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Syntheses, characterization and crystal structures of the boron–antimony adducts $BX_3 \cdot Sb(SiMe_3)_3$ (X = Cl, Br or I)

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The crystal structures of the 1:1 Lewis acid–base adducts $BX_3 \cdot Sb(SiMe_3)_3$ (X = Cl, Br or I) have been determined and they are the first reported for such boron–antimony adducts.

Recently, we have isolated and characterized the 1:1 Lewis acid–base adducts $BX_3 \cdot E(SiMe_3)_3$ (X = Cl, Br or I; E = P or As) in our laboratories.[1,2] Success with these compounds prompted us to look further down Group 15 to investigate boron–antimony systems. Previously, it has been shown that trivalent boron compounds (BX_3, X = F, Cl, Br, I or H) form 1:1 Lewis acid–base adducts with trialkyl- or triaryl-stibines (R_3Sb, R = Me[3–6] or Ph[7]). Although these compounds were characterized by a range of techniques, no crystal structures were reported. To our knowledge, the only reported X-ray structural determination of a B–Sb bond-containing compound is in a cluster compound, *closo*-1,1-$(PMe_2Ph)_2$-1,2,3-$PdSb_2B_9H_9$.[8] Herein, we report the syntheses and characterizations of three novel B–Sb 1:1 Lewis acid–base adducts, $BX_3 \cdot Sb(SiMe_3)_3$ (X = Cl, Br or I), along with their crystal structures, the first reported for such B–Sb adducts.

The three adducts $BX_3 \cdot Sb(SiMe_3)_3$ (X = Cl **1**, Br **2** or I **3**) were synthesized from the separate 1:1 mole ratio reactions of the respective boron trihalides with a pentane or hexane solution of $Sb(SiMe_3)_3$ at −78 °C.† The $Sb(SiMe_3)_3$ solution was added slowly to the cooled, stirring pentane or hexane solutions of BCl_3 or BBr_3, however due to the extreme sensitivity of BI_3 to solvents, a pentane solution of $Sb(SiMe_3)_3$ was added to neat BI_3. The initial products were white powders which turned light brown (Br, I) to brown (Cl) when warmed to room temperature. Clear crystals were grown from toluene solutions of these powders at −30 °C. Upon exposure to light, ambient atmosphere or room temperature, these crystals rapidly turned brown-black. Yields obtained for the bulk powders were 79.8 for **1**, 92.0 for **2** and 82.8% for **3**.

Proton and ^{13}C NMR of these compounds showed a singlet in the range expected for the resonance of a trimethylsilyl group bound to a pnictogen, based on previous observations of similar boron–pnictogen adducts:[1,2] **1** ^1H δ 0.37, ^{13}C δ 2.40; **2** ^1H δ 0.31, ^{13}C δ 3.76; **3** ^1H δ 0.49, ^{13}C δ 5.18. Boron-11 spectra were also recorded, displaying singlets and chemical shifts consistent with the parent boron trihalide:[2] **1** δ 5.35, **2** −24.71, **3** −99.32. Electron ionization mass spectra of these adducts showed various fragmentation peaks which can be derived from the original structure: **1** *m*/*z* 389.9 $[Cl(H)_2BSb(SiMe_3)_3]^+$, 340.0 $[Sb(SiMe_3)_3]^+$, 252.2 $[Sb(SiMe_3)_2SiMe_2]^+$, 116.1 $[BCl_3]^+$; **2** *m*/*z* 340.1 $[Sb(SiMe_3)_3]^+$, 325.0 $[Sb(SiMe_3)_2(SiMe_2)]^+$, 252.0 $[BBr_3]^+$, 170.8 $[BBr_2]^+$; **3** *m*/*z* 536.3 $[I_2(H)BSb(H)(SiMe_3)_2 + 2\,H]^+$, 396.9 $[BI_3]^+$, 340.2 $[Sb(SiMe_3)_3]^+$. Elemental analyses of compounds **1**–**3** were conducted, and the expected C and H values for **2** and **3** matched well with those found. However, C and H analyses for **1** were greatly inconsistent with the expected calculated values for this compound.† This was likely due to the aforementioned sensitivity of **1** to light and temperature, as the bulk powder was observed to turn a much darker shade of brown as compared to **2** and **3** when exposed to room temperature.

