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Preparation and Characterization of Halogen−Boron−Phosphorus Compounds. X-ray Crystal Structures of $X_3B{\cdot}P(SiMe_3)_3$ and $[X_2BP(SiMe_3)_2]_2$ (X = Cl, Br)

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The 1:1 mole ratio reactions of boron trihalides (BX_3) with tris(trimethylsilyl)phosphine [$P(SiMe_3)_3$] produced 1:1 Lewis acid/base adducts [$X_3B{\cdot}P(SiMe_3)_3$, X = Cl (**1**), Br (**2**), I (**5**)]. Analogous 1:1 mole ratio reactions of these boron trihalides with lithium bis(trimethylsilyl)phosphide [$LiP(SiMe_3)_2$] produced dimeric boron−phosphorus ring compounds {$[X_2BP(SiMe_3)_2]_2$, X = Br (**3**), Cl (**4**)}. X-ray crystallographic studies were successfully conducted on compounds **1**−**4**. Compound **1** crystallized in the orthorhombic space group *Pbca*, with $a = 13.420(3)$ Å, $b = 17.044(5)$ Å, $c = 21.731(7)$ Å, $V = 4970.6(25)$ Å^3, and $D_{calc} = 1.229$ g cm^{-3} for $Z = 8$; the B−P bond length was 2.022(9) Å, Compound **2** crystallized in the orthorhombic space group *Pbca*, with $a = 13.581(6)$ Å, $b = 17.106(7)$ Å, $c = 22.021(9)$ Å, $V = 5116(4)$ Å^3, and $D_{calc} = 1.540$ g cm^{-3} for $Z = 8$; the B−P bond length was 2.00(2) Å. Compound **3** crystallized in the monoclinic space group $P2_1/n$, with $a = 9.063(5)$ Å, $b = 16.391(8)$ Å, $c = 9.331(4)$ Å, $V = 1379.2(12)$ Å^3, and $D_{calc} = 1.676$ g cm^{-3} for $Z = 2$; the B−P bond length was 2.023(10) Å. Compound **4** crystallized in the monoclinic space group $P2_1/n$, with $a = 9.143(5)$ Å, $b = 16.021(8)$ Å, $c = 9.170(4)$ Å, $V = 1342.2(11)$ Å^3, and $D_{calc} = 1.282$ g cm^{-3} for $Z = 2$; the B−P bond length was 2.025(3) Å. Thermal decomposition studies were performed on compounds **1**−**4**, yielding colored powders with boron: phosphorus ratios greater than 1:1 and significant C and H contamination indicated by elemental analyses.

Introduction

In the past decade, research in our laboratories has produced numerous potential precursors to group 13−15 semiconductors by two different routes: silyl cleavage (elimination of a trimethylsilyl halide) or lithium halide elimination.[1] In addition, the former methodology has been utilized by us and others to produce group 13−15 semiconductor materials.[2−13] Because of the recent interest in boron−phosphorus[14−16] and boron−arsenic[17,18] compounds, we decided to apply both methodologies to the boron−phosphorus and boron−arsenic[19] systems in an attempt to isolate potential precursors which contain only halogens as substituents on the boron. Reactions of boron trihalides (BX_3, X = F, Cl, Br) with (trimethylsilyl)phosphines to form boron−phosphorus compounds were originally reported by Nöth and Schrägle in 1961,[20] but only partial elemental analyses were offered as characterizations of these species. However, as a result of our investigations, we have prepared and characterized five potential precursors to boron phosphide from the separate reactions of boron trihalides (BX_3, X = Cl, Br, I) with tris(trimethylsilyl)phosphine, $P(SiMe_3)_3$, or lithium bis(trimethylsilyl)phosphide, $LiP(SiMe_3)_2$: $Cl_3B{\cdot}P(SiMe_3)_3$ (**1**), $Br_3B{\cdot}P(SiMe_3)_3$ (**2**), $[Br_2BP(SiMe_3)_2]_2$ (**3**), $[Cl_2BP(SiMe_3)_2]_2$ (**4**), and $I_3B{\cdot}P(SiMe_3)_3$ (**5**), respectively. These compounds have been characterized by multinuclear NMR, electron ionization mass spectrometry (EIMS), and elemental analyses; X-ray crystal structures were also determined for **1**−**4**.

