REACTIONS OF BORON TRIHALIDES WITH TRIS(TRIMETHYLSILYL)ARSINE AND LITHIUM BIS(TRIMETHYLSILYL)ARSENIDE; X-RAY CRYSTAL STRUCTURES OF $Br_3B{\bullet}As(SiMe_3)_3$ AND $[X_2BAs(SiMe_3)_2]_2$ (X = Cl, Br)

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Abstract

The 1:1 mole ratio reactions of boron trihalides, BX_3, with tris(trimethylsilyl)arsine, $As(SiMe_3)_3$, produced the 1:1 Lewis acid-base adducts $X_3B{\bullet}As(SiMe_3)_3$ [X = Cl (**1**), Br (**2**)] and the dimeric compound $[I_2BAs(SiMe_3)_2]_2$ (**3**). Dimers were also isolated from the separate 1:1 mole ratio reactions of boron trihalides [X = Cl (**4**), Br (**5**)] with lithium bis(trimethylsilyl)arsenide, $LiAs(SiMe_3)_2$. X-ray crystal structures were obtained for **2**, **4** and **5**. Compound **2** crystallized in the orthorhombic space group *Pbca*, with a = 13.644(3), b = 17.2564(17), c = 22.184 Å, V = 5223.0(14) Å^3, D_{calc} = 1.621 g cm^{-3} for Z = 8; the B-As bond length is 2.108(11) Å. Compound **4** crystallized in the monoclinic space group $P2_1/n$, with a = 9.1273(8), b = 16.2295(16), c = 9.2550(11) Å, V = 1369.13(24) Å^3, D_{calc} = 1.470 g cm^{-3} for Z = 2; the B-As bond length is 2.109(8) Å. Compound **5** crystallized in the monoclinic space group $P2_1/n$, with a = 9.1071(12), b = 16.552(3), c = 9.424(4) Å, V = 1413.4(6) Å^3, D_{calc} = 1.842 g cm^{-3} for Z = 2; the B-As bond length is 2.113(6) Å.

Introduction

Interest in boron chemistry with Group 15 elements has been directed mainly towards boron-nitrogen systems,[1] with significant attention given to boron-phosphorus reactions.[2-3] Recently, an interest has developed regarding boron-arsenic compounds,[4-11] and methods previously used for reactions of the heavier Group 13 elements with these pnicogens have been applied to boron systems. Drake synthesized three boron-arsenic Lewis acid-base adducts $[X_3B{\bullet}AsMe_3$ (X = Cl, Br, I)] from the direct reactions of the respective boron trihalides with trimethylarsine.[9] Power *et al.* reported the syntheses of boron-arsenic compounds, including the dimer $[PhB(Cl)As(t\text{-}Bu)_2]_2$, *via* a lithium halide elimination route.[10] Likewise, Cowley and co-workers isolated two monomeric arsinoboranes, $R_2AsB(Mes)_2$ (R = *i*-Pr, *t*-Bu; Mes = mesityl) by the same method.[11] Thus, we were encouraged to apply our methods of dehalosilylation and lithium halide elimination, which were successful in producing 13-15 compounds from the heavier elements,[12] to the boron-arsenic system.

As a result of our investigations, we have isolated and characterized five boron-arsenic compounds from the reactions of boron trihalides, BX_3 (X = Cl, Br, or I) with tris(trimethylsilyl)arsine, $As(SiMe_3)_3$, or lithium bis(trimethylsilyl)arsenide, $LiAs(SiMe_3)_2$: $Cl_3B{\bullet}As(SiMe_3)_3$ (**1**), $Br_3B{\bullet}As(SiMe_3)_3$ (**2**), $[I_2BAs(SiMe_3)_2]_2$ (**3**), $[Cl_2BAs(SiMe_3)_2]_2$ (**4**), $[Br_2BAs(SiMe_3)_2]_2$ (**5**), respectively. These compounds have been characterized by multinuclear NMR, electron ionization mass spectrometry and elemental analyses. The X-ray crystal structures of **2**, **4** ,and **5** are also presented.

Materials and Methods

General Considerations. All manipulations were performed under an inert atmosphere using general Schlenk and dry box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. Literature methods were used to prepare $As(SiMe_3)_3$.[13] $LiAs(SiMe_3)_2$[13] was prepared *via* the 1:1 mole reaction of MeLi with $As(SiMe_3)_3$. BCl_3 was obtained as a 1 *M* solution in hexanes from Aldrich and used as received. BBr_3 (99.999% purity) was obtained from Strem Chemicals, Inc. and used as

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received. 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. All NMR spectra were obtained in 5 mm tubes using dry degassed C_6D_6 or C_7D_8 (as indicated) as the solvent. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively, and referenced to TMS using the residual protons or carbons of deuterated toluene at δ 2.09 or 20.4 ppm, or deuterated benzene at δ 7.15 or 128 ppm. ^{11}B NMR spectra were obtained on a Varian Unity 500 spectrometer operating at 160.5 MHz, and referenced externally to $BF_3{\bullet}OEt_2$ at δ 0.00 ppm. Single-crystal X-ray diffraction data were collected on a Rigaku AFC6/S diffractometer using the ω scan mode (λ = 0.71073 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.