All three adducts crystallized in the orthorhombic space group *Pbca*, and were solvated with one molecule of toluene per molecule of adduct.‡ The ORTEP[10] diagrams of **1**, **2** and **3** are shown in Figs. 1, 2 and 3, respectively, along with selected bond lengths and angles. The B–Sb bond lengths were 2.259(21) for **1**, 2.268(17) for **2** and 2.257(8) Å for **3**, all slightly shorter than the sum of the covalent radii of B and Sb (2.31 Å),[13] and the average B–Sb distance in the cluster compound *closo*-1,1-

† All manipulations were performed using general Schlenk and dry box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. Literature methods were used to prepare $Sb(SiMe_3)_3$.[9] Boron trichloride was obtained from Aldrich as a 1 mol dm^{-3} solution in hexanes and used as received, BBr_3 (99.999% purity) was obtained from Strem Chemicals, Inc. and used as received and BI_3 (98% purity) was obtained from Aldrich and sublimed before use. Mass spectra were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV (≈ 3.204×10^{-18} J). All NMR spectra were obtained in 5 mm tubes using dry degassed $C_6D_5CD_3$ as the solvent. Proton, ^{13}C-{^1H} and ^{11}B-{^1H} NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 400, 100.6 and 128.3 MHz, respectively, referenced to $SiMe_4$ using the residual protons or carbons of deuteriated toluene at δ 2.09 or 20.4 and to $BF_3 \cdot OEt_2$ externally at δ 0.00. The ^{11}B-{^1H} NMR spectrum for compound **2** was obtained on a Varian Unity 500 spectrometer operating at 160.4 MHz and referenced to $BF_3 \cdot OEt_2$ externally at δ 0.00. Single-crystal X-ray diffraction data were collected on a Rigaku AFC6/S diffractometer using the ω scan mode (λ = 0.710 73 Å) at the University of North Carolina at Chapel Hill Single Crystal X-Ray Facility. Elemental analyses were performed by E + R Microanalytical Laboratories, Inc., Corona, NY. General synthetic technique: a solution of $Sb(SiMe_3)_3$ (0.500 g, 1.46 mmol) in pentane (30 cm^3) was placed in the upper (100 cm^3) bulb of a two-bulbed screwtop reaction flask equipped with Teflon valves and a magnetic stir bar and the bulb was sealed. Boron trichloride (0.171 g, 1.46 mmol) was dissolved in pentane (60 cm^3) in the lower (300 cm^3) bulb of this flask. The flask was sealed and the lower bulb placed in a −78 °C dry ice–acetone bath. The $Sb(SiMe_3)_3$ solution was then added slowly to the cooled, stirring BCl_3 solution. A white precipitate formed immediately, along with some pentane vapour due to the heat released in the reaction. The mixture was allowed to stir for 15 min after addition was complete. The bath was then changed to ice–water and the solvent removed *in vacuo*, yielding an off-white powder which browned upon warming to room temperature. Yield 0.534 g (1.16 mmol, 79.8%), brown powder identified as **1** [Calc. (Found) for $C_9H_{27}BCl_3SbSi_3$ **1**: C, 23.60 (27.20); H, 5.95 (5.55). Calc. (Found) for $C_9H_{27}BBr_3SbSi_3$ **2**: C, 18.25 (18.00); H, 4.60 (4.35). Calc. (Found) for $C_9H_{27}BI_3SbSi_3$ **3**: C, 14.75 (14.90); H, 3.70 (3.95%)].

‡ Crystal structure solution and refinement. The crystals of **1**–**3** used were colourless blocks which were mounted separately on glass fibres with a viscous oil under a stream of cold dinitrogen. These crystals were orthorhombic with space group *Pbca*. X-Ray intensity data were recorded using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) at −120 °C for **1**–**3** and corrected for absorption using ψ scans. The structures were solved by direct methods. Full-matrix

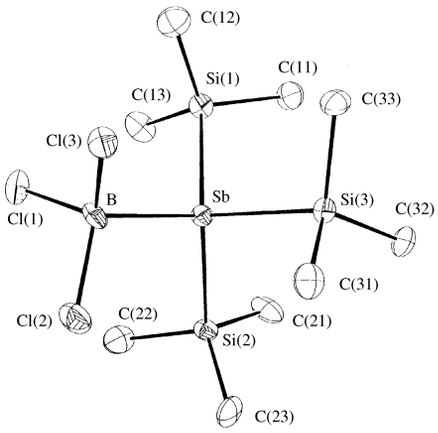

Fig. 1 An ORTEP diagram (30% probability ellipsoids) of BCl_3·Sb-$(SiMe_3)_3$ **1**, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sb–B 2.259(21), Sb–Si(1) 2.566(5), Sb–Si(2) 2.573(5), Sb–Si(3) 2.565(5), Cl(1)–B 1.842(21), Cl(2)–B 1.864(21), Cl(3)–B 1.858(23); Si(1)–Sb–Si(2) 110.11(15), Si(1)–Sb–B 109.9(6), Sb–B–Cl(1) 109.0(11), Cl(1)–B–Cl(2) 110.3(10)

