra of **2a** – **3b** reveal two broad signals for the BH_2 moieties in the range of $\delta = -6.4$ to -10.8 ppm and $\delta = -37.2$ to -43.5 ppm. In contrast to the NMe_3-stabilized compounds **2a** – **3b**, the ^{11}B NMR spectra of **5a** and **5b** show a significantly upfield-shifted signal for the terminal boron atom within the Ge–B–E–B chain (**5a** $\delta = -34.8$ ppm; **5b** $\delta = -33.3$ ppm) due to the exchange of NMe_3 with IDipp. This is also observed for the substitution with IMes in compound **4** ($\delta = -35.3$ ppm). Similar to the NMe_3-stabilized compounds, a broad signal for the second boron atom is found in the range of $\delta = -39.6$ to -42.8 ppm. Moreover, all molecular ion peaks of the products **2a–5b** (except **4**) are detected in the ESI-MS spectra (see ESI† for details).

The solid state structures of **2a** and **2b** reveal similar C–Ge bond lengths [**2a**: 2.009(2) Å; **2b**: 2.0075(18) Å] (Fig. 1). In addition, the Ge–B distances are almost identical [**2a**: 2.051(3) Å; **2b**: 2.054(2) Å]. The P–B bond lengths of **2a** [1.937(3) and 1.969(3) Å] and the As–B bond lengths of **2b** [2.047(2) and 2.072(2) Å] are in the expected range for single bonds. The B–P–B angle measures 119.27(13)°, while the corresponding B–As–B angle is slightly wider [122.45(9)°]. Both B–N distances [**2a**: 1.609(3) Å; **2b**: 1.599(3) Å] are within the expected range of single bonds.[18] In the Ge–B–E–B chain (**2a**: E = P, **2b**: E = As) all substituents adopt a staggered conformation about the Ge–B and both E–B bond



Scheme 2 Synthesis of the parent compounds **5a** and **5b**. Yields are given in parentheses.

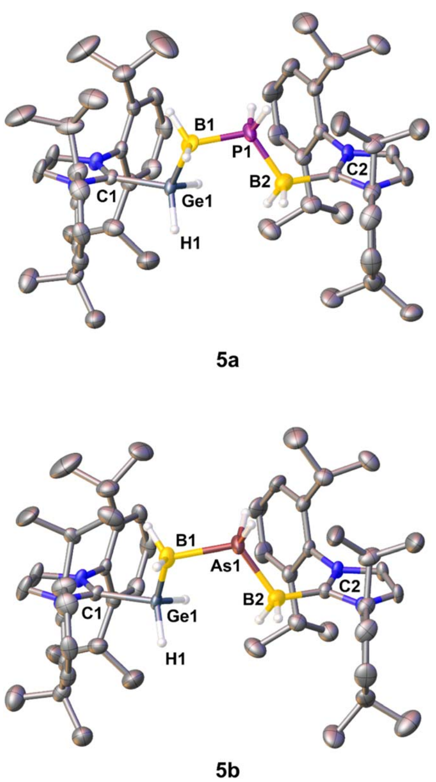


Fig. 2 Major parts of the disordered molecular structures of the cations in **5a** (top) and **5b** (bottom) in the solid state with thermal ellipsoids at a 50% probability level. Only one cation of the asymmetric unit is depicted, respectively. Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5a**: C1–Ge1 1.955(3), Ge1–B1 2.014(7), B1–P1 1.934(6), P1–B2 1.922(13), B2–C2 1.665(11); C1–Ge1–B1 111.3(2), Ge1–B1–P1 105.7(3), B1–P1–B2 114.8(4), P1–B2–C2 116.1(8). **5b**: C1–Ge1 1.994(3), Ge1–B1 2.055(8), B1–As1 2.076(6), As1–B2 2.034(10), B2–C2 1.595(9); C1–Ge1–B1 112.1(2), Ge1–B1–As1 103.4(3), B1–As1–B2 119.0(4), As1–B2–C2 112.2(7).

