EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202100930

Chemistry Europe
European Chemical Societies Publishing

Very Important Paper

Synthesis and Reactivity of a Lewis-Base-Stabilized *tert*-Butyl Arsanylborane: A Versatile Building Block for Arsenic-Boron Oligomers

Felix Lehnfeld,[a] Michael Seidl,[a] Alexey Y. Timoshkin,[b] and Manfred Scheer*[a]

The synthesis and reactivity of the *tert*-butyl-substituted arsanylborane tBuAsHBH$_2$·NMe$_3$ (**1**) stabilized by a Lewis base (LB) are reported. Compound **1** is obtained by the reaction of *in situ* generated NatBuAsH with IBH$_2$·NMe$_3$. By the reaction of **1** with Lewis acids the neutral compounds BBr$_3$·tBuAsHBH$_2$·NMe$_3$ (**2**) and BH$_3$·tBuAsHBH$_2$·NMe$_3$ (**3**) as well as coordination products towards Group 6 metal complexes [M(CO)$_4$(tBuAsHBH$_2$·NMe$_3$)$_2$] (M = Cr, Mo, W; **4a–c**) are obtained. Upon reaction with IBH$_2$·LB (LB = SMe$_2$, NMe$_3$), the cationic oligomeric arsanylboranes [(Me$_3$N·BH$_2$$t$BuAsHBH$_2$·NMe$_3$)]I (**5**) and [H$_2$B($t$BuAsHBH$_2$·NMe$_3$)$_2$]I (**6**) were isolated. Compound **1** was also used as starting material for the synthesis of the first oligomeric arsanylboranes obtained by thermal oligomerization under different conditions. DFT computations support the experimental observations.

Introduction

Inorganic main-group-based polymers are attractive materials for many different applications, e.g. as ceramic precursors, polyelectrolytes or in optoelectronics due to their broad variety of properties.[1] Therefore, the targeted catenation of non-carbon elements has been receiving increasing attention. In the case of phosphorus, not only several chains of polyphosphines and polyphosphorus anions are known,[2] but also different *catena*-phosphorus cations, as reported by Burford and Weigand et al.[3] On the other hand, for boron, mainly the formation of higher aggregated clusters is known with only few exceptions.[4] Besides some references to a linear B$_8$(NMe$_2$)$_{10}$,[5] only B$_4$(NMe$_2$)$_6$[6] and cyclic B$_6$(NMe$_2$)$_6$[7] have structurally been characterized. Additionally, B$_4$R$_4$ was reported as a ligand in the coordination sphere of a transition metal complex,[8] but, as for all other examples, organic substituents are necessary for their stabilization.

Due to the isoelectronic relation between carbon compounds and compounds consisting of group 13 and 15 elements, such compounds possess great potential as starting material for main group-based *catena* compounds. In addition to poly(amino)- and poly(phosphinoborane)s based on Lewis acid/base adducts of the type R$_3$E·E′R$_3$ (E = group 15 element; E′ = group 13 element) obtained by dehydrogenation/dehydrocoupling reactions,[9] recently the polymerization of Zintl type anions [BP$_2$]$^{3-}$ to 1D boron-phosphorus chains, composed of pentagonal B$_2$P$_3$ rings, has been reported. Similar arsenic based Zintl anions are known, but no similar polymerizations have been reported to date.[10] Especially Lewis base-stabilized pnictogenylboranes of the type R$_2$EBH$_2$·LB (E = group 15 element; LB=Lewis base) exhibit a very promising reactivity owing to their lone pair. Our group has reported numerous different compounds of this type over the past years, including the only hydrogen-substituted parent pnictogenylboranes H$_2$PBH$_2$·LB and H$_2$AsBH$_2$·LB in addition to organosubstituted derivatives.[11]

For Lewis base-stabilized phosphanylboranes, a very rich chemistry was observed. Among the reported results are Lewis acid adducts resulting in neutral catena compounds,[11a,b,12] anionic chains obtained by the substitution of the Lewis base by phoshanides[11a,13] as well as cationic group 13/15 *catena* compounds by the reaction with IBH$_2$·LB.[11a,14] By reaction of (OC)$_5$W·PH$_2$BH$_2$·SMe$_2$ with LB-stabilized pnictogenylboranes, neutral mixed pnictogenylborane chains are accessible.[15] For the parent phosphanylborane PH$_2$BH$_2$·NMe$_3$, oligomeric compounds can be obtained by reaction with [Cp$_2$Ti(btmsa)] (btmsa = bis(trimethylsilyl)acetylene)[16] as well as polymeric materials under thermolytic conditions.[11c]

The mono tert-butyl-substituted phosphanylborane, tBuPHBH$_2$·NMe$_3$, exhibits a good combination of steric bulk and donor strength, making it an excellent starting material for the generation of stable high-molecular weight polymers by metal-free head-to-tail polymerization.[11c]

In contrast to the variety of phosphorus-boron *catena* compounds, there are very few examples known for oligomeric compounds based on the heavier pnictogen homologue arsenic. Reported examples require bulky organic substituents on both the B and As atoms (**I**) or the stabilization by

[a] F. Lehnfeld, Dr. M. Seidl, Prof. Dr. M. Scheer
Institut für Anorganische Chemie, Universität Regensburg
93040 Regensburg, Germany
E-mail: manfred.scheer@ur.de
www.uni-regensburg.de/chemie-pharmazie/anorganische-chemie-scheer
[b] Prof. Dr. A. Y. Timoshkin
Institute of Chemistry, St. Petersburg State University
199034 Universitetskaya emb. 7/9, St. Petersburg, Russia

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202100930

Part of the "44th ICCC Conference" Special Collection.

Research Article
doi.org/10.1002/ejic.202100930

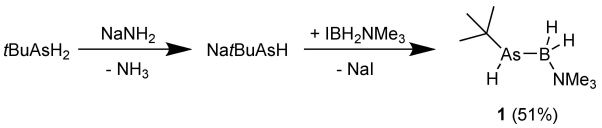
thermodynamically favorable ring systems (**II**) (Scheme 1).[17] Only few *catena* compounds based on Lewis-base-stabilized arsanylboranes (**III** and **IV**) have been reported recently. Noteworthy examples include the neutral LA adducts $BH_3 \cdot AsR_2BH_2 \cdot NMe_3$ (R=Ph or H; **V**)[11a,b] as well as the cationic chain compounds $[BH_2(R_2AsBH_2 \cdot NMe_3)_2]I$ (R=Ph, H; **VI**) and $[Me_3N \cdot BH_2AsR_2BH_2 \cdot NMe_3]I$ (R=Ph, H; **VII**).[11a,14] But neither the parent arsanylborane $H_2AsBH_2 \cdot NMe_3$ nor the diphenyl-substituted arsanylborane $Ph_2AsBH_2 \cdot NMe_3$ are suitable as precursors for neutral oligo- or poly(arsinoborane)s due to thermal cleavage of the As–B bond in case of **III** or insufficient donor strength of the arsenic atom in case of **IV**.