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Experimental Section

General Considerations. All manipulations were performed using general Schlenk and drybox techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. Literature methods were used to prepare $P(SiMe_3)_3$.[21] $LiP(SiMe_3)_2{\cdot}1.8THF$[22] was prepared *via* the 1:1 mole reaction of MeLi with $P(SiMe_3)_3$. 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 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 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 and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Unity 500 spectrometer operating at 160.5 and 202.3 MHz, respectively. ^{11}B spectra were referenced externally to $BF_3{\cdot}OEt_2$ at δ 0.00 ppm, while $^{31}P\{^1H\}$ spectra were referenced externally to H_3PO_4 at δ 0.00 ppm. Variable-temperature ^1H NMR experiments were performed on a Varian Unity 400 spectrometer using vacuum-sealed 5 mm tubes, with dry degassed C_7D_8 as the solvent. The temperature was increased in 15−25 °C increments from 25−90 °C, then decreased in similar increments back to room temperature (25 °C). Melting points (uncorrected) were taken on a Thomas/Hoover Uni-Melt capillary melting point apparatus. Single-crystal X-ray diffraction data were collected on a Rigaku AFC6/S diffractometer using the ω scan mode ($\lambda = 0.710\ 73$ 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.

Preparation of $Cl_3B{\cdot}P(SiMe_3)_3$ (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. $P(SiMe_3)_3$ (0.293 g, 1.17 mmol, 10% excess) dissolved in 30 mL of pentane was added *via* pipet to the stirring BCl_3 solution. During addition, the solution turned from clear to cloudy, and clear/white crystals formed on the walls and base of the flask. The reaction mixture was stirred for 24 h under an argon atmosphere in the dark at room temperature. The solvents were then removed *in vacuo* to afford a white powder, which was rinsed in pentane and collected to yield 0.369 g (1.00 mmol, 93.5% yield based on BCl_3) of **1**, mp 73 °C dec. Crystals of **1** suitable for X-ray structure determination were grown from toluene at −15 °C. Anal. Calcd (found) for $C_9H_{27}BCl_3PSi_3$: C, 29.40 (29.57); H, 7.40 (7.39); B, 2.94 (3.17); Cl, 28.92 (28.65); P, 8.42 (8.31). Titration of hydrolyzed volatiles with a standardized NaOH solution revealed no elimination of Me_3SiCl. ^1H NMR (C_7D_8): δ 0.49 (t (vw), PSi*Me*$_3$, $^3J_{P-H} = 2.7$ Hz, dimer), 0.35 (d, PSi*Me*$_3$, $^3J_{P-H} = 5.1$ Hz), 0.19 (s, *Me*$_3$SiCl). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 1.48 (d, PSi*Me*$_3$, $^2J_{P-C} = 6.5$ Hz). ^{11}B NMR (C_6D_6): δ 5.04 (d, *B*P, $^1J_{B-P} = 102.4$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −154.40 (quartet, B*P*, $^1J_{P-B} = 100.7$ Hz). Mass spectrum (EI, 20 eV): *m/z* 250.1 $(P(SiMe_3)_3)^+$, 116.0 $(BCl_3)^+$.

Preparation of $Br_3B{\cdot}P(SiMe_3)_3$ (2). BBr_3 (0.283 g, 1.13 mmol) dissolved in 60 mL of pentane was added to a 200 mL screwtop reaction flask equipped with a Teflon valve and a magnetic stirbar. $P(SiMe_3)_3$ (0.313 g, 1.25 mmol, 10% excess) dissolved in 60 mL of pentane was added *via* pipet to the stirring BBr_3 solution. During the addition, the colorless solution turned cloudy and a white precipitate formed. The reaction mixture was stirred for 48 h under argon atmosphere and in the dark at room temperature. The solvents were then removed *in vacuo* to afford a white powder, which was rinsed in pentane and collected to yield 0.419 g (0.84 mmol, 74.0% yield based on BBr_3) of **2**, mp 90 °C dec. Crystals of **2** suitable for X-ray structure determination were grown from toluene at −15 °C. Anal. Calcd (found) for $C_9H_{27}BBr_3PSi_3$: C, 21.57 (21.75); H, 5.43 (5.23); B, 2.16 (2.23); Br, 47.84 (47.88); P, 6.18 (6.03). Titration of hydrolyzed volatiles with a standardized NaOH solution revealed no elimination of Me_3SiBr. ^1H NMR (C_6D_6): δ 0.36 (d, PSi*Me*$_3$, $^3J_{P-H} = 4.8$ Hz). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 1.90 (d, PSi*Me*$_3$, $^2J_{P-C} = 6.9$ Hz). ^{11}B NMR (C_6D_6): δ −16.64 (d, *B*P, $^1J_{B-P} = 94.9$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −145.94 (quartet, B*P*, $^1J_{P-B} = 94.6$ Hz). Mass spectrum (EI, 20 eV): *m/z* 420.8 $(M - Br)^+$.