Preparation of $Cl_3B{\bullet}As(SiMe_3)_3$ (1). BCl_3 (0.125 g, 1.07 mmol; as a 1.0*M* solution in hexanes) was added to a 200 mL screwtop reaction flask equipped with a Teflon valve and a magnetic stir bar, and dissolved in 50 mL pentane. $As(SiMe_3)_3$ (0.346 g, 1.17 mmol, 10% excess) was dissolved in 30 mL pentane and added *via* pipet to the stirred BCl_3 solution. During addition, the solution turned cloudy white, a fluffy solid formed in the base of the flask, and clear crystals formed along the solvent line. The reaction was stirred for 48 h under argon atmosphere in the dark. The solvents were removed *in vacuo* to yield an off-white/yellow solid which was washed in pentane and collected to yield 0.389 g (0.945 mmol, 88.3% yield based on BCl_3) of (**1**). Anal. Calcd. (Found) for $C_9H_{27}AsBCl_3Si_3$: C, 26.26 (26.39); H, 6.61 (6.50); As, 18.20 (18.28); B, 2.63 (2.90); Cl, 25.83 (25.58). ^1H NMR (C_7D_8): δ 0.35 (s). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 1.64 (s). ^{11}B NMR (C_6D_6): δ 4.33 (s). Mass Spectrum (EI, 20 eV): m/z 302.0 $(Cl_2BAs(SiMe_3)_2)^+$, 294.0 $(As(SiMe_3)_3)^+$, 117.9 $(BCl_3)^+$.

Preparation of $Br_3B{\bullet}As(SiMe_3)_3$ (2). BBr_3 (0.319 g, 1.27 mmol) was dissolved in 60 mL pentane and added to a 200 mL flask equipped with a Teflon valve and a magnetic stir bar. $As(SiMe_3)_3$ (0.411 g, 1.40 mmol, 10% excess) was dissolved in 30 mL pentane and added to the stirred BBr_3 solution *via* pipet. During addition, the solution turned cloudy white. The flask was allowed to stir at room temperature for 48 h in the dark. The solvent was removed *in vacuo* to yield an off-white powder, which was collected and rinsed in pentane to yield 0.609 g (1.12 mmol, 88.0% yield based on BBr_3) of (**2**). Crystals of **2** suitable for X-ray structure determination were grown from toluene at -15 °C. Anal. Calcd. (Found) for $C_9H_{27}AsBBr_3Si_3$: C, 19.83 (20.11); H, 4.99 (5.11); As, 13.75 (13.90); B, 1.98 (2.40); Br, 43.98 (43.83). ^1H NMR (C_7D_8): δ 0.39 (s). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 1.87 (s). ^{11}B NMR (C_6D_6): δ -18.70 (s). Mass Spectrum (EI, 20 eV): m/z 448.2 $(Br_2BAs(SiMe_3)_2SiMe_2)^+$, 391.8 $(Br_2BAs(SiMe_3)_2^+$, 294.0 $(As(SiMe_3)_3)^+$, 249.8 $(BBr_3)^+$.

Preparation of $[I_2BAs(SiMe_3)_2]_2$ (3). BI_3 (0.250 g, 0.639 mmol) was added neat to a 250 mL reaction flask equipped with a Teflon valve and magnetic stirring bar. $As(SiMe_3)_3$ (0.206 g, 0.702 mmol, 10% excess) was dissolved in 30 mL pentane and added to the BI_3 *via* pipet. Immediately upon addition, a white powder was formed from the crystalline BI_3 and clear $As(SiMe_3)_3$ solution. After completion of addition, an additional 30 mL pentane was added to the mixture to increase the volume for stirring. The flask was then allowed to stir at room temperature in the dark for 64 h. The solvent was removed *in vacuo*, revealing a yellow-white powder which was collected and washed in pentane to yield 0.276 g (0.284 mmol, 44.4% yield by B) of (**3**). Anal. Calcd. (Found) for $C_{12}H_{36}As_2B_2I_4Si_4$: C, 14.83 (15.10); H, 3.73 (3.79); As, 15.42 (15.66); B, 2.22 (2.27); I, 52.23 (51.94). ^1H NMR (C_6D_6): δ 0.64 (s). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 3.45 (s). ^{11}B NMR (C_7D_8): δ -55.61 (s). Mass Spectrum (EI, 20 eV): m/z 971.7 $(M)^+$, 485.8 $(I_2BAs(SiMe_3)_2)^+$, 285.9 $(IBAs(SiMe_3))^+$.

Preparation of $[Cl_2BAs(SiMe_3)_2]_2$ (4). BCl_3 (0.250 g, 2.13 mmol; as a 1.0*M* solution in hexanes) was dissolved in 50 mL pentane and added to the upper (100 mL) bulb of a two-bulb reaction flask equipped with a Teflon valve and a magnetic stir bar. $LiAs(SiMe_3)_2$ (0.393 g, 2.13 mmol) was dissolved in 60 mL toluene and placed in the lower (300 mL) bulb of this flask. The flask was sealed and the lower bulb immersed in a -78 °C dry ice/acetone bath. The BCl_3 solution was added dropwise over 15-20 minutes to the stirred $LiAs(SiMe_3)_2$ solution. Upon addition, the initially clear solutions turned a cloudy yellow. The reaction mixture was allowed to warm to room temperature and stir in the dark for 48 h, after which it was filtered over a glass frit to remove LiCl, yielding a yellow solution. The solvents were removed *in vacuo* revealing a yellow powder, which was recovered and washed in pentane to yield 0.465 g (0.767 mmol, 36.0% by B) of (**4**). Crystals of **4** suitable for X-ray structure determination were grown from toluene at -15 °C. Anal. Calcd. (Found) for $C_{12}H_{36}As_2B_2Cl_4Si_4$: C, 23.78 (24.88); H, 5.99 (5.39); As, 24.72 (27.84);