Therefore, transferring the very versatile reactivity of tBuPHBH$_2 \cdot$NMe$_3$ to the corresponding arsanylborane chemistry should allow for a relatively stable, while reactive arsanylborane. Therefore, we targeted the synthesis of a similar, monoalkyl-substituted arsanylborane as model compound to be used as potential precursor for the generation of oligomers.

Herein, we report the synthesis of tBuAsHBH$_2 \cdot$NMe$_3$, which represents the first monoalkyl-substituted arsanylborane only stabilized by a LB. The successful synthesis allows to investigate the reactivity of this new compound as a potential starting material for both neutral and cationic arsenic-boron-based *catena* compounds and oligomers.

Results and Discussion

The one-pot reaction of *in situ* generated NatBuAsH with IBH$_2 \cdot$NMe$_3$ in THF leads to the LB-stabilized arsanylborane tBuAsHBH$_2 \cdot$NMe$_3$ (**1**) in 51 % yield. After metalation of tBuAsH$_2$, the dark brown suspension undergoes a color change to colorless upon addition of IBH$_2 \cdot$NMe$_3$ and stirring overnight, while showing full conversion to **1** according to ^{11}B NMR spectroscopy (Equation 1). In the ^{11}B NMR spectrum of isolated **1**, a triplet at $\delta = -5.26$ ppm with a coupling constant of $^1J_{B,H} =$ 109 Hz is observed, which is similar to already reported arsanylboranes.[11a,b]

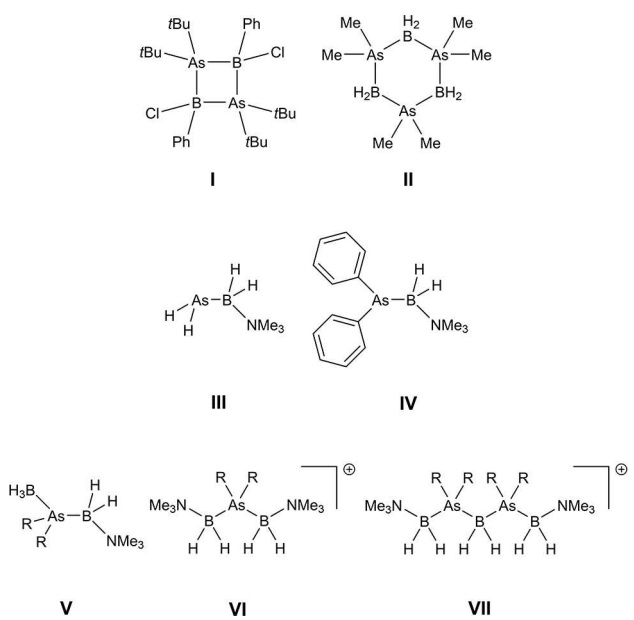


(1)

In the ^{1}H NMR spectrum among the signals corresponding to the NMe$_3$ and the tBu groups at $\delta = 1.92$ ppm and $\delta =$ 1.62 ppm, respectively, two overlapping broad pseudo-quartets for the diastereotopic hydrogen atoms bound to the boron atom can be detected. In the ^{1}H{^{11}B} NMR spectrum, the signals appear as two pseudo-triplets at $\delta = 2.99$ ppm and $\delta =$ 2.50 ppm with two very similar $^{2/3}J_{H,H}$ coupling constants of about 8 Hz. The resonance signal corresponding to the As–H is observed as a triplet at $\delta = 1.89$ ppm with a $^3J_{H,H}$ coupling constant of 7.4 Hz, but the signal is partly overlapped by the signal of the NMe$_3$ group.

In contrast to the already reported arsanylboranes such as AsH$_2$BH$_2 \cdot$NMe$_3$ and Ph$_2$AsBH$_2 \cdot$NMe$_3$, compound **1** is asymmetrically substituted on the arsenic atom and therefore occurs as two enantiomers. In the solid-state structure (Figure 1), both enantiomers are incurred as a racemate. The As–B bond length of 2.079(5) Å is in the range of a single bond. The boron atom shows a nearly tetrahedral environment, whereas the arsenic atom possesses a distorted trigonal pyramidal arrangement, with a B–As–C bond angle of 101.0(4)° which is slightly more distorted in comparison to the phosphorus analogue tBuPHBH$_2 \cdot$NMe$_3$.[11c]

As the donor strength of the As atom is essential for its potential use as building block for oligomeric compounds, its reactivity towards Lewis acids (LAs) was investigated



Scheme 1. Selected examples of cyclic arsanylboranes, monomeric arsanylboranes and derived *catena* compounds. R=H, Ph. Counterions are omitted for clarity.

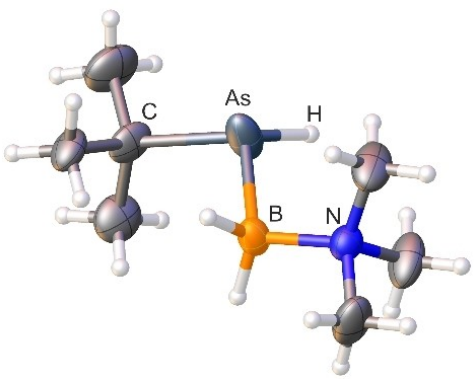
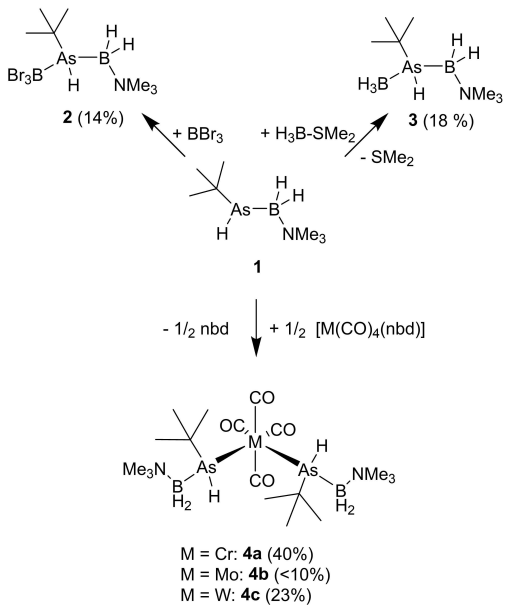


Figure 1. Molecular structure of **1**. Only the S enantiomer is shown for clarity. Thermal ellipsoids displayed at 50 % probability. Selected bond distances (Å) and angles [°]: N–B 1.619(3), B–As 2.079(5), As–C 1.941(18); N–B–As 109.7(2), C–As–B 101.0(4).

