Main-Group Chemistry

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Isolation and Characterization of Lewis Base Stabilized Monomeric Parent Stibanylboranes

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Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: *The synthesis of the Lewis base stabilized monomeric parent compound of stibanylboranes, "$H_2Sb{-}BH_2$", is reported. Through a salt metathesis route, the silyl-substituted compounds $(Me_3Si)_2Sb{-}BH_2{\cdot}LB$ ($LB = NMe_3$, NHC^{Me}) were synthesized as representatives of derivatives with a Sb−B σ bond. Under very mild conditions, they could be transformed into the target compounds $Me_3N{\cdot}H_2B{-}HSb{-}BH_2{\cdot}NMe_3$ and $H_2Sb{-}BH_2{\cdot}NHC^{Me}$, respectively. The products were characterized by X-ray structure analysis, NMR spectroscopy, IR spectroscopy, and mass spectrometry. DFT calculations give further insight into the stability and bonding of these unique compounds.*

Binary group 13/15 compounds have been extensively investigated in recent decades owing to their interesting physical properties, particularly their semiconducting properties. Because of their narrow direct bandgaps (from 0.17 eV for InSb to 3.44 eV for GaN), they are potential candidates for applications in micro- and optoelectronic devices. Combination with even more group 13/15 elements facilitates tuning of the band gaps, thereby leading to ternary and quarternary materials.[1] The hitherto unknown BSb compound in particular might possess some interesting features for optoelectric devices.[2–4] However, examples for compounds with a direct Sb−B bond are very rare. Besides the three Lewis acid/base adducts of the type $X_3B{\cdot}Sb(SiMe_3)_3$ (X = Cl, Br, or I)[5] and the stibaborane cluster *closo*-1,1-$(Me_2PPh)_2$-1,2,3-$PdSb_2B_9H_9$,[6] no well-defined molecular stibaboranes have been isolated so far. The published $(H_3C)_2Sb{-}BH_2$,[7] which was obtained through the reaction of $(H_3C)_2SbBr$ with $NaBH_4$, later proved to be a mixture of $(H_3C)_3Sb$, $(H_3C)_2SbH$, and B_5H_9.[8] Reactive main-group compounds like the elusive $H_2N{-}BH_2$ can be stabilized by applying donor–acceptor complexation[9] in the coordination sphere of transition metals,[10] or with the support of strong donors like N-heterocyclic carbenes.[11] In our group, we are especially interested in the stabilization of the monomeric parent compounds of the type $H_2E{-}E'H_2$ (E = group 15 atom, E′ = group 13 atom). We initially discovered the synthesis of the Lewis base stabilized phosphanylborane $H_2P{-}BH_2{\cdot}NMe_3$[12] through the photochemically induced elimination of $W(CO)_5$ from $(CO)_5W{\cdot}H_2P{-}BH_2{\cdot}NMe_3$ in the presence of $P(OMe)_3$. Subsequently, we found that a salt metathesis reaction between $LiE(SiMe_3)_2{\cdot}2\,thf$ (E = P, As) and $ClBH_2{\cdot}NMe_3$ in boiling *n*-hexane yielded $(Me_3Si)_2E{-}BH_2{\cdot}NMe_3$, which could then be transformed into the parent compounds by methanolysis, thereby enabling the generation of $H_2As{-}BH_2{\cdot}NMe_3$ for the first time.[13] The first route is restricted to the phosphanylborane while the second route can also be used for the arsanylborane but could not be transferred to the heavier stibanylborane analogue. In this context, the extreme thermal instability of primary stibines containing small substituents is well known.[14] Simple primary stibines[15,16] decompose within minutes or hours at room temperature.[17] Primary stibines, which are sufficiently stable at ambient temperatures, require sterically demanding substituents like neopentyl (Me_3CCH_2)[18] or $CH(SiMe_3)_2$,[19] and have to be stored in the dark. For $(Me_3Si)_2CHSbH_2$, it was possible to investigate its coordination behavior.[20] Sterically crowded substituents like 9-trypticenyl[21] or terphenyl[22] lead to primary stibines that are stable up to 195 °C. Herein, we present a selective synthesis of the stibanylboranes $H_2Sb{-}BH_2{\cdot}LB$ as the first stable primary stibines without a bulky substituent and the first stibanylboranes with a σ bond between the two elements.