Table 1. Crystallographic Data and Measurements for $Br_3B{\bullet}As(SiMe_3)_3$ (**2**), $[Cl_2BAs(SiMe_3)_2]_2$ (**4**) and $[Br_2BAs(SiMe_3)_2]_2$ (**5**).

	(**2**)	(**4**)	(**5**)
molec formula	$C_{16}H_{35}AsBBr_3Si_3$	$C_{12}H_{36}As_2B_2Cl_4Si_4$	$C_{12}H_{36}As_2B_2Br_4Si_4$
formula weight	637.15	606.03	783.83
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/n$
a (Å)	13.644(3)	9.1273(8)	9.1071(12)
b (Å)	17.2564(17)	16.2295(16)	16.552(3)
c (Å)	22.184(4)	9.2550(11)	9.424(4)
V (Å^3)	5223.0(14)	1369.13(24)	1413.4(6)
Z	8	2	2
D_{calcd} (g cm^{-3})	1.621	1.470	1.842
radiation (λ, Å)	Mo- $K\alpha$ (0.71073)	Mo- $K\alpha$ (0.71073)	Mo- $K\alpha$ (0.71073)
μ (mm^{-1})	5.98	3.00	8.13
temp (°C)	-120	-120	-120
cryst dimens (mm)	0.35 x 0.35 x 0.30	0.25 x 0.25 x 0.20	0.20 x 0.20 x 0.35
T_{max}, T_{min}	0.2873; 0.2318	0.5649; 0.4524	0.2489; 0.1458
scan type	ω	ω	ω
scan width (deg)	1.00	1.00	1.00
$2\Theta_{max}$ (deg)	50.0	50.0	50.0
no. reflections recorded	3742	2411	2506
no. non-equiv reflns rec	3648	2409	2498
R_{merg} (on I)	0.051	0.058	0.016
reflns retained, I>2.5σ(I)	2227	1524	1731
no. parameters refined	217	109	110
R; R_w[a]	0.041; 0.043	0.045; 0.052	0.031; 0.037
goodness of fit[b]	1.12	1.36	1.06
max shift/esd. in final least-squares cycle	0.002	0.001	0.001
final max, min Δρ, e/Å^3	0.850; -0.530	1.050, -0.490	0.590, -0.600

[a] $R = \Sigma(||Fo| - |Fc||)/\Sigma|Fo|$; $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

[b] Goodness-of-fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$

B, 3.57 (4.03); Cl, 23.40 (21.36). ^{1}H NMR (C_7D_8): δ 0.50 (s), 0.35 (s), 0.19 (s). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 2.43 (s). ^{11}B NMR (C_7D_8): δ 4.23 (s), -1.89 (s). Mass Spectrum (EI, 20 eV): m/z 302.0 $(Cl_2BAs(SiMe_3)_2)^+$, 194.0 $(ClBAs(SiMe_3))^+$.

Preparation of $[Br_2BAs(SiMe_3)_2]_2$ (5). BBr_3 (0.400 g, 1.60 mmol) was dissolved in 30 mL pentane and placed in the upper (100 mL) bulb of a two-bulb reaction flask equipped with a Teflon valve and magnetic stir bar. $LiAs(SiMe_3)_2$ (0.364 g, 1.60 mmol) was dissolved in 40 mL toluene and added to the lower (300 mL) bulb of this flask. The flask was sealed and the lower bulb immersed in a -78 °C dry ice/acetone bath. The BBr_3 solution was then added dropwise over 15-20 min to the stirred $LiAs(SiMe_3)_2$ solution. Upon addition, the mixture turned cloudy, then cloudy yellow. The reaction mixture was allowed to warm to room temperature and stir in the dark for 12 h, after which it was filtered over a glass frit to remove the precipitated LiBr, yielding a pale yellow solution. Removal of solvents *in vacuo* revealed an off-white powder, which was rinsed in pentane to yield 0.261 g (0.333 mmol, 20.8% by B) of (**5**). Crystals of **5** suitable for X-ray structure determination were grown from toluene at -15 °C. Anal. Calcd. (Found) for $C_{12}H_{36}As_2B_2Br_4Si_4$: C, 18.39 (18.61); H, 4.63 (4.63); As, 19.12 (19.10); B, 2.76 (2.70); Br 40.78 (40.79). ^{1}H NMR (C_6D_6): δ 0.56 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.81 (s). ^{11}B NMR (C_7D_8): δ -15.78 (s). Mass Spectrum (EI, 20 eV): m/z 783.7 $(M)^+$, 391.9 $(Br_2BAs(SiMe_3)_2)^+$, 239.9 $(BrBAs(SiMe_3))^+$.