Research Article
doi.org/10.1002/ejic.202100930

(Scheme 2). The reactions with the main group LAs BBr_3 and $BH_3 \cdot SMe_2$ lead to the formation of the LA-LB-stabilized *tert*-butylarsanylboranes $BBr_3 \cdot t$BuAsHBH$_2 \cdot$NMe$_3$ (**2**) and $BH_3 \cdot t$BuAsHBH$_2 \cdot$NMe$_3$ (**3**), respectively. Both reactions proceed almost quantitatively according to the ^{11}B NMR spectroscopy, but the products are only accessible in lower crystalline yields due to the good solubility of **2** and **3**. The signals corresponding to the BBr_3 and BH_3 moiety in **2** and **3** can be observed at $\delta = -15.77$ ppm and $\delta = -35.87$ ppm, respectively. In comparison to the starting material **1**, the signals for the BH_2 groups are slightly high-field shifted at $\delta = -7.55$ ppm and $\delta = -8.60$ ppm for **2** and **3**, respectively. For compound **2**, the ^{1}H NMR spectrum exhibits low field shifts both for the signal corresponding to the As–H to 3.88 ppm and for the *t*Bu-group to 2.82 ppm. The ^{1}H NMR spectrum of **3** exhibits two broad pseudo quartets for the BH_2- and BH_3-groups in the range of 1.7–2.7 ppm and 0.4–1.2 ppm, respectively. In addition to multinuclear NMR spectroscopy, both compounds have been characterized by X-ray structure analysis (Figure 2).



Scheme 2. Reaction of **1** with main group and transition metal Lewis acids; isolated crystalline yields in parentheses (nbd = norbornadiene).

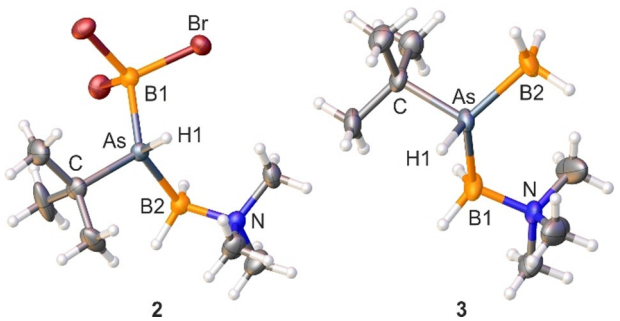


Figure 2. Molecular structure of **2** and **3**. Thermal ellipsoids displayed at 50% probability. Selected bond distances (Å) and angles [°]: **2**) As–B1 2.064(5), As–B2 2.093(5), As–C 1.986(5), N–B2 1.597(7); C–As–B1 116.1(2), C–As1–B2 108.8(2), B1–As–B2 111.9(2), N–B2–As 114.9(3); **3**) As–C 1.976(5), As–B1 2.075(6), As–B2 2.070(6), N–B1 1.583(7); C–As–B1 104.1(2), C–As–B2 111.7(3), B2–As–B1 123.6(3), N–B1–As 115.0(4).

The inner As–B distances in **2** (2.093(5)) and **3** (2.070(6)) are in the range of an As–B single bond and only slightly elongated in **3** in comparison to the starting material **1** due to the stronger Lewis acidity and steric bulk of BBr_3. The As–B distances towards the LA are in both cases very similar (2.064(5) (**2**) and 2.070(6) (**3**)) and in the range of an As–B single bond.

For **2** and **3**, two enantiomers are present in the solid state due to the chirality of the arsenic atom. Whereas **3** crystallizes in the space group $P2_1/n$ with both enantiomers in the unit cell, **2** crystallizes in the acentric space group $P2_12_12_1$, but represents inversion twins.

Computed thermodynamic characteristics for the formation of **2** and **3** are summarized in Table S4. Reactions of tBuAsHBH$_2 \cdot$NMe$_3$ with BBr_3 and $BH_3 \cdot SMe_2$ are predicted to be exergonic in solution, in agreement with experimental observations.

In addition to the reactivity towards main group LAs, also the coordination chemistry towards Lewis acidic transition metal complexes of group 6 metals was investigated. The reaction of **1** with *in situ* prepared [W(CO)$_5$(thf)] leads to a slight color change to darker yellow, but no solid product could be isolated (only an oily product).

To yield crystalline products, the group 6 complexes [M(CO)$_4$(nbd)] (M = Cr, Mo, W; nbd = norbornadiene) were used as transition metal LAs instead. In all three cases, the elimination of nbd and the coordination of two equivalents of **1** to the metal centre are observed in a quantitative reaction according to ^{11}B NMR spectra of the reaction solutions. In the ^{11}B NMR spectra of **4a** and **4c**, only a slight change in the chemical shift to $\delta = -4.6$ ppm could be observed, but it was possible to obtain crystals of **4a–c** suitable for X-ray diffraction analysis, with moderate yields for **4a** and **4c**, but only few single crystals for **4b** (Figure 3). Also, the DFT computations reveal that these reactions are exergonic in solution (Table S4).

4a–c crystallize in the monoclinic space group $P2_1/n$. All relevant bond lengths and bond angles are depicted in Table 1. Whereas **4b** and **4c** show very similar structural features, the Cr–As distance and bond angles such as the As1–Cr–As2 one differ slightly for **4a** due to the smaller atom

Table 1. Selected bond distances [Å] and angles [°] of compounds **4a–c**.

	4a	**4b**	**4c**
M–As1/M–As2 [Å]	2.5168(2)/2.5163(2)	2.6666(3)/2.6595(3)	2.6513(4)/2.6501(5)
As1–M–As1 [°]	90.417(7)	88.895(8)	88.719(14)
C–As1–M/C–As2-M [°]	117.35(4)/117.92(4)	119.34(8)/118.05(7)	118.36(12)/119.16(12)

Research Article
doi.org/10.1002/ejic.202100930

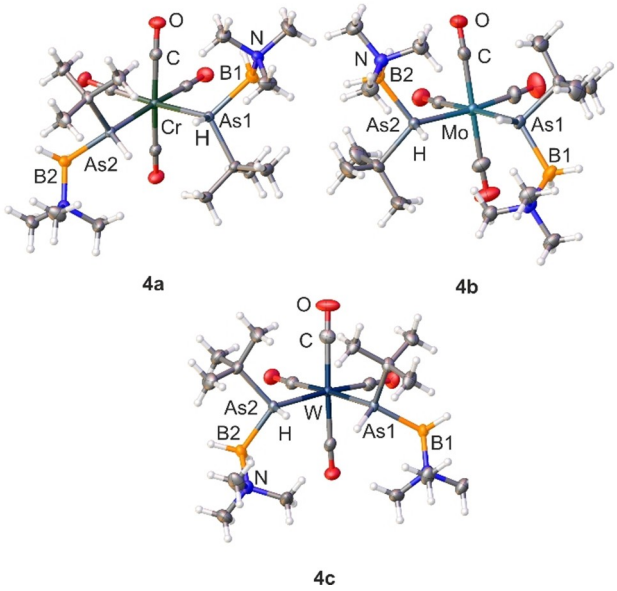


Figure 3. Molecular structure of 4**a**–**c**. Thermal ellipsoids displayed at 50% probability. Selected bond distances (Å) and angles [°] are found in Table 1.

radius compared to **4b** and **4c**. Concerning the stereochemistry of **4a**–**c**, one important difference was observed: Whereas in **4a** and **4b**, two molecules of **1** with the same configuration coordinate to the metal centre, leading to RR or SS configuration with both enantiomers found in the unit cell, the tungsten derivative **4c** exists as a *meso*-isomer.