DFT calculations[23] (Table 1) show that stronger donors significantly weaken the E−B bond (E = group 15 element) of the pnictogenylboranes. This is in part a reflection of a greater stabilization of radical BH_2 species by stronger Lewis bases. The B−Sb bond energy of approximately 162–264 $kJ\,mol^{-1}$ is sufficiently strong for compounds containing this bond to be isolable. However, the monomeric parent compound $H_2Sb{-}BH_2{\cdot}LB$ has not yet been obtained.

When the iodo derivative is used instead of $ClBH_2{\cdot}NMe_3$ in the reaction with $KSb(SiMe_3)_2$, the salt metathesis occurs even at low temperatures (Scheme 1). Therefore, by using $IBH_2{\cdot}NMe_3$ and $IBH_2{\cdot}NHC^{Me}$ (NHC^{Me} = 1,3,4,5-tetramethyl-

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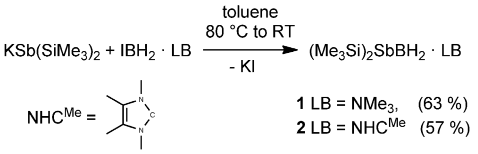
Table 1: Standard dissociation enthalpies ΔH°_{298} in kJ mol^{-1} for homolytic B–E bond breaking processes. B3LYP/def2-TZVPP level of theory.

Process	N	P	As	Sb	Bi
$H_2EBH_2 \rightarrow H_2E^{\bullet} + {}^{\bullet}BH_2$	576	355	314	264	234
$H_2EBH_2{\cdot}NMe_3 \rightarrow H_2E^{\bullet} + {}^{\bullet}BH_2{\cdot}NMe_3$	441	300	271	231	207
$H_2EBH_2{\cdot}NHC^{Me} \rightarrow H_2E^{\bullet} + {}^{\bullet}BH_2{\cdot}NHC^{Me}$	309	210	189	162	155

NHC^{Me} = 1,3,4,5-tetramethylimidazolylidene.



Scheme 1. Synthesis of silylated stibanylboranes **1** and **2**. Yields in parentheses.

imidazolylidene), respectively, the silylated stibanylboranes $(Me_3Si)_2Sb{-}BH_2{\cdot}LB$ [**1**: LB = NMe_3 (63 %), **2**: LB = NHC^{Me} (57 %)] were obtained in good yields. Compounds **1** and **2** can easily be isolated through extraction with *n*-hexane, followed by crystallization at −28 °C.

Apart from the already mentioned Lewis acid/base adducts,[5] compounds **1** and **2** are the first examples of compounds with a well-defined 2-center-2-electron σ bond between antimony and boron. In the EI-MS spectra, the molecular ion peak is detected for **1** and **2**. The IR spectra of **1** and **2** show absorptions for the B–H stretches between 2306 cm^{-1} and 2406 cm^{-1}. The ^{11}B NMR spectra reveal signals at $\delta = -8.5$ ppm (**1**) and −39.0 ppm (**2**), which split into triplets with typical $^{1}J_{B,H}$ coupling constants (**1**: $^{1}J_{B,H} = 114$ Hz, **2**: $^{1}J_{B,H} = 103$ Hz). The solid-state structures of the stibanylboranes (Figure 1) show a bond length of 2.295(6) Å for the Sb–B bonds of **1** and 2.350(2) Å for those of **2**. The values are in good agreement with the calculated sum of the covalent radii of boron and antimony ($\Sigma r_{cov}(Sb,B) = 2.29$ Å).[24] Compound **1** shows a similar E-B-N bond angle to that of $(Me_3Si)_2E{-}BH_2{\cdot}NMe_3$ (E = P, As)[13] and also adopts a synperiplanar arrangement (for $SiMe_3$ and H substituents, view along Sb–B axis), whereas **2** deviates slightly from the synperiplanar arrangement.

