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Main-Group Chemistry

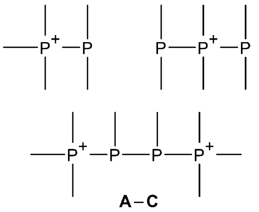
Cationic Chains of Phosphanyl- and Arsanylboranes**

*Christian Marquardt, Christine Thoms, Andreas Stauber, Gábor Balázs, Michael Bodensteiner, and Manfred Scheer**

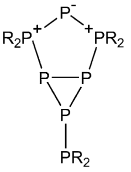
Dedicated to Professor Don Tilley on the occasion of his 60th birthday

Abstract: *Whilst catena-phosphorus cations have been intensively studied in the last years, mixed Group 13/15 element cationic chains have not yet been reported. Reaction of the pnictogenboranes $H_2EBH_2{\cdot}NMe_3$ (E = P, As) with monohalideboranes lead to the cationic chain compounds $[Me_3N{\cdot}BH_2EH_2BH_2{\cdot}NMe_3][X]$ (E = P, As; X = $AlCl_4$, I) and $[Me_3N{\cdot}BH_2PH_2BH_2PH_2BH_2{\cdot}NMe_3][X]$ (X = I, $VCl_4(thf)_2$), respectively. All of the compounds have been characterized by X-ray structure analysis, NMR spectroscopy, IR spectroscopy, and mass spectrometry. DFT calculations elucidate the reaction pathway, the high thermodynamic stability, the charge distribution within the chain and confirm the observed solid-state structures.*

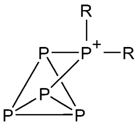
Over the last years, efforts at catenation of non-carbon elements have gained increasing attention. Whereas several chains of polyphosphines and polyphosphorus anions have been reported,[1–6] only recently the chemistry of catena-phosphorus cations has been discovered by Burford et al., leading to a wide variety of new catena-phosphorus species (see **A**–**C**).[7] Apart from linear chains, other structural motifs were found. Particularly cationic cycles[8,9] such as **D** and cages such as **E** are known, and their reactivity has been studied.[10]



A–C



D

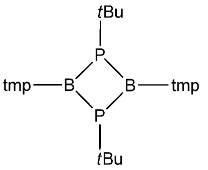


E

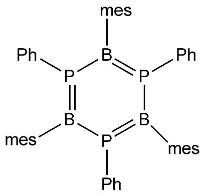
Boron compounds otherwise tend to form higher aggregated clusters rather than linear chains.[11] Although hints were given for the existence of a linear $B_8(NMe_2)_{10}$ compound,[12] the only structurally characterized longer derivatives are $B_4(NMe_2)_6$[13] and a cyclic species, $B_6(NMe_2)_6$.[14] Recently, a B_4R_4 chain was stabilized in the coordination sphere of a transition metal.[15] All of the examples reveal the requirement of organic substituents for catenation. A similar need was found for a reported In_6 chain.[16]

Lewis acid–base adduct compounds for Group 13/15 elements of the type $R_3E{\cdot}E'R_3$ (E = Group 15 element, E' = Group 13 element) are electronically and structurally related to hydrocarbons. The polyamino- and polyphosphinoboranes are mainly obtained by dehydrogenation/dehydrocoupling reactions mediated by metal catalysts and are the inorganic analogues of polymers such as polyolefins.[17,18]

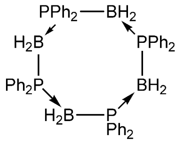
Among the different structural motifs of oligophosphinoboranes only the ring systems (**F**,[19] **G**,[19c] and **H**[20]) and the short four-membered chain **I**[21] have been characterized by X-ray structural analysis for which the presence of organic substituents is very helpful. Longer chain molecules such as **J**[22] were only characterized by spectroscopy.



F

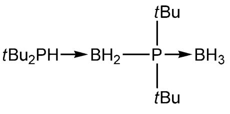


G



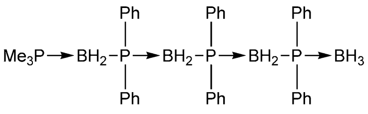
H

tmp = 2,2,6,6-tetramethylpiperidino mes = mesityl



$$tBu_2PH \rightarrow BH_2-\overset{tBu}{\underset{tBu}{P}} \rightarrow BH_3$$

I



$$Me_3P \rightarrow BH_2-\overset{Ph}{\underset{Ph}{P}} \rightarrow BH_2-\overset{Ph}{\underset{Ph}{P}} \rightarrow BH_2-\overset{Ph}{\underset{Ph}{P}} \rightarrow BH_3$$