Preparation of $[Br_2BP(SiMe_3)_2]_2$ (3). Method a. BBr_3 (0.283 g, 1.13 mmol) dissolved in 30 mL of pentane was added to a 200 mL screwtop reaction flask equipped with a Teflon valve and a magnetic stirbar. $P(SiMe_3)_3$ (0.313 g, 1.25 mmol, 10% excess) dissolved in 30 mL of pentane was added *via* pipet to the BBr_3 solution. Immediately upon addition, the solution turned from clear to cloudy and a white precipitate formed. This mixture was allowed to stir under argon at room temperature, in the dark, for 48 h. The solvent and volatile reaction products were then removed *in vacuo*, revealing an off-white powder, which was washed in pentane to yield 0.343 g (0.492 mmol, 87.1% yield based on B) of **3**, mp 140 °C dec. Crystals suitable for X-ray structural determination were grown from toluene at −15 °C but were found to be **2**. Anal. Calcd (found) for $C_{12}H_{36}B_2Br_4P_2Si_4$: C, 20.71 (20.96); H, 5.21 (5.27); B, 3.11 (3.49); Br, 45.93 (46.19); P, 8.90 (8.64). Titration of hydrolyzed volatiles required 7.5 mL of NaOH (0.11 M), corresponding to an elimination of 0.80 mmol (23.7%) of Me_3SiBr. ^1H NMR (C_6D_6): δ 0.56 (t, PSi*Me*$_3$, $^3J_{P-H} = 2.4$ Hz, dimer), 0.36 (d, PSi*Me*$_3$, $^3J_{P-H} = 5.1$ Hz, adduct), 0.28 (s, *Me*$_3$SiBr). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.28 (t, PSi*Me*$_3$, $^2J_{P-C} = 3.5$ Hz, dimer), 1.83 (d, PSi*Me*$_3$, $^2J_{P-C} = 6.3$, adduct). ^{11}B NMR (C_7D_8): δ −12.15 (t, *B*P, $^1J_{B-P} = 72.2$ Hz, dimer), −16.63 (d, *B*P, $^1J_{B-P} = 94.9$ Hz, adduct). $^{31}P\{^1H\}$ NMR (C_7D_8): δ −96.54 (septet, B*P*, $^1J_{P-B} = 68.4$ Hz, dimer). Mass spectrum (EI, 20 eV): *m/z* 695.9 $(M)^+$.

Method b. BBr_3 (0.319 g, 1.27 mmol) dissolved in 60 mL of toluene was placed in the upper (100 mL) bulb of a two-bulb screwtop reaction flask equipped with a Teflon valve and a magnetic stirbar. $LiP(SiMe_3)_2{\cdot}1.8THF$ (0.234 g, 0.712 mmol) dissolved in 60 mL of toluene was placed in the lower (200 mL) bulb of this flask. The flask was sealed, and the lower bulb was placed in a −78 °C dry ice/acetone bath. The BBr_3 solution was added dropwise to the $LiP(SiMe_3)_2{\cdot}1.8THF$ solution over 15−20 min. The clear solution turned first cloudy and then dark yellow upon complete addition. The mixture was allowed to warm to room temperature under stirring in the dark overnight, during which it turned cloudy orange. The mixture was filtered over a glass frit to remove LiBr, yielding an orange-yellow solution. Removal of the solvent yielded a light orange powder, which was rinsed in pentane to yield 0.172 g (0.247 mmol, 69.4% based on P) of **3**, mp 140 °C dec. Crystals of **3** suitable for X-ray structure determination were grown from toluene at −15 °C. Anal. Calcd (found) for $C_{12}H_{36}B_2Br_4P_2Si_4$: C, 20.71 (20.97); H, 5.21 (4.99); B, 3.11 (2.96); Br, 45.93 (45.69); P, 8.90 (8.78). ^1H NMR (C_6D_6): δ 0.57 (t, PSi*Me*$_3$, $^3J_{P-H} = 2.7$ Hz, dimer), 0.36 (d, PSi*Me*$_3$, $^3J_{P-H} = 5.1$ Hz, adduct), 0.28 (s, *Me*$_3$SiBr). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.32 (t, PSi*Me*$_3$, $^2J_{P-C} = 3.7$ Hz, dimer). ^{11}B NMR (C_7D_8): δ −12.13 (t, *B*P, $^1J_{B-P} = 72.7$ Hz, dimer), −16.65 (d, *B*P, $^1J_{B-P} = 94.9$ Hz, adduct). $^{31}P\{^1H\}$ NMR (C_7D_8): δ −95.68 (septet, B*P*, $^1J_{P-B} = 73.2$ Hz, dimer). Mass spectrum (EI, 20 eV): *m/z* 695.9 $(M)^+$.