Table 1 Thermodynamic characteristics for gas phase processes. Reaction energies $\Delta E_0°$, standard enthalpies $\Delta H_{298}°$ and Gibbs energies $\Delta G_{298}°$ in kJ mol^{-1}, standard reactions entropies $\Delta S_{298}°$ in J mol^{-1} K^{-1}. B3LYP/def2-TZVP level of theory

Process	$\Delta E_0°$	$\Delta H_{298}°$	$\Delta S_{298}°$	$\Delta G_{298}°$
1 + $Ph_2PBH_2 \cdot NMe_3$ = **2a**	−77.9	−69.0	−183.6	−14.3
1 + $Ph_2AsBH_2 \cdot NMe_3$ = **2b**	−51.3	−43.8	−168.9	6.6
1 + $H_2PBH_2 \cdot NMe_3$ = **3a**	−67.5	−58.1	−173.9	−6.2
1 + $H_2AsBH_2 \cdot NMe_3$ = **3b**	−39.9	−31.8	−168.5	18.4
1 + $H_2PBH_2 \cdot$IDipp = **5a**	−122.8	−113.8	−151.0	−68.7
1 + $H_2AsBH_2 \cdot$IDipp = **5b**	−88.1	−80.0	−146.7	−36.3
3a + IDipp = **5a** + NMe_3	−79.4	−82.0	−33.7	−72.0
3b + IDipp = **5b** + NMe_3	−75.8	−78.2	−35.4	−67.6

axes. Specifically, an antiperiplanar conformation is present about the Ge1–B1 axis, whilst a synperiplanar arrangement is found about the B1–E1-axis, and a synclinal arrangement exists about the E1–B2-axis. Similar to **2a** and **2b**, single crystals of **5a** and **5b** could be obtained by layering of a CH_2Cl_2 solution of the products with *n*-hexane at room temperature. Both compounds **5a** and **5b** crystallize with two independent molecules in the asymmetric unit and show a very disordered Ge–B–E–B (E = P, As) chain (Fig. 2; see the ESI† for details). In the solid state both compounds reveal Ge–B single bond distances. The P–B bond lengths of compound **5a** and the As–B bond lengths of **5b** are in the expected range for single bonds.[18]

Computational studies of the gas phase reactions of $IDipp \cdot GeH_2BH_2OTf$ with $R_2EBH_2 \cdot LB$ leading to the ion pairs reveal that those processes are exothermic for all cases (Table 1). The favorability increases in the order **3b** < **2b** < **3a** < **2a** < **5b** < **5a** and thus, confirms the experimental findings well. In detail, the formation of the phosphorus derivatives is more exothermic (by 18–35 kJ mol^{-1}) than for the corresponding arsenic compounds. Furthermore, the formal substitution of NMe_3 by IDipp is exothermic by 75–80 kJ mol^{-1} and therefore significantly increases the stability of the respective hydride-only-substituted products.

Conclusions

The results show that the synthetic concept to generate cationic linear chain compounds by using $IDipp \cdot GeH_2BH_2OTf$ (**1**) in the reactions with different pnictogen sources could be successfully applied to obtain the longer, parent, mixed group 13/14/15 chain compounds containing a Ge–B–E–B (E = P, As) sequence. As a result, the diphenyl-substituted compounds **2a** and **2b** were synthesized in very good yields and were fully characterized. In addition, the cationic chain compounds of only hydrogen-substituted parent group 13/14/15 elements $[IDipp \cdot GeH_2BH_2EH_2BH_2 \cdot NMe_3][OTf]$ (**3a** E = P; **3b** E = As) could be isolated successfully. Subsequent substitution of NMe_3 with IDipp for the group 13/14/15 chains containing only hydrogen substituents allowed X-ray structure analysis on the unprecedented parent compounds **5a** and **5b**. Further investigations are directed to generate anionic or neutral chain compounds of mixed group 13/14/15 elements.

Data availability

All experimental procedures, spectroscopic data, information on the theoretical calculations and crystallographic data can be found in the ESI.†

Author contributions

M. T. A. and R. C. performed the experimental work. M. T. A wrote the original draft. A. Y. T. performed the DFT calculations. M. Seidl, Y. Z. and M. J. F. performed single crystal X-ray experiments and interpreted the structural data. E. R. and M. Scheer supervised and acquired funding for the project.

Conflicts of interest

There are no conflicts to declare.

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