J

We are especially interested in the synthesis of parent Group 13/15 compounds containing E−H bonds,[23] and reported recently the high-yield synthesis of the pnictogenboranes $H_2EBH_2{\cdot}NMe_3$ (E = P, As).[24] As they possess a Lewis basic lone pair, they are an ideal starting material for the synthesis of oligomeric compounds containing mixed Group 13/15 element chains by NMe_3 elimination. For instance, dehydro-oligomerization by titanocene leads to unprecedented phosphinoborane chain complexes.[25] As only neutral and complex-bound chain compounds have been reported to date,[23b,25] the quest for cationic chain molecules remains open. Herein we report the synthesis and characterization of the first cationic chain compounds con-

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[*] C. Marquardt, Dr. C. Thoms, A. Stauber, Dr. G. Balázs, Dr. M. Bodensteiner, Prof. Dr. M. Scheer
University of Regensburg, Institut für Anorganische Chemie
93040 Regensburg (Germany)
E-mail: manfred.scheer@ur.de

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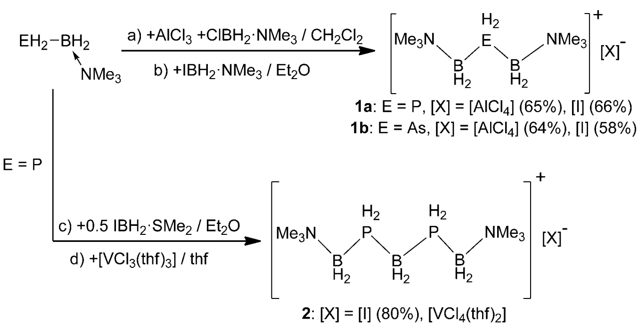
taining mixed Group 13/15 elements, including the first arsenic-containing chain molecules.

The reaction of the phosphanyl- or the arsanyl-borane $H_2EBH_2{\cdot}NMe_3$ (E = P, As) with one equivalent of $AlCl_3$ and $ClBH_2{\cdot}NMe_3$ leads to the formation of **1** revealing the cationic chain $[Me_3N{\cdot}BH_2{-}EH_2{-}BH_2{\cdot}NMe_3]^+$ (**1a**: E = P, **1b**: E = As; Scheme 1 a).



Scheme 1. Synthesis of cationic phosphanylborane chain compounds (yields in parentheses): a) $+AlCl_3+ClBH_2{\cdot}NMe_3$ in CH_2Cl_2; b) $+IBH_2{\cdot}NMe_3$ in Et_2O; c) $+0.5\,IBH_2{\cdot}SMe_2$ in Et_2O; d) $+[VCl_3(thf)_3]$ in THF.

According to ^{31}P NMR investigations, the reaction proceeds without any formation of side products, and salts of **1a,b** can be isolated as crystalline solids in good yields (**1a**[$AlCl_4$]: E = P 65%, **1b**[$AlCl_4$]: E = As 64%). For **1a**[$AlCl_4$], the ^{31}P NMR spectrum shows a very broad triplet at $\delta = -135.0$ ppm. The ^{11}B NMR spectra of **1a**[$AlCl_4$] and **1b**[$AlCl_4$] show similar chemical shifts at $\delta = -11.7$ ppm (**1a**[$AlCl_4$]) and $\delta = -9.1$ ppm (**1b**[$AlCl_4$]). In the solid state, **1a** adopts a zigzag conformation, with all substituents being in an antiperiplanar position (Figure 1). The P–B bond length of 1.957(3) Å is slightly shortened compared to the starting material (1.976(2) Å for $H_2PBH_2{\cdot}NMe_3$[23b]). The dihedral angle defined by the two N–P–B units is only 6.4(1)°, indicating an almost ideal zigzag conformation. In the solid state, weak H···Cl interactions between the PH_2 groups of the cation and $AlCl_4$ are observed (H···Cl distances 2.83 Å), which are slightly below the sum of the van der Waals radii of chlorine and hydrogen (Σr_{cov}H,Cl = 2.85 Å).[26]

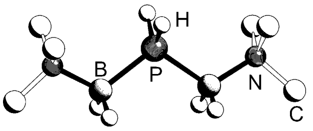


Figure 1. Molecular structure of the cation in **1a**[$AlCl_4$] and **1a**[I] in the solid state. Hydrogen atoms at the methyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1a**[$AlCl_4$]: P–B 1.957(2), N–B 1.594(2)–1.600(2); B-P-B 107.5(8), N-B-P 114.6(1)–114.7(1); **1a**[I]: P–B 1.959(5)–1.966(5), N–B 1.601(6)–1.608(6); B-P-B 111.5(8), N-B-P 113.0(3)–113.8(3).