Preparation of $[Cl_2BP(SiMe_3)_2]_2$ (4). BCl_3 (0.250 g, 2.13 mmol; as a 1.0 M solution in hexanes) was diluted to 50 mL in pentane, and the solution was placed in the upper (50 mL) bulb of a two-bulb screwtop reaction flask equipped with a Teflon valve. $LiP(SiMe_3)_2{\cdot}1.8THF$ (0.393 g, 1.19 mmol) dissolved in 60 mL toluene was transferred into the lower (300 mL) bulb of this flask and stirred in a −78 °C dry ice/acetone bath for 15 min. The BCl_3 solution was then added slowly (over 10−15 min) to the stirring $LiP(SiMe_3)_2{\cdot}1.8THF$ solution, during which the initially clear solutions turned a cloudy yellow-brown. The mixture was allowed to warm to room temperature and stir in the dark for 3 days, after which it was filtered under slight vacuum to remove LiCl, yielding a clear yellow solution. Removal of solvents in vacuo gave a yellow-white powder, which was rinsed in pentane to yield 0.298 g (0.575 mmol, 96.2% yield by P) of **4**, mp 135 °C dec. Crystals suitable for X-ray structural determination were grown from toluene at −15 °C. Anal. Calcd (found) for $C_{12}H_{36}B_2Cl_4P_2Si_4$: C, 27.82 (28.06); H, 7.00 (7.06); B, 4.17 (4.49); Cl, 27.37 (27.13); P, 11.96 (11.68). ^1H NMR (C_7D_8): δ 0.49 (t, PSi*Me*$_3$, $^3J_{P-H} = 2.7$ Hz, dimer), 0.35 (d (w), PSi*Me*$_3$, $^3J_{P-H} = 5.1$ Hz, adduct), 0.19 (s, *Me*$_3$SiCl). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 2.69 (t, PSi*Me*$_3$, $^2J_{P-C} = 3.5$ Hz, dimer). ^{11}B

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Table 1. Crystallographic Data and Measurements for $Cl_3B{\cdot}P(SiMe_3)_3$ (**1**), $Br_3B{\cdot}P(SiMe_3)_3$ (**2**), $[Br_2BP(SiMe_3)_2]_2$ (**3**), and $[Cl_2BP(SiMe_3)_2]_2$ (**4**)

	1	**2**	**3**	**4**
empirical formula	$C_{16}H_{35}BCl_3PSi_3$	$C_{16}H_{35}BBr_3PSi_3$	$C_{12}H_{36}B_2Br_4P_2Si_4$	$C_{12}H_{36}B_2Br_4P_2Si_4$
fw	459.85	593.20	695.94	518.13
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	*Pbca*	$P2_1/n$	$P2_1/n$
a (Å)	13.420(3)	13.581(6)	9.063(5)	9.143(5)
b (Å)	17.044(5)	17.106(7)	16.391(8)	16.021(8)
c (Å)	21.731(7)	22.021(9)	9.331(4)	9.170(4)
V (Å^3)	4970.6(25)	5116(4)	1379.2(12)	1342.2(11)
Z	8	8	2	2
D_{calcd} (g cm^{-3})	1.229	1.540	1.676	1.282
radiation (λ (Å))	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ (mm^{-1})	0.58	4.89	6.07	0.73
temp (°C)	−130	−135	−130	−170
cryst dimens (mm)	0.50 × 0.30 × 0.25	0.30 × 0.25 × 0.14	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.30
T_{max}; T_{min}	0.8776; 0.7040	0.4404; 0.2942	0.2817; 0.2735	0.8471; 0.7508
scan type	ω	ω	ω	ω
scan width (deg)	1.00	1.00	1.00	1.00
θ_{max} (deg)	46.0	46.0	50.0	46.0
no. of reflns recorded	6492	4098	2810	5438
no. of nonequiv reflns recorded	3444	3540	2425	1860
R_{merg} (on I)	0.080	0.058	0.071	0.051
no. of reflns retained, $I > 2.5\sigma(I)$	1681	1563	1598	1591
no. of params refined	217	218	110	128
R; R_w[a]	0.053; 0.054	0.059; 0.054	0.051; 0.055	0.027; 0.042
goodness of fit[b]	1.32	1.25	1.57	1.55
max shift/esd in final least-squares cycle	0.000	0.005	0.005	0.002
final max, min $\Delta\rho$ (e/Å^3)	0.470; −0.380	0.900; −0.810	1.580; −1.210	0.370; −0.240