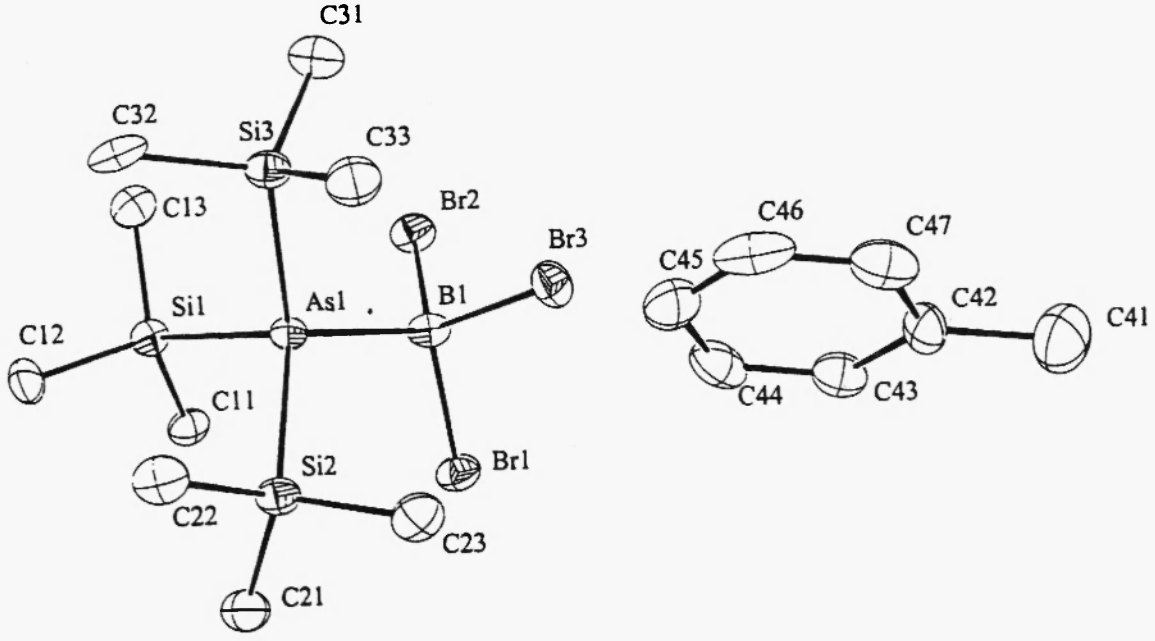
X-ray structural solution and refinement. Crystallographic data are summarized in Table 1. The crystals of **2**, **4**, and **5** used were colorless blocks which were mounted on glass fibers with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -120 °C for **2**, **4**, and **5**, and the

structures were solved by direct methods. Full-matrix 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 which converged at $R = 0.041$ ($R_w = 0.043$) for **2**, $R = 0.045$ ($R_w = 0.052$) for **4**, and $R = 0.031$ ($R_w = 0.037$) for **5**. A final difference-Fourier synthesis revealed no unusual features (max. 0.850, min. -0.530 $Å^{-3}$ for **4**; max. 1.050, min. -0.490 $Å^{-3}$ for **4**; max. 0.590, min. -0.600 $Å^{-3}$ for **5**). Crystallographic calculations were performed using the NRCVAX[14] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from Ref. 15. Interatomic distances and angles are given for **2** in Table 2, for **4** in Table 3, and for **5** in Table 4. ORTEP[16] diagrams showing the solid-state conformations and atom numbering schemes of **2**, **4**, and **5** are presented in Figures 1, 2, and 3, respectively. Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, thermal and positional parameters, and observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Center.

Results and Discussion

The separate 1:1 mole ratio reactions of BCl_3 and BBr_3 with $As(SiMe_3)_3$ produced the 1:1 Lewis acid-base adducts $Cl_3B{\bullet}As(SiMe_3)_3$ (**1**) and $Br_3B{\bullet}As(SiMe_3)_3$ (**2**) respectively. The X-ray crystal structure of **2** was solved and confirms this formulation. Compound **2** crystallized in the orthorhombic space group *Pbca*, isostructural to the analogous phosphorus compound, $Br_3B{\bullet}P(SiMe_3)_3$.[17] Both the B-As and corresponding B-P adduct were found to be solvated with one molecule of toluene per molecule of adduct. When the toluene was removed and the crystals were allowed to dry, they crumbled to a white powder. The B-As bond length of **2** was 2.108(11) A, longer than that observed by Drake for $Br_3B{\bullet}AsMe_3$ [2.04(1) Å],[9] and by Power for either $Cp^*B(Cl)As(t\text{-}Bu)_2$ [2.085(4) Å] or $Mes_2BAs(Ph)SiMe_3$ [2.031(8) A].[10] In comparing the adducts, the larger trimethylsilyl groups on **2** were likely the cause of the longer B-As bond length. The greater B-As length of **2** as compared to the three-coordinate monomeric arsinoboranes was likely due to the additional substituent present on both the B and As for **2** . Compound **2** displayed a tetrahedral coordination geometry around the B and As centers [B-As-Si 110.2° (avg), Br-B-As 109.1° (avg)], with the bromine and trimethylsilyl groups arranged in a staggered conformation, matching the features observed by Drake for $Br_3B{\bullet}AsMe_3$.[9] This was also the observed geometry for other 13-15 Lewis acid-base adducts synthesized in our group, most notably the analogous halogen-substituted adducts in the boron-phosphorus[17] and aluminum-phosphorus[18] systems.