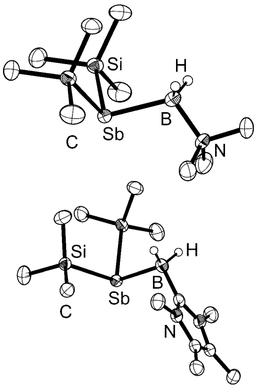
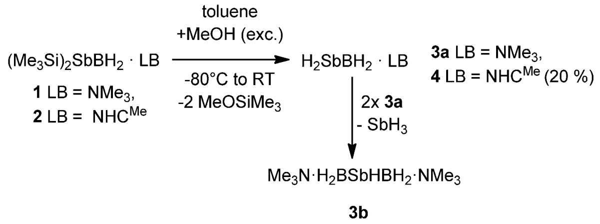


Figure 1. Molecular structures of **1** (top) and **2** (bottom) in the solid state. Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms on the methyl groups are omitted for clarity.[25]

Subsequent methanolysis of **1** and **2** at low temperatures, however, leads to the monomeric parent compound of the stibanylboranes, $H_2Sb{-}BH_2{\cdot}LB$ (Scheme 2).



Scheme 2. Methanolysis of the silylated stibanylboranes **1** and **2**. Yields in parentheses.

In the case of **1**, even with a large excess of methanol and a long reaction time, complete cleavage of the $SiMe_3$ groups does not occur, although DFT studies suggest that methanolysis reactions of both **1** and **2** are highly exothermic and exergonic (by more than 180 kJ mol^{-1} at 298 K). The stibanylborane $H_2Sb{-}BH_2{\cdot}NMe_3$ (**3a**) can be observed in the ^{1}H and ^{11}B NMR spectra ($\delta(^{1}H) = -0.78$ ppm, SbH_2), however only about 50 % of the $SiMe_3$ groups of **1** are cleaved and a mixture of **1**, **3a**, and other reaction products that are not assignable is obtained. All attempts to isolate **3a** from the reaction mixture failed because decomposition occurs. Numerous attempts were made to isolate **3a**. Instead, a few crystals of $Me_3N{\cdot}H_2B{-}HSb{-}BH_2{\cdot}NMe_3$ (**3b**) were obtained and characterized by X-ray structure analysis. The decomposition pathway of **3a** is not known, but we suppose that **3a** is generated concomitantly with the elimination of SbH_3 to yield the secondary stibine **3b**. This assumption is further supported by the observation of precipitation of elemental antimony. Computations show that the reaction 2 **3a**(sol) → SbH_3(g) + **3b**(sol) in toluene is exergonic by 12 kJ mol^{-1} at 298 K. In the ^{1}H NMR spectrum of the mixture, a signal centered at $\delta = -2.45$ ppm was tentatively attributed to the SbH group in **3b**. The central structural motif of **3b** is the B–Sb–B backbone. In the solid-state structure of **3b** (Figure 2), one of the two Sb–B subunits adopts an antiperiplanar conformation, whereas the second subunit shows a synclinal conformation, thereby leading to a dihedral angle defined by the two N–Sb–B units of 32.3(3)°. The Sb–B bond lengths of 2.291(4) Å and 2.297(4) Å are identical to those in the starting material **1** (2.295(6) Å). Compound **3b**

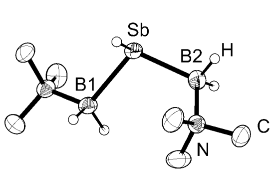


Figure 2. Molecular structure of **3b** in the solid state. Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms on the methyl groups are omitted for clarity.[25]

is a neutral species and is reminiscent of the recently discovered cationic chains of pnictogenylboranes.[26]