Interestingly, **1b** shows a distorted zigzag chain in the solid state (Figure 2) with two nearly identical As–B bond lengths (2.076(3)–2.086(3) Å, 2.071(4) Å for $H_2AsBH_2{\cdot}NMe_3$[24]). One of the two B–As units adopts an antiperiplanar conformation, whereas the second unit shows a synclinal conformation, leading to a dihedral angle of 58.5(2)°. According to DFT calculations, the conformation with two antiperiplanar B–As units is more stable by 3.5 kJ mol^{-1} in solution. Thus, the conformation found in the solid state of **1b** is probably a result of packing effects. It is noteworthy that for **1b**[$AlCl_4$] no H···Cl interactions are observed in the solid state.

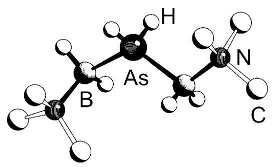


Figure 2. Molecular structure of the cation in **1b**[$AlCl_4$] and **1b**[I] in the solid state. The hydrogen atoms at the methyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1b**[$AlCl_4$]: As–B 2.076(3)–2.086(4), N–B 1.590(4)–1.595(5); B-As-B 123.0(1), N-B-As 113.3(2)–113.8(2); **1b**[I]: As–B 2.076(5)–2.077(6), N–B 1.587(6)–1.591(6); B-As-B 123.3(2), N-B-As 112.2(4)–112.8(3).

To elucidate the formation pathway, different experiments were carried out. Reacting $H_2EBH_2{\cdot}NMe_3$ (E = P, As) with $AlCl_3$ results in the formation of the Lewis acid–base adduct $AlCl_3{\cdot}H_2EBH_2{\cdot}NMe_3$ (E = P, As). The subsequent addition of $ClBH_2{\cdot}NMe_3$ in CH_2Cl_2 neatly yields **1**[$AlCl_4$], probably via the intermediary hyper-coordinated Al species $Me_3N{\cdot}BH_2Cl{\cdot}AlCl_3{\cdot}H_2EBH_2{\cdot}NMe_3$ (E = P, As). If $ClBH_2{\cdot}NMe_3$ is first treated with $AlCl_3$, followed by $H_2EBH_2{\cdot}NMe_3$ (E = P, As), the yield of the reaction decreases significantly. This is probably a consequence of the less-stable intermediate boranylium cation $[Me_3N{\cdot}BH_2][AlCl_4]$. Note that no change of reactivity is observed if $AlCl_3$ is added to a mixture of the corresponding Group 15 borane and $ClBH_2{\cdot}NMe_3$.

This reaction pathway is further supported by DFT calculations. The overall reaction of $H_2PBH_2{\cdot}NMe_3$ with $AlCl_3$ and $ClBH_2{\cdot}NMe_3$ to form [**1a**][$AlCl_4$] is endothermic by 95.9 kJ mol^{-1} in the gas phase. However, it becomes exothermic by -140.7 kJ mol^{-1} when the solvent effects are incorporated. The initial step towards the Lewis acid–base adduct $Me_3N{\cdot}BH_2PH_2{\cdot}AlCl_3$ is exothermic by -116.9 kJ mol^{-1}, whereas the formation of the boranylium cation $Me_3N{\cdot}BH_2^+$ is endothermic by 19.5 kJ mol^{-1}, but followed by the strongly exothermic addition of the phosphanylborane unit (Figure 3). Thus, both energy profiles are feasible and in a good agreement with the experimental observations.

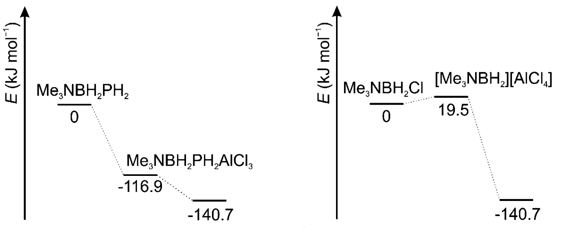


Figure 3. Energy profile of the reaction of $PH_2BH_2{\cdot}NMe_3$, $AlCl_3$ and $ClBH_2{\cdot}NMe_3$, starting from: a) $PH_2BH_2{\cdot}NMe_3$ and b) $ClBH_2{\cdot}NMe_3$.

When $IBH_2{\cdot}NMe_3$, is treated with $H_2EBH_2{\cdot}NMe_3$ (E = As, P), no halogen abstracting agent is necessary to form **1**[I] (**1a**: E = P, **1b**: E = As) in good yields, which is due to the much better leaving group iodine (Scheme 1 b). The spectroscopic data and geometric parameters of **1** are essentially identical with the compounds **1**[$AlCl_4$]. In the solid state **1a**[I] and **1b**[I] are isostructural to their [$AlCl_4$] derivatives. Even the weak interactions between the hydrogen atoms of the EH_2 groups and the counterion are present.