Figure 1. ORTEP Diagram (30% probability ellipsoids) of **2**, hydrogen atoms omitted for clarity.



Multinuclear NMR of Compounds **1** and **2** displayed signals characteristic of those expected for these adducts. A singlet in the respective ^{1}H (**1**, δ 0.35; **2**, δ 0.39) ^{13}C (**1**, δ 1.64; **2**, δ 1.87), and ^{11}B (**1**, d 4.33; **2**, δ -18.70) spectra of these compounds are indicative of where the unsplit proton, carbon, and boron nuclei should appear based on previous observations of similar 13-15 adducts synthesized in our laboratory,[12d,17-19] including the analogous boron-phosphorus adducts.[17] The mass spectrum of **1** showed a fragmentation peak corresponding to the elimination of one molar equivalent of trimethylsilylchloride from the adduct ($Cl_2BAs(SiMe_3)_2^+$, m/z 302.0), as

Table 2. Bond Distances (Å) and Angles (degrees) for $Br_3B{\bullet}As(SiMe_3)_3$ (**2**), standard deviations in parentheses.

Bond Lengths			
As(1) - B(1)	2.108(11)	Si(2) - C(22)	1.858(10)
Br(1) - B(1)	2.012(10)	Si(2) - C(23)	1.859(10)
Br(2) - B(1)	1.996(10)	Si(3) - C(31)	1.857(10)
Br(3) - B(1)	2.034(10)	Si(3) - C(32)	1.847(10)
As(1) - Si(1)	2.392(3)	Si(3) - C(33)	1.859(10)
As(1) - Si(2)	2.394(3)	C(41) - C(42)	1.499(15)
As(1) - Si(3)	2.389(3)	C(42) - C(43)	1.370(14)
Si(1) - C(11)	1.836(9)	C(42) - C(47)	1.394(14)
Si(1) - C(12)	1.861(10)	C(43) - C(44)	1.375(15)
Si(1) - C(13)	1.856(9)	C(44) - C(45)	1.399(16)
Si(2) - C(21)	1.862(9)	C(45) - C(46)	1.363(16)
C(46) - C(47)	1.379(17)		

Bond Angles			
Si(1) - As(1) - Si(1)	108.54(9)	As(1) - Si(3) - C(32)	107.8(3)
Si(1) - As(1) - Si(3)	107.90(10)	As(1) - Si(3) - C(33)	108.6(3)
Si(1) - As(1) - B(1)	109.0(3)	C(31) - Si(3) - C(32)	111.5(4)
Si(2) - As(1) - Si(3)	109.63(9)	C(31) - Si(3) - C(33)	111.1(5)
Si(2) - As(1) - B(1)	110.8(3)	C(32) - Si(3) - C(33)	110.0(4)
Si(3) - As(1) - B(1)	110.9(3)	As(1) - B(1) - Br(1)	109.4(5)
As(1) - Si(1) - C(11)	106.8(3)	As(1) - B(1) - Br(2)	109.7(5)
As(1) - Si(1) - C(12)	108.1(3)	As(1) - B(1) - Br(3)	108.2(4)
As(1) - Si(1) - C(13)	108.3(3)	Br(1) - B(1) - Br(2)	110.6(4)
C(11) - Si(1) - C(12)	111.3(4)	Br(1) - B(1) - Br(3)	108.9(5)
C(11) - Si(1) - C(13)	112.5(4)	Br(2) - B(1) - Br(3)	110.0(5)
C(12) - Si(1) - C(13)	109.7(4)	C(41) - C(42) - C(43)	120.9(9)
As(1) - Si(2) - C(21)	108.1(3)	C(41) - C(42) - C(47)	120.1(9)
As(1) - Si(2) - C(22)	108.1(3)	C(43) - C(42) - C(47)	118.9(9)
As(1) - Si(2) - C(23)	106.6(3)	C(42) - C(43) - C(44)	121.2(9)
C(21) - Si(2) - C(22)	109.9(4)	C(43) - C(44) - C(45)	120.2(9)
C(21) - Si(2) - C(23)	111.9(4)	C(44) - C(45) - C(46)	118.2(10)
C(22) - Si(2) - C(23)	112.0(4)	C(45) - C(46) - C(47)	112.0(10)
As(1) - Si(3) - C(31)	107.6(3)	C(42) - C(47) - C(46)	119.5(9)

well as peaks for $As(SiMe_3)_3$ (m/z 294.0) and BCl_3 (m/z 117.9). Analogous fragmentation peaks were observed in the mass spectrum of **2**, and also a peak corresponding to the loss of MeBr from the parent ion ($Br_2BAs(SiMe_3)_2SiMe_2^+$, m/z 448.2). Accurate elemental analyses were also obtained for these compounds (within experimental error for C, H, As, B, and halogen), further supporting the identification of **1** as the aforementioned adduct by comparison to the data for the known adduct structure of **2**.