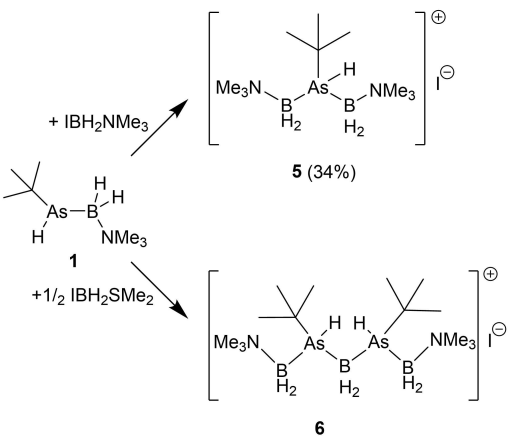
Having established that the donor strength of the As atom in the *tert*-butyl-substituted arsanylborane is sufficient, we were furthermore interested in the formation of cationic oligomeric chain-like compounds by reacting **1** with $IBH_2 \cdot LB$ (LB=NMe_3, SMe_2). Depending on the substituted LB, the formation of $[Me_3N \cdot BH_2 tBuAsHBH_2 \cdot NMe_3]I$ (**5**) or $[H_2B(tBuAsHBH_2 \cdot NMe_3)_2]I$ (**6**) is observed (Scheme 3).

Both reactions show full conversion according to the ^{11}B NMR spectroscopy of the reaction mixture, with **5** and **6** as the only products. Whereas **5** could be isolated in a crystalline yield of 34%, **6** could only be obtained in solution. All attempts to grow single crystals of **6** suitable for X-ray diffraction analysis or precipitation of **6** failed due to decomposition. Both **5** and **6** were characterized by multinuclear NMR spectroscopy and **5** also by single crystal X-ray structure analysis.

Both compounds **5** and **6** show a very similar high field shifted signals for the NMe_3-bonded BH_2 groups at $\delta = -7.7$ ppm (**5**) and $\delta = -7.8$ ppm (**6**), respectively. The signal for the BH_2 moiety between the two As centres in **6** is observed as a broadened triplet at $\delta = -34.4$ ppm (Figure 4).[11a,14a] In the ^1H NMR spectra of **5**, the As–H signal is shifted to lower field compared to **1** where it is found at around $\delta = 4.0$ ppm. The signals corresponding to the BH_2-groups appear as a broad overlapping signal in the range between 2 and 3 ppm. The signals corresponding to the NMe_3 and *t*Bu groups are shifted by about 1 ppm to lower field compared to **1**.

5 crystallizes as colorless blocks in the space group $Pca2_1$. The solid-state structure reveals a central *tert*-butyl-substituted AsH moiety that is connected to two BH_2NMe_3 groups via As–B single bonds (Figure 5). The conformation of both As–B bonds is almost eclipsed, leading to an overall almost symmetric arrangement, as both As–B distances are very similar (As–B1 2.074(5), As–B2 2.070(5)). The arsenic atom reveals a distorted tetrahedral arrangement, with all non-hydrogen-substituents exhibiting bond angles of approximately 114° around the As atom.

According to DFT calculations, the reaction of $tBuAsHBH_2 \cdot NMe_3$ with $IBH_2 \cdot SMe_2$ is predicted to be exergonic in solution, in agreement with experimental observations. The reaction with $IBH_2 \cdot NMe_3$ under formation of **5** is predicted to be slightly endergonic, but the crystal lattice energy favors the formation of a solid product (Table S4).



Scheme 3. Synthesis of three- and five-membered cationic chain-like compounds starting from **1**; yields of isolated product in parentheses.

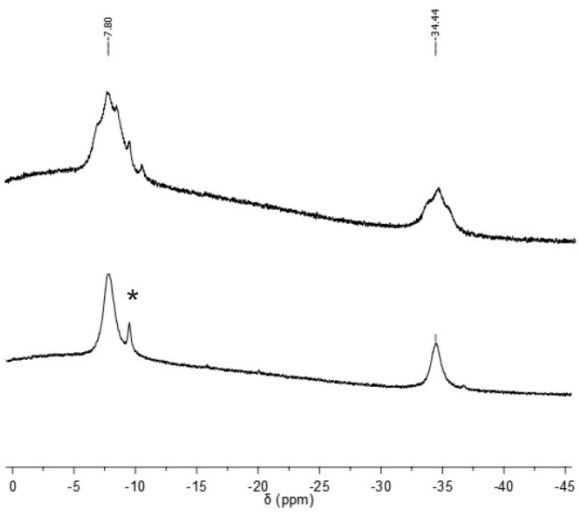


Figure 4. $^{11}B\{^1H\}$ NMR spectrum (bottom) and ^{11}B NMR spectrum (top) of **6** in CD_2Cl_2 (* = impurity of IBH_2SMe_2).

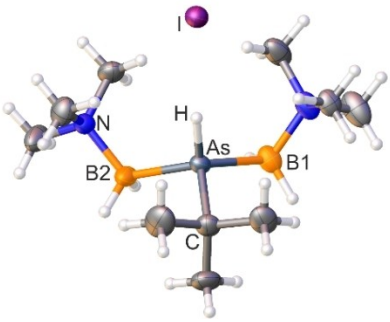
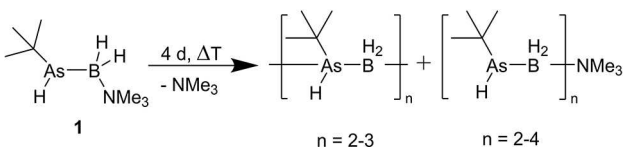


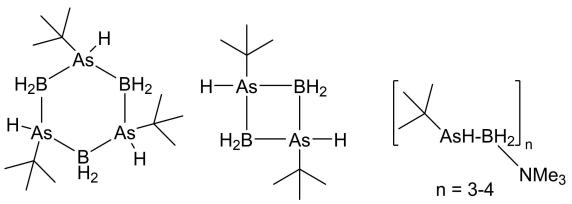
Figure 5. Molecular structure of **5**. The thermal ellipsoids are displayed at 50% probability. Selected bond distances (Å) and angles [°]: As–C 1.978(5), As–B1 2.074(5), As–B2 2.070(5), N–B1 1.591(6), C–As1–B1 110.8(2), C–As1–B2 107.6(2), B2–As1–B1 114.2(2), N1–B1–As 114.2(3), N2–B2–As 114.3(3).