Reacting the NHC^{Me}-stabilized species **2** with an excess of methanol leads to the formation of the monomeric parent compound $H_2Sb{-}BH_2{\cdot}NHC^{Me}$ (**4**), which can be isolated as a colorless solid in 20% yield. Compound **4** is highly unstable and decomposes during crystallization into elemental antimony (most likely through SbH_3 elimination)[27] and the borane adduct $BH_3{\cdot}NHC^{Me}$. Besides high sensitivity towards moisture and oxygen, the decomposition of **4** is readily induced by exposure to light and temperatures above −30 °C. DFT computations show that the reaction $\mathbf{4}(g) \rightarrow Sb(s) + BH_3NHC^{Me}(g) + {}^1\!/_2\,H_2(g)$ is exergonic by 133 kJ mol^{-1} at 298 K. The stibanylborane **4** represents the first example of a Lewis base stabilized monomeric parent compound of a stibanylborane. In the ^{1}H NMR spectrum of **4**, the signal for the SbH_2 group arises at $\delta = -0.96$ ppm as a pseudo-triplet owing to coupling to the boranyl moiety, which arises as a broad quartet at $\delta = 2.44$ ppm. This was further confirmed by ^{1}H,^{1}H COSY NMR experiments, which clearly indicate cross-peaks for the $^3J_{H,H}$ coupling between the H atoms of the SbH_2 and BH_2 groups. The ^{11}B NMR spectrum of **4** shows a signal at $\delta = -38.6$ ppm, which splits into a triplet ($^1J_{B,H} = 103$ Hz). In the EI-MS spectra, the molecular ion peak can be detected for **4**. The IR spectra of **4** reveal absorptions for the B−H stretches between 2395 cm^{-1} and 2281 cm^{-1} and a very prominent absorption for the Sb−H stretches at 1818 cm^{-1} (1870 cm^{-1} for $Me_3CCH_2SbH_2$[18] and 1860 cm^{-1} for $(Me_3Si)_2CHSbH_2$[19]). Crystals of **4** were obtained by storing an *n*-hexane solution at −28 °C. In the solid state, stibanylborane **4** shows a staggered arrangement for the substituents around the Sb−B moiety (the lone pair at the Sb atom is in an antiperiplanar conformation with respect to NHC^{Me}; Figure 3). The parent compounds $H_2E{-}BH_2{\cdot}NMe_3$ (E = P, As) show the same conformation of the lone pair at the pnictogen atom and the Lewis base.[12,13] Calculations on stabilized pnictogenylboranes have shown that the energy differences to the synperiplanar conformation calculated for the gas phase are very small (6–7 kJ mol^{-1}) and that the observed conformation most probably originates from packing effects in the solid state.[28] The Sb−B bond length is 2.318(2) Å and therefore within the expected range for a Sb−B single bond ($\Sigma r_{cov}(Sb,B) = 2.29$ Å,[24] the calculated Sb−B bond length for compound **4** is 2.3448 Å[23]). It is slightly shorter compared to the starting material **2** (2.350(2) Å) and similar to the Sb−B bond lengths in **1** (2.295(6) Å) and the adducts $X_3B{\cdot}Sb(SiMe_3)_3$ (X = Cl, Br, or I; 2.257(8)–2.268(17) Å).[5]

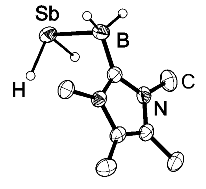


Figure 3. Molecular structure of **4** in the solid state. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms on methyl groups are omitted for clarity.[29]

In summary, by using $IBH_2{\cdot}LB$ (LB = NMe_3, NHC^{Me}), a direct synthesis and isolation of a series of stable stibanylboranes was achieved. The silylsubstituted compounds **1** and **2** are unique representatives with a well-defined 2-center-2-electron σ-bond between antimony and boron. Furthermore, it was possible for the first time to synthesize, isolate, and comprehensively characterize the Lewis base stabilized monomeric parent compound **4** of the stibanylboranes, “H_2SbBH_2”. This compound represents a unique primary stibine without the bulky substituent that is usually needed for stable primary stibines. Furthermore, the diboranylstibine **3b** was obtained as a decomposition product of the primary stibine, thereby revealing a first example of a longer neutral B−Sb−B chain.

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Keywords: antimony · boron · group 13/15 elements · pnictogenylboranes · primary stibines

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