Considerable difficulties were encountered when solution reactions of BI_3 were attempted. Upon dissolution, these white/light pink crystals immediately turned the solution a dark orange color. After reaction with tris(trimethylsilyl)arsine and removal of solvents, an insoluble orange powder or intractable orange oil were frequently the products. Therefore, to circumvent this problem, the BI_3 was reacted neat, in a 1:1 mole ratio with a solution of $As(SiMe_3)_3$. However, the expected adduct was not produced; rather, the characterization data indicate a dimeric compound, $[I_2BAs(SiMe_3)_2]_2$, (**3**). Singlets in the multinuclear

NMR spectra were observed in the locations expected for a dimeric boron-Group 15 compound (ref. 12 and discussion *vide infra*): ^{1}H (δ 0.64) ^{13}C (δ 3.45), and ^{11}B (δ -55.61). The parent ion peak for **3** was present in the mass spectrum at m/z 971.7, as well as fragmentation peaks corresponding to the monomeric unit of **3** ($I_2BAs(SiMe_3)_2^+$, m/z 485.8), and the elimination of one molar equivalent of Me_3SiI from the monomer ($IBAs(SiMe_3)^+$, m/z 285.9). Positive identification of this compound as **3** was further strengthened by the elemental analyses (C, H, As, B, I), within experimental error for all elements studied.

Figure 2. ORTEP Diagram (30% probability ellipsoids) of **4**, hydrogen atoms omitted for clarity.

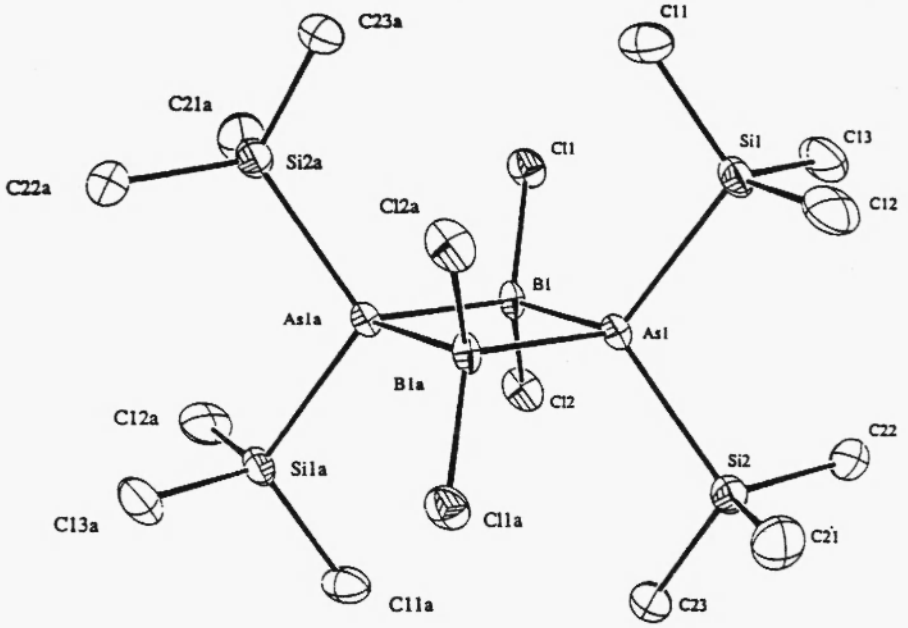


Table 3. Bond Distances (Å) and Angles (degrees) for $[Cl_2BAs(SiMe_3)_2]_2$ (**4**), standard deviations in parentheses.

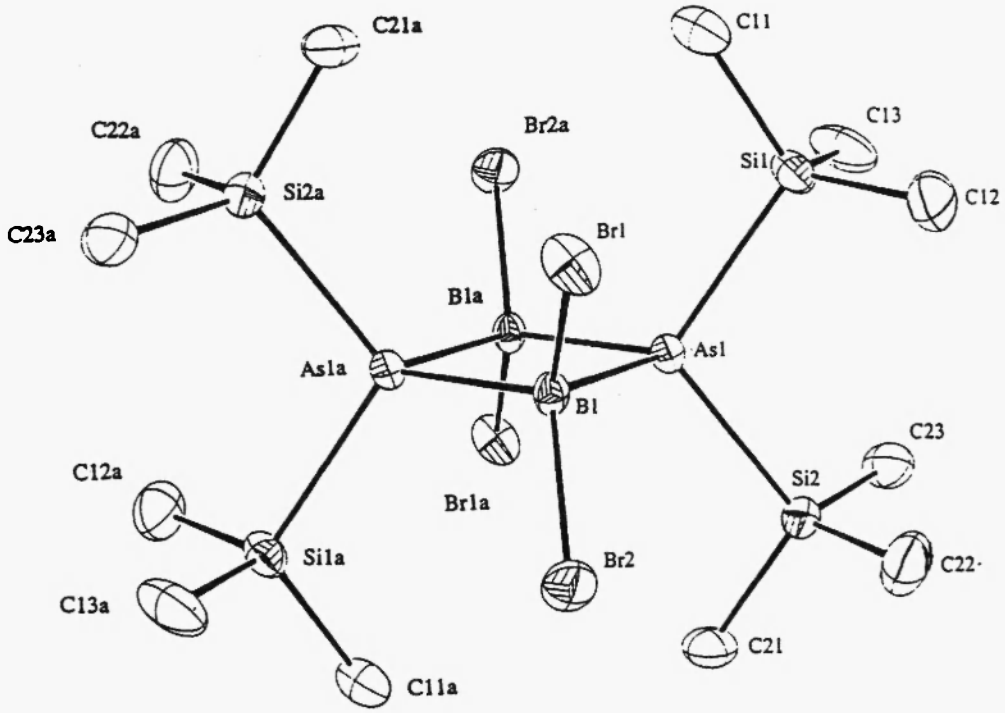
Bond Lengths			
As(1) - B(1)	2.109(8)	Si(1) - C(11)	1.859(8)
As(1) - B(1a)	2.122(8)	Si(1) - C(12)	1.866(9)
As(1) - Si(1)	2.3869(22)	Si(1) - C(13)	1.873(9)
As(1) - Si(2)	2.3822(21)	Si(2) - C(21)	1.854(9)
Cl(1) - B(1)	1.850(8)	Si(2) - C(22)	1.859(8)
Cl(2) - B(1)	1.841(9)	Si(2) - C(23)	1.854(8)
B(1) - As(1a)	2.122(8)		