Having established **1** as a suitable starting material for the targeted synthesis of cationic oligomeric compounds, the next step was the synthesis of neutral oligomers. As in the case of tBuPHBH$_2$·NMe$_3$, this was achieved by thermolysis (Scheme 4).[11c] After already 40 h stirring at 80 °C, about 50% conversion was detected in the ^{11}B NMR spectrum, indicated by a broad multiplet at $\delta = -36.8$ ppm. The conversion can be increased by longer reaction times as well as higher temperatures. However, the thermolysis is always accompanied by decomposition, visible in the precipitation of an insoluble orange solid, which increases over time and with more elevated temperatures.

Besides the insoluble orange solid, the obtained oil is very soluble in polar and nonpolar organic solvents and was characterized by ESI mass spectrometry. Hereby, it was possible to identify NMe$_3$-capped oligomeric fragments with up to n = 4 as well as oligomers missing the NMe$_3$ group with up to n = 3. This indicates that, very probably, cyclic oligomers are formed among presumably NMe$_3$-capped linear oligomers.



Scheme 4. Thermal oligomerization of **1**.



Scheme 5. Structures of the most likely formed oligomers according to ESI-MS results and DFT calculations. Reaction Gibbs energies ΔG°_{373} for the formation of oligomer compounds from **1** (in kJ per mole of **1**) (−53 (left), −21 (middle), −5 (right, n = 3), −20.5 (right, n = 4)).

To investigate the nature of the formed oligomers and their relative stability, DFT computations were performed. According to the calculations, the oligomerization processes of **1** to form *catena*-(tBuAsHBH$_2$)$_n$ oligomers are thermodynamically unfavorable and therefore highly unlikely even at 373 K, while the formation of *catena*-(tBuAsHBH$_2$)$_n$NMe$_3$ oligomers is exergonic for $n = 3$, 4 and *cyclo*-(tBuAsHBH$_2$)$_n$ is exergonic for n = 2, 3, 4.

For the oligomerization of tBuAsHBH$_2$·NMe$_3$ per one mole of starting material, the formation of the trimeric *cyclo*-(tBuAsHBH$_2$)$_3$ is predicted to be the most thermodynamically favorable product both at 298 and at 373 K, followed by the ring tetramer *cyclo*-(tBuAsHBH$_2$)$_4$, the ring dimer *cyclo*-(tBuAsHBH$_2$)$_2$, the NMe$_3$-stabilized chain tetramer *catena*-(tBuAsHBH$_2$)$_4$NMe$_3$ and the NMe$_3$-stabilized chain trimer *catena*-(tBuAsHBH$_2$)$_3$NMe$_3$. Taking all information into account, the most likely formed oligomers are summarized in Scheme 5.

Conclusion

In summary, a straightforward synthesis of an alkyl-substituted monomeric arsanylborane tBuAsHBH$_2$·NMe$_3$ (**1**) stabilized only by a Lewis base was developed. It was isolated in good yields and showed high thermal stability. Using **1** as starting material, it was possible to access numerous new products. In addition to the neutral arsanylborane chain compounds BBr$_3$·tBuAsHBH$_2$·NMe$_3$ (**2**) and BH$_3$·tBuAsHBH$_2$·NMe$_3$ (**3**) obtained by the reaction with main group Lewis acids, also coordination products with transition metal centres were obtained. Taking into account the asymmetric nature of **1**, these coordination products as well as the crystallization of **2** in the acentric space group $P2_12_12_1$ allow for some fascinating insights into the stereochemistry of **1** and its products. It was also shown that **1** is a suitable precursor for larger arsanylborane oligomers. Not only the cationic group 13/15-based oligomers [Me$_3$N·BH$_2$$t$BuAsHBH$_2$·NMe$_3$]I (**5**) or [H$_2$B-($t$BuAsHBH$_2$·NMe$_3$)$_2$]I (**6**) are accessible via reactions with IBH$_2$·LB (LB=NMe$_3$, SMe$_2$), but it is also possible to obtain neutral oligo(arsanylborane)s through thermolysis of **1**. This makes **1** not only the first asymmetrically substituted arsanylborane only stabilized by an LB, but also the first isolable arsanylborane to undergo metal-free head-to-tail oligomerization under thermolytic conditions.

Experimental Section

Synthesis of tBuAsHBH$_2$·NMe$_3$ (1)

A solution of tBuAsH$_2$ (5 mmol, 670 mg) in 5 mL toluene is added to a suspension of NaNH$_2$ (5 mmol, 195 mg) in 10 ml thf at 193 K. After stirring for 16 h while slowly warming up to r.t., a deep brown solution is obtained. A suspension of IBH$_2$·NMe$_3$ (5 mmol, 994 mg) in 5 mL thf is added to this solution cooled to 193 K. After stirring for 16 h while slowly warming up to r.t., a colorless solution and a white precipitate are obtained. After carefully removing the solvent under reduced pressure at 253 K, compound **1** is extracted with *n*-

hexane (3x 10 mL) and filtrated over diatomaceous earth. After carefully removing the solvent, compound 1 can be obtained as a colorless liquid. **1** can be isolated as colorless blocks by storing a saturated solution of **1** in n-hexane at 243 K. Yield: 523 mg (2.55 mmol, 51 %). ^{1}H NMR (C_6D_6, 293 K) δ = 3.5–2.0 (2H, br, $^1J_{H,B}$ = 109 Hz, BH_2), 1.92 (9H, s, NMe_3), 1.85 (1H, d, $^3J_{H,H}$ = 7.4 Hz), 1.62 (9H, s, *t*Bu). ^{11}B NMR (C_6D_6, 293 K) δ = −5.26 (t, $^1J_{H,B}$ = 109 Hz, BH_2). ^{11}B{^{1}H} NMR (C_6D_6, 293 K) δ = −5.26 (s, BH_2). ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ = 27.18 (s, $(CH_3)_3$**C**, 34.10 (s, (**C**H$_3$)$_3$C), 52.74 (s, NMe_3). ESI-MS (CH_2Cl_2): m/z = 205.98. Elemental analysis (%) calculated for $C_7H_{21}AsBN$: C: 41.02, H: 10.33, N: 6.83; found: C: 41.16, H: 10.01, N: 6.72.