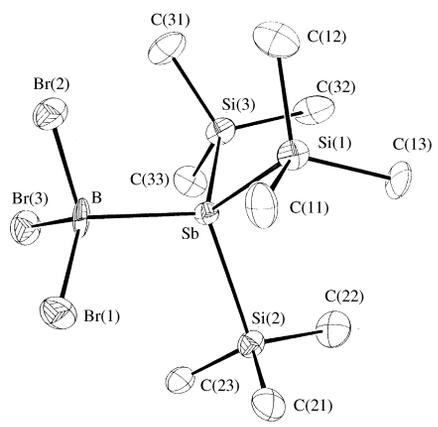

Fig. 2 An ORTEP diagram (30% probability ellipsoids) of BBr_3·Sb-$(SiMe_3)_3$ **2**, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sb–B 2.268(17), Sb–Si(1) 2.572(4), Sb–Si(2) 2.571(3), Sb–Si(3) 2.573(4), Br(1)–B 2.014(16), Br(2)–B 2.032(17), Br(3)–B 2.008(17); Si(1)–Sb–Si(2) 109.48(13), Si(1)–Sb–B 109.2(4), Sb–B–Br(1) 109.2(7), Br(1)–B–Br(2) 109.4(7)

least-squares refinements with weights based upon counter statistics were performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at $R = 0.060$ ($R' = 0.069$) for **1**, $R = 0.048$ ($R' = 0.046$) for **2** and $R = 0.027$ ($R' = 0.035$) for **3**. A final Fourier-difference synthesis revealed no unusual features (maximum 1.450, minimum −0.980 e Å^{-3} for **1**; 0.800, −0.750 for **2**; 0.700, −0.600 for **3**). Crystallographic calculations were performed using the NRCVAX[11] suite of structure-determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 12. Crystal data. $C_9H_{27}BCl_3SbSi_3$·$C_6H_5CH_3$ **1**, $M = 550.62$, $a = 12.921(7)$, $b = 17.460(5)$, $c = 23.607(5)$ Å, $U = 5326(3)$ Å^3, $Z = 8$, crystal size 0.25 × 0.25 × 0.40 mm, $D_c = 1.373$ g cm^{-3}, $F(000) = 2238.84$, $\mu = 1.48$ mm^{-1}, no. reflections measured 3897, no. independent reflections 3696. $C_9H_{27}BBr_3SbSi_3$·$C_6H_5CH_3$ **2**, $M = 683.97$, $a = 13.688(7)$, $b = 17.599(4)$, $c = 22.546(4)$ Å, $U = 5431(3)$ Å^3, $Z = 8$, crystal size 0.25 × 0.25 × 0.25 mm, $D_c = 1.673$ g cm^{-3}, $F(000) = 2660.76$, $\mu = 5.53$ mm^{-1}, no. reflections measured 5188, no. independent reflections 3758. $C_9H_{27}BI_3SbSi_3$·$C_6H_5CH_3$ **3**, $M = 824.97$, $a = 13.9064(9)$, $b = 17.8576(4)$, $c = 23.2343(8)$, $U = 5769.9(5)$ Å^3, $Z = 8$, crystal size 0.35 × 0.35 × 0.30 mm, $D_c = 1.899$ g cm^{-3}, $F(000) = 3082.98$, $\mu = 4.26$ mm^{-1}, no. reflections measured 4019, no. independent reflections 4015. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/362.

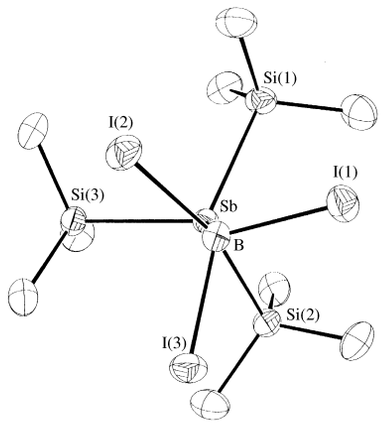

Fig. 3 An ORTEP diagram (30% probability ellipsoids) of BI_3·Sb-$(SiMe_3)_3$ **3**, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sb–B 2.257(8), Sb–Si(1) 2.5839(19), Sb–Si(2) 2.5794(19), Sb–Si(3) 2.5793(19), I(1)–B 2.231(8), I(2)–B 2.259(8), I(3)–B 2.235(8); Si(1)–Sb–Si(2) 108.74(6), Si(1)–Sb–B 110.67(20), Sb–B–I(1) 109.3(3), I(1)–B–I(2) 110.1(13)

$(PMe_2Ph)_2$-1,2,3-$PdSb_2B_9H_9$ (2.397 Å).[8] This was likely a result of increased Lewis acidity due to the electronegative halogens on the boron centre of **1**–**3**. Compounds **1**–**3** display a distorted tetrahedral co-ordination geometry around the B and Sb centres, with the halogen atoms and trimethylsilyl groups arranged in a staggered configuration. These features were similar to those observed for other Group 13–Group 15 adducts isolated in our laboratories.[14–16]

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