Bond Angles			
B(1) - As(1) - B(1a)	88.5(3)	As(1) - Si(1) - C(11)	110.1(3)
B(1) - As(1) - Si(1)	113.73(23)	As(1) - Si(1) - C(12)	107.6(3)
B(1) - As(1) - Si(2)	118.67(23)	As(1) - Si(1) - C(13)	108.0(3)
B(1a) - As(1) - Si(1)	114.91(24)	C(11) - Si(1) - C(12)	109.1(4)
B(1a) - As(1) - Si(2)	111.81(22)	C(11) - Si(1) - C(13)	110.1(4)
Si(1) - As(1) - Si(2)	108.34(8)	C(12) - Si(1) - C(13)	112.0(4)
As(1) - B(1) - As(1a)	91.5(3)	As(1) - Si(2) - C(21)	106.4(3)
As(1) - B(1) - Cl(1)	111.9(4)	As(1) - Si(2) - C(22)	108.0(3)
As(1) - B(1) - Cl(2)	115.6(4)	As(1) - Si(2) - C(23)	110.5(3)
As(1a) - B(1) - Cl(1)	112.8(4)	C(21) - Si(2) - C(22)	110.8(4)
As(1a) - B(1) - Cl(2)	113.8(4)	C(21) - Si(2) - C(23)	111.5(4)
Cl(1) - B(1) - Cl(2)	110.1(4)	C(22) - Si(2) - C(23)	109.6(4)

Lithium halide elimination has been observed to be a reliable method for producing dimeric compounds from Group 13 halides and lithium bis(trimethylsilyl)arsenide.[20] Based on this success, we were encouraged to apply this method to the analogous boron-arsenic system. Thus, BCl_3 and BBr_3 were combined in a 1:1 mole ratio with $LiAs(SiMe_3)_2$ in separate reactions to form $[Cl_2BAs(SiMe_3)_2]_2$ (**4**) and $[Br_2BAs(SiMe_3)_2]_2$ (**5**), respectively. The X-ray crystal structures of **4** and **5** were solved and confirm these formulations. Compounds **4** and **5** both crystallize in the monoclinic system, space group $P2_1/n$. The B-As bond lengths for **4** and **5** are 2.109(8) Å and 2.113(6) Å, respectively, slightly shorter than that seen by Power for $[PhB(Cl)As(t\text{-}Bu)_2]_2$ (2.200(5) Å),[10] but longer than that observed by Cowley for $i\text{-}Pr_2AsB(Mes)_2$ (2.019(7) Å).[11] Increased Lewis acidity at the boron centers of **4** and **5** due to the presence of two halogen ligands can be cited as a reason for their shorter B-As bond length when compared to $[PhB(Cl)As(t\text{-}Bu)_2]_2$, as well as the smaller size of the halogen ligands when compared to a phenyl group. The longer bond lengths when compared to the monomer $i\text{-}Pr_2AsB(Mes)_2$ were likely the result of the steric requirements of the dimeric structures of **4** and **5**. Both **4** and **5** have a central four-membered boron-arsenic-boron-arsenic ring, configured in a distorted square planar geometry with the B-As-B angle (88.5° for **4**, 88.2° for **5**) slightly smaller than the As-B-As angle (91.5° for **4**, 91.8° for **5**). This also was in contrast to $[PhB(Cl)As(t\text{-}Bu)_2]_2$, which has a smaller As-B-As angle (88.6°). Such a difference can again be explained by the greater steric requirements of the phenyl groups, as well as solid-state packing of the molecule in the crystal. Distorted tetrahedral geometry around the B and As centers was present in both **4** (Cl-B-Cl, 110.1°; Si-As-Si, 108.3°) and **5** (Br-B-Br, 108.7°; Si-As-Si, 107.9°); these angles were larger than the analogous angles in $[PhB(Cl)As(t\text{-}Bu)_2]_2$ (C-B-Cl, 105.6°; C-As-C, 106.9°), once again likely due to the different steric requirements of the phenyl group. The slightly longer B-As bond length for **5** as compared to **4**, as well as variances in bond angles between these molecules, are likely due to the different steric requirements of the Br ligands of **5** as compared to the Cl ligands of **4**.