Synthesis of $BBr_3 \cdot$ *t*BuAsHBH$_2 \cdot$ NMe$_3$ (2)

To a solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 41 mg) in 4 mL toluene, BBr_3 (0.2 mmol, 50 mg) is added at 273 K. After stirring at 273 K for 1 h, the solution is slowly warmed up to r.t. and continued to be stirred for 16 h hours at r.t. All volatiles are removed under reduced pressure and the obtained white, oily solid is washed with two times 2 ml of *n*-hexane. **2** can be isolated as colorless blocks by storing a saturated solution in CH_3CN at 243 K. Yield: 13 mg (0.03 mmol, 14 %). ^{1}H NMR (CD_3CN, 293 K) δ = 3.89 (1H, br, AsH), 2.83 (9H, s, NMe_3) 3.0-2.0 (br, 2H, BH_2), 1.48 (9H, s, *t*Bu). ^{11}B NMR (CD_3CN, 293 K) δ = −15.77 (s, BBr_3), −7.55 (t, $^1J_{H,B}$ = 117 Hz, BH_2). ^{11}B {^{1}H} NMR (CD_3CN, 293 K) δ = −15.77 (s, BBr_3), −7.55 (s, BH_2). ESI-MS (CH_3CN): m/z = 375.9 (M-Br$^-$). Elemental analysis (%) calculated for $C_7H_{21}AsB_2Br_3N$: C: 18.46, H: 4.65, N: 3.08; found: C: 19.26, H: 4.44, N: 3.09; containing 1/12 n-hexane.

Synthesis of $BH_3 \cdot$ *t*BuAsHBH$_2 \cdot$ NMe$_3$ (3)

To a solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 41 mg) in 3 ml toluene, a solution of $BH_3 \cdot SMe_2$ (0.2 mmol, 15 mg) in 0.4 mL toluene is added at r.t. After stirring for 16 h at r.t., all volatiles are removed under reduced pressure. The remaining solid is dissolved in 5 mL *n*-hexane and filtrated over diatomaceous earth. **3** can be isolated as colorless needles by storing a saturated solution in *n*-hexane at 243 K. Yield: 8 mg (0.04 mmol, 18 %). ^{1}H NMR (C_6D_6, 293 K) δ = 2.78 (9H, s, NMe_3), 2.73–1.73 (2H, br, $^1J_{H,B}$ = 112 Hz, BH_2), 2.28 (1H, m, AsH), 1.2 (9H, s, *t*Bu), 1.2–0.4 (3H, brq, $^1J_{H,B}$ = 103 Hz, BH_3). ^{11}B NMR (C_6D_6, 293 K) δ = −35.87 (q, $^1J_{H,B}$ = 103 Hz, BH_3), −8.60 (t, $^1J_{H,B}$ = 112 Hz, BH_2). ^{11}B{^{1}H} NMR (CD_3CN, 293 K) δ = −35.87 (s, BH_3), −8.60 (s, BH_2). ESI-MS (CH_3CN): m/z = 217.9 (M-H$^-$). Elemental analysis (%) calculated for $C_7H_{24}AsB_2N$: C: 38.42, H: 11.06, N: 6.40; found: C: 39.53, H: 10.61, N: 6.45; containing 1/8 n-hexane.

Synthesis of [Cr(CO)$_4$(*t*BuAsHBH$_2 \cdot$ NMe$_3$)$_2$] (4 a)

To a solution of [Cr(CO)$_4$(nbd)] (nbd = norbornadiene, 0.1 mmol, 26 mg) in 2 mL CH_2Cl_2, a solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 41 mg) in 2 mL toluene is added at r.t.. After stirring for 16 h at r.t., the solution is filtrated. **4 a** can be isolated as yellow blocks by layering a saturated CH_2Cl_2/toluene solution with *n*-hexane at 273 K. Yield: 23 mg (0.04 mmol, 40 %). ^{1}H NMR (CD_2Cl_2, 293 K) δ = 3.0–2.0 (4H, br, BH_2), 2.78 (18H, s, NMe_3), 1.68 (2H, s, AsH), 1.29 (18H, s, *t*Bu). ^{11}B NMR (CD_2Cl_2, 293 K) δ = −4.51 (t (br), $^1J_{H,B}$ = 114 Hz, BH_2). ^{11}B{^{1}H} NMR (CD_2Cl_2, 293 K) δ = −4.51 (br, BH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K) δ = 231.4 (s, $(CH_3)_3$**C**, 231.2(s, (**C**H$_3$)$_3$C), 225.9 (s, NMe_3), 32.54 (s, CO), 32.19 (s, CO), 31.87 (s, CO), 31.58 (s, CO).

Synthesis of [Mo(CO)$_4$(*t*BuAsHBH$_2 \cdot$ NMe$_3$)$_2$] (4 b)

To a solution of [Mo(CO)$_4$(nbd)] (nbd = norbornadiene, 0.1 mmol, 30 mg) in 2 mL CH_2Cl_2, a solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 41 mg) in 2 mL toluene is added at r.t. After stirring for 16 h at r.t., the solution is filtrated. **4 b** can be isolated as yellow blocks by layering a saturated CH_2Cl_2/toluene solution with *n*-hexane at 273 K. Yield: few crystals (< 10 %).

Synthesis of [W(CO)$_4$(*t*BuAsHBH$_2 \cdot$ NMe$_3$)$_2$] (4 c)

To a solution of [W(CO)$_4$(nbd)] (nbd = norbornadiene, 0.1 mmol, 39 mg) in 2 mL CH_2Cl_2, a solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 41 mg) in 2 mL toluene is added at r.t.. After stirring for 16 h at r.t., the solution is filtrated. **4 c** can be isolated as yellow blocks by layering a saturated CH_2Cl_2/toluene solution with *n*-hexane at 273 K. Yield: 16 mg (0.023 mmol, 23 %). ^{1}H NMR (CD_2Cl_2, 293 K) δ = 3.0–2.0 (4H, br, BH_2), 2.78 (18H, s, NMe_3), 1.68 (2H, m, AsH), 1.30 (18H, s, *t*Bu). ^{11}B NMR (CD_2Cl_2, 293 K) δ = −4.96 (t (br), $^1J_{H,B}$ = 105 Hz, BH_2). ^{11}B{^{1}H} NMR (CD_2Cl_2, 293 K) δ = −4.96 (br, BH_2).

Synthesis of [Me$_3$N $\cdot$ BH$_2$-*t*BuAsH-BH$_2 \cdot$ NMe$_3$]$^+$I$^-$ (5)

To a solution of IBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 40 mg) in 3 mL CH_2Cl_2, a solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 41 mg) in 2 mL toluene is added dropwise at 243 K. The solution is stirred for 16 h while allowed to reach r.t. After removing all volatiles under reduced pressure, the obtained yellowish oil is suspended in benzene. Benzene is removed under reduced pressure and the oil is dried in vacuo. **5** can be isolated as colorless blocks by layering a saturated CH_2Cl_2 solution with *n*-hexane at 273 K. Yield: 28 mg (0.07 mmol, 34 %). ^{1}H NMR (CD_2Cl_2, 293 K) δ = 4.01 (1H, s, AsH), 3.1–1.8 (4H, br, BH_2), 2.91 (18H, s, NMe_3), 1.32 (9H, s, *t*Bu). ^{11}B NMR (CD_2Cl_2, 293 K) δ = −7.72 (t, $^1J_{H,B}$ = 116 Hz, BH_2). ^{11}B{^{1}H} NMR (CD_2Cl_2, 293 K) δ = −7.72 (s, BH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K) δ = 45.1 (s, $(CH_3)_3$**C**), 32.3 (s, (**C**H$_3$)$_3$C), 29.6 (s, NMe_3). ESI-MS (CH_3CN): m/z = 277.3 (M$^+$). Elemental analysis (%) calculated for $C_{10}H_{32}AsB_2N_2I$: C: 29.74, H: 7.99, N: 6.94; found: C: 30.08, H: 7.77, N: 7.04.