The natural population analysis (NPA) shows a relatively strong charge separation within the cationic chain of **1**, the positive charge being accumulated on the central P (+0.52e) and As (+0.53e) atom, whereas the B atoms are negatively charged (−0.22e and −0.18e for **1a** and **1b**, respectively). Based on the charge distribution the B−E−B unit (E = P, As) can formally be described as a phosphonium or arsonium cation.

Furthermore, we tried to create more extended B−P frameworks by combining the good leaving group iodide with an even more labile Lewis base. The corresponding reaction of $IBH_2{\cdot}SMe_2$ with $H_2PBH_2{\cdot}NMe_3$ leads to the formation of $[Me_3N{\cdot}BH_2{-}PH_2{-}BH_2{-}PH_2{-}BH_2{\cdot}NMe_3]^+[I]^-$ (**2**[I], Scheme 1 c) in high yields. Interestingly, when $H_2PBH_2{\cdot}NMe_3$ is reacted with [$VCl_3(thf)_3$], **2**[$VCl_4(thf)_2$] is obtained (Scheme 1 d). However, the exact yield of the reaction could not be determined, as $HNMe_3[VCl_4(thf)_2]$ co-crystallizes with **2**[$VCl_4(thf)_2$]. We attribute the formation of **2**[$VCl_4(thf)_2$] to the presence of $ClBH_2{\cdot}NMe_3$ in the starting material $H_2PBH_2{\cdot}NMe_3$.[24] [$VCl_3(thf)_3$] acts as halide abstractor, leading to the formation of the boranylium cation $BH_2{\cdot}NMe_3^+$, which reacts with $H_2PBH_2{\cdot}NMe_3$ to give **2**[$VCl_4(thf)_2$]. The NMR spectra of **2**[$VCl_4(thf)_2$] and **2**[I] show similar chemical shifts. The solid-state structures of **2**[I] and **2**[$VCl_4(thf)_2$] show the cation **2** in an all-antiperiplanar conformation in **2**[$VCl_4(thf)_2$] featuring an ideal zigzag chain, whereas in **2**[I] the arrangement along the two central B−P bonds is synclinal (Figure 4 and Figure 5). According to DFT calculations, the energy difference between the both alignments in solution is only 5.8 kJ mol^{-1}, favoring the all-antiperiplanar conformation. Thus, the observed different conformations of **2** probably originate from the size of the counterion and packing effects.

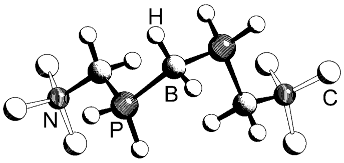


Figure 4. Molecular structure of the cation of **2**[I] in the solid state. The hydrogen atoms at the methyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: P–B 1.948(3)–1.949(5), N–B 1.595(6); B-P-B 110.6(2), P-B-P 108.2(1), N-B-P 116.9(3), B-P-B-P 51.7(2).

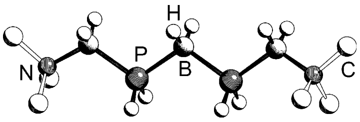


Figure 5. Molecular structure of the cation of **2**[$VCl_4(thf)_2$]. The hydrogen atoms at the methyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: P–B 1.930(3)–1.954(3), N–B 1.600(3)–1.604(4), B-P-B 109.7(1)–110.5(1), P-B-P 111.4(1), N-B-P 114.6(2)–115.5(2), B-P-B-P 171.3(2)–174.6(2).

An NPA analysis for **2** shows a more accentuated charge separation compared to **1**. The positive charge is equally localized on the two phosphorus atoms (+0.58e), whereas the negative charge is considerably higher on the central boron atom (−0.74e) relative to the peripheral boron atoms (−0.23e). Thus, the charge distribution again shows the pronounced ionicity of the B−P−B−P−B chains.

The results show the advantages of use of the parent phosphinoborane $PH_2BH_2NMe_3$ as a remarkable monomer to build-up unprecedented cationic chain compounds in a stepwise manner, and in high yields, which are structurally and electronically related to *n*-alkanes. These first phosphanylborane chains are unique representatives of the cationic class of Group 13/15 catena compounds, and they are the longest Group 13/15 chain compounds characterized by X-ray diffraction. The first arsenic-containing chain compound has now also been isolated. The chains show excellent thermodynamic stability, and the presented concepts will allow the formation of more extended chain molecules and also of more complex hydrocarbon-related structures. This will contribute to our knowledge about the C/PB relationship, and in future the chemical behavior will be investigated in more detail.

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Keywords: arsenic · boron · cationic chains · pentelylboranes · phosphorus

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