Analysis of the NMR data of **4** and **5** supports retention of the dimeric structures of these compounds when dissolved. The multinuclear NMR spectra of **4** all show singlets in the range expected for a 13-15 dimeric compound: ^1H, δ 0.50; ^{13}C, δ 2.43; ^{11}B, δ -1.89. Likewise, the signals in the NMR spectra of **5** show up as singlets in a similar range: ^1H, δ 0.56; ^{13}C, δ 2.53; ^{11}B, δ -15.78. The peak

Figure 3. ORTEP Diagram (30% probability ellipsoids) of **5**, hydrogen atoms omitted for clarity.



locations in the ^{11}B spectra of the dimeric compounds **4** and **5** vary greatly due to the location of the parent boron trihalide: BCl_3 ^{11}B, δ 46.23; BBr_3 ^{11}B, δ 38.73; BI_3 ^{11}B δ -7.88. An additional set of peaks is also present in the ^{1}H (δ 0.35) and ^{11}B (δ 4.23) NMR spectra of **4**; these peaks correspond with those observed for **1**, and could indicate some rearrangement of the dimer to the analogous adduct in solution. It is interesting to note that similar adduct peaks are not seen in the spectra of **3** or **5**, nor are peaks assignable to the dimers present in the NMR spectra of either **1** or **2**. Rearrangement or a mixture of products could also explain the variant elemental analysis data for **4**; several samples were sent, and the data was not once consistent beyond C and H for the calculated values of **4**. Elemental analyses of **5**, however, were consistent for all elements evaluated, as were the analyses conducted for **3** (*vide supra*).

The mass spectrum of **4** showed two major peaks: m/z 302.0, corresponding to the monomeric unit $(Cl_2BAs(SiMe_3)_2)^+$; and m/z 194.0, corresponding to the loss of one Me_3SiCl unit from this monomer, $(ClBAsSiMe_3)^+$. A parent ion peak was obtained in the mass spectrum of **5** at m/z 783.7, along with fragmentation peaks analogous to those observed for **4**: the monomeric unit (m/z 391.9, $Br_2BAs(SiMe_3)_2^+$) and the monomer less Me_3SiBr (m/z 239.9, $BrBAsSiMe_3^+$). Peaks assigned to the parent ion and similar fragments of **3** were also observed (*vide supra*). Thus by comparison of the available data with that of the structurally confirmed dimeric compounds **4** and **5**, we can confidently assign a dimeric formulation to compound **3**.

Table 4. Bond Distances (Å) and Angles (degrees) for $[Br_2BAs(SiMe_3)_2]_2$ (**5**), standard deviations in parentheses.

Bond Lengths			
As(1) - B(1)	2.113(6)	Si(1) - C(11)	1.849(7)
As(1) - B(1a)	2.108(7)	Si(1) - C(12)	1.850(8)
As(1) - Si(1)	2.3993(18)	Si(1) - C(13)	1.852(7)
As(1) - Si(2)	2.3935(19)	Si(2) - C(21)	1.855(7)
Br(1) - B(1)	1.995(7)	Si(2) - C(22)	1.854(7)
Br(2) - B(1)	2.024(7)	Si(2) - C(23)	1.845(7)
B(1) - As(1a)	2.108(7)		

Bond Angles			
B(1) - As(1) - B(1a)	88.21(25)	As(1) - Si(1) - C(11)	111.41(21)
B(1) - As(1) - Si(1)	114.57(19)	As(1) - Si(1) - C(12)	106.59(24)
B(1) - As(1) - Si(2)	118.04(19)	As(1) - Si(1) - C(13)	108.19(22)
B(1a) - As(1) - Si(1)	114.83(19)	C(11) - Si(1) - C(12)	109.1 (13)
B(1a) - As(1) - Si(2)	112.51(19)	C(11) - Si(1) - C(13)	109.8 (13)
Si(1) - As(1) - Si(2)	107.87(6)	C(12) - Si(1) - C(13)	111.7 (4)
As(1) - B(1) - As(1a)	91.8 (3)	As(1) - Si(2) - C(21)	111.08(22)
As(1) - B(1) - Br(1)	116.1 (3)	As(1) - Si(2) - C(22)	106.79(24)
As(1) - B(1) - Br(2)	111.5 (3)	As(1) - Si(2) - C(23)	108.22(22)
As(1a) - B(1) - Br(1)	114.7 (3)	C(21) - Si(2) - C(22)	111.4 (3)
As(1a) - B(1) - Br(2)	113.3 (3)	C(21) - Si(2) - C(23)	109.1 (3)
Br(1) - B(1) - Br(2)	108.7 (3)	C(22) - Si(2) - C(23)	110.2 (3)

The ultimate goal of producing the boron-arsenic compounds discussed in this work is to decompose them to the 13-15 material BAs *via* a thermolysis route. Fragmentation peaks in the mass spectra of these compounds indicating the loss of trimethylsilylhalide groups in the gas phase is encouraging, however preliminary thermal decompositions of these compounds have yielded powders which have heavy contamination of C, H, Si, and halogens. Work is continuing in our laboratories to develop methods to utilize the potential of these compounds as single-source precursors.

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Supplementary Material Available: Tables of non-hydrogen atom fractional coordinates and equivalent thermal parameters (8 pages); list of observed and calculated structure amplitudes (24 pages); unit cell diagrams (3 pages). Ordering information is given on any current masthead page.

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