Synthesis of [Me$_3$N $\cdot$ BH$_2$-*t*BuAsH-BH$_2$-*t*BuAsH-BH$_2 \cdot$ NMe$_3$]$^+$I$^-$ (6)

To a solution of IBH$_2$SMe$_2$ (0.2 mmol, 40 mg) in 1 mL CH_2Cl_2, a solution of *t*BuAsHBH$_2$NMe$_3$ (0.4 mmol, 82 mg) in 2 mL toluene is added dropwise at 243 K. The solution is stirred for 16 h while allowed to reach r.t. All attempts to isolate **6** as solid failed due to decomposition, but it can be characterized in solution.

Thermolytic oligomerization of *t*BuAsHBH$_2 \cdot$ NMe$_3$

A solution of *t*BuAsHBH$_2 \cdot$ NMe$_3$ (0.2 mmol, 40 mg) in 1 mL toluene is stirred at 80 °C for 40 h, the colorless solution turns slightly yellow during that time. According to the ^{11}B NMR, the reaction shows 50 % conversation to oligomeric species. Increasing the reaction time to 65 h or the temperature to 100 °C, augments conversion to 70 %, but more decomposition product is formed as an orange precipitate. ^{11}B NMR (CD_2Cl_2, 293 K) δ = −36.75 (t (br), $^1J_{H,B}$ = 109 Hz). ^{11}B{^{1}H} NMR (CD_2Cl_2, 293 K) δ = −36.75 (m (br))

DFT computations

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[18] with def2-SVP[19] all electron basis set (ECP on Mo, W). Gaussian 09 program package[20] 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.[21] Standard entropies of the

reactions in solution were estimated by taking into account the loss of translational degrees of freedom upon solvation of one gaseous mole in the inert solvent (90 J mol^{-1} K^{-1}).[22]

Deposition Numbers 2117548 (for **1**), 2117549 (for **2**), 2117530 (for **3**), 2117531 (for **4a**), 2117532 (for **4b**), 2117533 (for **4c**), and 2117534 (for **5**) 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 www.ccdc.cam.ac.uk/structures.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the project Sche 384/41-1. This work was supported by the joint DFG-RSF grant (RSF project 21-43-04404). Use of computational resources of the Research center «Computing Center» of the research park of St. Petersburg State University is acknowledged. Open Access funding enabled and organized by Projekt DEAL.

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: Arsenic · Boron · Group 13/15 compounds · LA/LB adducts · Oligomers

[1] a) J. Linshoeft, E. J. Baum, A. Hussain, P. J. Gates, C. Näther, A. Staubitz, *Angew. Chem. Int. Ed.* **2014**, *53*, 12916–12920; *Angew. Chem.* **2014**, *126*, 13130–13134; b) A. Hübner, Z.-W. Qu, U. Englert, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 4596–4609; c) R. H. Neilson, P. Wisian-Neilson, *Chem. Rev.* **1988**, *88*, 541–562; d) R. D. Jaeger, M. Gleria, *Prog. Polym. Sci.* **1998**, *23*, 179–276; e) M. Liang, I. Manners, *J. Am. Chem. Soc.* **1991**, *113*, 4044–4045; f) A. M. Priegert, B. W. Rawe, S. C. Serin, D. P. Gates, *Chem. Soc. Rev.* **2016**, *45*, 922–953; g) I. Manners, *Angew. Chem. Int. Ed.* **1996**, *35*, 1602–1621; *Angew. Chem.* **1996**, *108*, 1712–1731; h) R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359–1410; i) F. Choffat, S. Käser, P. Wolfer, D. Schmid, R. Mezzenga, P. Smith, W. Caseri, *Macromolecules* **2007**, *40*, 7878–7889; j) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985–4022; k) B. W. Rawe, C. P. Chun, D. P. Gates, *Chem. Sci.* **2014**, *5*, 4928–4938; l) Z. M. Hudson, D. J. Lunn, M. A. Winnik, I. Manners, *Nat. Commun.* **2014**, *5*; m) X. He, T. Baumgartner, *RSC Adv.* **2013**, *3*, 11334–11350; n) H. R. Allcock, *Chem. Mater.* **1994**, *6*, 1476–1491; o) G. Zhang, G. M. Palmer, M. W. Dewhirst, C. L. Fraser, *Nat. Mater.* **2009**, *8*, 747–751; p) P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen, L. G. Sneddon, *Chem. Mater.* **1990**, *2*, 96–97.

[2] a) M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623–1667; b) M. Baudler, K. Glinka, *Chem. Rev.* **1994**, *94*, 1273–1297; c) M. Baudler, *Angew. Chem. Int. Ed.* **1982**, *21*, 492–512; *Angew. Chem.* **1982**, *94*, 520–539; d) M. Baudler, *Angew. Chem. Int. Ed.* **1987**, *26*, 419–441; *Angew. Chem.* **1987**, *99*, 429–451; e) H. G. Von Schnering, W. Hoenle, *Chem. Rev.* **1988**, *88*, 243–273; f) I. Jevtovikj, P. Lönnecke, E. Hey-Hawkins, *Chem. Commun.* **2013**, *49*, 7355–7357.

[3] a) C. A. Dyker, N. Burford, *Chem. Asian J.* **2008**, *3*, 28–36; b) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford, J. J. Weigand, *Angew. Chem. Int. Ed.* **2012**, *51*, 2964–2967; *Angew. Chem.* **2012**, *124*, 3018–3021; c) J. J. Weigand, N. Burford, M. D. Lumsden, A. Decken, *Angew. Chem. Int. Ed.* **2006**, *45*, 6733–6737; *Angew. Chem.* **2006**, *118*, 6885–6889; d) C. Taube, K. Schwedtmann, M. Noikham, E. Somsook, F. Hennersdorf, R. Wolf, J. J. Weigand, *Angew. Chem. Int. Ed.* **2020**, *59*, 3585–3591; *Angew. Chem.* **2020**, *132*, 3613–3619; e) J. J. Weigand, M. Holthausen, R. Fröhlich, *Angew. Chem. Int. Ed.* **2009**, *48*, 295–298; *Angew. Chem.* **2009**, *121*, 301–304; f) M. H. Holthausen, C. Richter, A. Hepp, J. J. Weigand, *Chem. Commun.* **2010**, *46*, 6921–6923; g) K.-O. Feldmann, J. J. Weigand, *Angew. Chem. Int. Ed.* **2012**, *51*, 7545–7549; *Angew. Chem.* **2012**, *124*, 7663–7667; h) J. J. Weigand, N. Burford, R. J. Davidson, T. S. Cameron, P. Seelheim, *J. Am. Chem. Soc.* **2009**, *131*, 17943–17953.

[4] a) H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.* **2013**, *52*, 3574–3583; *Angew. Chem.* **2013**, *125*, 3658–3667; b) E. Osorio, J. K. Olson, W. Tiznado, A. I. Boldyrev, *Chem. Eur. J.* **2012**, *18*, 9677–9681.

[5] K. H. Hermannsdörfer, E. M. Und, H. Nöth, *Chem. Ber.* **1970**, *103*, 516–527.

[6] G. Linti, D. Loderer, H. Nöth, K. Polborn, W. Rattay, *Chem. Ber.* **1994**, *127*, 1909–1922.

[7] H. Nöth, H. Pommerening, *Angew. Chem. Int. Ed.* **1980**, *19*, 482–483.

[8] H. Braunschweig, Q. Ye, A. Vargas, R. D. Dewhurst, K. Radacki, A. Damme, *Nat. Chem.* **2012**, *4*, 563–567.

[9] a) H. C. Johnson, A. S. Weller, *Angew. Chem. Int. Ed.* **2015**, *54*, 10173–10177; *Angew. Chem.* **2015**, *127*, 10311–10315; b) H. C. Johnson, E. M. Leitao, G. R. Whittell, I. Manners, G. C. Lloyd-Jones, A. S. Weller, *J. Am. Chem. Soc.* **2014**, *136*, 9078–9093; c) A. N. Marziale, A. Friedrich, I. Klopsch, M. Drees, V. R. Celinski, J. Schmedt auf der Günne, S. Schneider, *J. Am. Chem. Soc.* **2013**, *135*, 13342–13355; d) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023–4078; e) A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne, I. Manners, *J. Am. Chem. Soc.* **2010**, *132*, 13332–13345; f) R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott, N. C. Smythe, *J. Am. Chem. Soc.* **2012**, *134*, 5598–5609; g) J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec, A.-C. Gaumont, *Chem. Commun.* **2003**,, 54–55; h) H. Dorn, J. M. Rodezno, B. Brunnhöfer, E. Rivard, J. A. Massey, I. Manners, *Macromolecules* **2003**, *36*, 291–297; i) A. Kumar, N. A. Beattie, S. D. Pike, S. A. Macgregor, A. S. Weller, *Angew. Chem. Int. Ed.* **2016**, *55*, 6651–6656; *Angew. Chem.* **2016**, *128*, 6763–6768; j) S. Pandey, P. Lönnecke, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2014**, *2014*, 2456–2465; k) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678.

[10] a) K. E. Woo, J. Wang, J. Mark, K. Kovnir, *J. Am. Chem. Soc.* **2019**, *141*, 13017–13021; b) H.-G. von Schnering, M. Somer, M. Hartweg, K. Peters, *Angew. Chem. Int. Ed.* **1990**, *29*, 65–67; *Angew. Chem.* **1990**, *102*, 63–65.

[11] a) O. Hegen, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2018**, *24*, 16521–16525; b) C. Marquardt, A. Adolf, A. Stauber, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2013**, *19*, 11887–11891; c) C. Marquardt, T. Jurca, K.-C. Schwan, A. Stauber, A. V. Virovets, G. R. Whittell, I. Manners, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13782–13786; *Angew. Chem.* **2015**, *127*, 13986–13991; d) A. Stauber, T. Jurca, C. Marquardt, M. Fleischmann, M. Seidl, G. R. Whittell, I. Manners, M. Scheer, *Eur. J. Inorg. Chem.* **2016**,, 2684–2687; e) U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519.

[12] C. Marquardt, T. Kahoun, J. Baumann, A. Y. Timoshkin, M. Scheer, *Z. Anorg. Allg. Chem.* **2017**, *643*, 1326–1330.

[13] C. Marquardt, T. Kahoun, A. Stauber, G. Balázs, M. Bodensteiner, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2016**, *55*, 14828–14832; *Angew. Chem.* **2016**, *128*, 15048–15052.

[14] a) C. Marquardt, G. Balázs, J. Baumann, A. V. Virovets, M. Scheer, *Chem. Eur. J.* **2017**, *23*, 11423–11429; b) C. Marquardt, C. Thoms, A. Stauber, G. Balázs, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 3727–3730; *Angew. Chem.* **2014**, *126*, 3801–3804.

[15] O. Hegen, C. Marquardt, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 12783–12787; *Angew. Chem.* **2017**, *129*, 12959–12963.

[16] C. Thoms, C. Marquardt, A. Y. Timoshkin, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 5150–5154; *Angew. Chem.* **2013**, *125*, 5254–5259.

[17] a) M. A. Petrie, M. M. Olmstead, H. Hope, R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 3221–3226; b) J. Burt, J. W. Emsley, W. Levason, G. Reid, I. S. Tinkler, *Inorg. Chem.* **2016**, *55*, 8852–8864; c) M. A. Mardones,

A. H. Cowley, L. Contreras, R. A. Jones, C. J. Carrano, *J. Organomet. Chem.* **1993**, *455*, C1–C2.

[18] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[19] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) K. A. Peterson, D. Figgen, E. Goll, H. Stoll, M. Dolg, *J. Chem. Phys.* **2003**, *119*, 11113.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford CT **2013**.

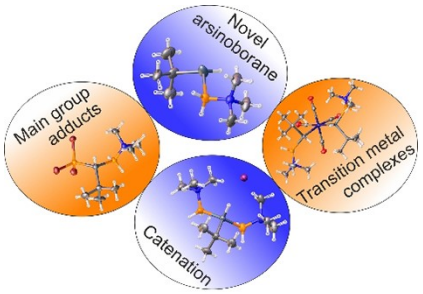
[21] a) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052; b) D. Feller, *J. Comput. Chem.* **1996**, *17*, 1571–1586.

[22] A. S. Lisovenko, A. Y. Timoshkin, *Inorg. Chem.* **2010**, *49*, 10357–10369.

Manuscript received: October 28, 2021
Revised manuscript received: November 11, 2021
Accepted manuscript online: November 11, 2021

RESEARCH ARTICLE

The synthesis of the *tert*-butyl-substituted arsanylborane $tBuAsHBH_2 \cdot NMe_3$ is reported. Its reactivity towards main group Lewis acids and transition metal complexes, yielding various coordination products, is discussed. Furthermore, it is used as starting material in catenation and oligomerization processes, leading to cationic *catena* compounds as well as to neutral oligomers obtained by thermolysis.



*F. Lehnfeld, Dr. M. Seidl, Prof. Dr. A. Y. Timoshkin, Prof. Dr. M. Scheer**