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [b] Goodness-of-fit $= [\sum w\Delta^2/(N_{observns} - N_{params})]^{1/2}$.

NMR (C_7D_8): δ −0.041 (t, *B*P, $^1J_{B-P} = 77.0$ Hz, dimer), 4.94 (d, *B*P, $^1J_{B-P} = 102.3$ Hz, adduct), −1.31 (m, *B*P, $^1J_{B-P} = 76.0$ Hz, oligomer). $^{31}P\{^1H\}$ NMR (C_7D_8): δ −69.81 (m, *B*P, $^1J_{B-P} = 74.7$ Hz, oligomer), −96.11 (septet, B*P*, $^1J_{P-B} = 74.7$ Hz, dimer), −154.34 (quartet, *B*P, $^1J_{B-P} = 98.5$ Hz, adduct). Mass spectrum (EI, 20 eV): *m*/*z* 518.1 (M)$^+$.

Preparation of $I_3B{\cdot}P(SiMe_3)_3$ (5). Solid BI_3 (0.250 g, 0.639 mmol) was added to a 200 mL flask equipped with a Teflon valve and a magnetic stir bar. $P(SiMe_3)_3$ (0.176 g, 0.702 mmol, 10% excess) dissolved in 30 mL of pentane was added to the BI_3 via pipet. A white precipitate formed immediately upon addition. After addition was complete, an additional 30 mL of pentane was added to increase the volume for stirring. The reaction mixture was stirred for 12 h at room temperature in the dark. The solvent was removed *in vacuo* to reveal a yellow-white powder, which was collected and washed in pentane to yield 0.338 g (0.526 mmol, 82.4% yield by BI_3) of **5**, mp 129 °C dec. Anal. Calcd (found) for $C_9H_{27}BI_3PSi_3$: C, 16.84 (16.93); H, 4.24 (4.26); B, 1.68 (1.95); I, 59.29 (59.16); P, 4.82 (4.92). Titration of hydrolyzed volatiles with a standardized NaOH solution revealed no elimination of Me_3SiI. ^1H NMR (C_7D_8): δ 0.46 (d, PSi*Me*$_3$, $^3J_{P-H} = 5.1$ Hz). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 2.53 (d, PSi*Me*$_3$, $^2J_{P-C} = 6.5$ Hz). ^{11}B NMR (C_7D_8): δ −83.69 (d, *B*P, $^1J_{B-P} = 75.5$ Hz). $^{31}P\{^1H\}$ NMR (C_7D_8): δ −155.17 (quartet, B*P*, $^1J_{P-B} = 74.8$ Hz). Mass spectrum (EI, 20 eV): *m*/*z* 515.0 (M − I)$^+$, 441.9 ($(I_2BP(SiMe_3)_2)^+$), 264.8 ($(BI_2)^+$), 250.1 ($(P(SiMe_3)_3)^+$).

X-ray Structure Solutions and Refinements. Crystallographic data are summarized in Table 1. The crystals of **1**−**4** used were colorless blocks, which were mounted separately on glass fibers with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at −130 °C for **1** and **3**, −135 °C for **2**, and −170 °C for **4**, 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 of refinement which converged at $R = 0.053$ ($R_w = 0.054$) for **1**, $R = 0.059$ ($R_w = 0.054$) for **2**, $R = 0.051$ ($R_w = 0.055$) for **3**, and $R = 0.027$ ($R_w = 0.042$) for **4**. A final difference-Fourier synthesis revealed no unusual features (maximum 0.470, minimum −0.380 e Å^{-3} for **1**; maximum 0.900, minimum −0.810 e Å^{-3} for **2**; maximum 1.580, minimum −1.210 e Å^{-3} for **3**; maximum 0.370, minimum −0.240 e Å^{-3} for **4**). Crystallographic calculations were performed using the NRCVAX[23] suite of structure determination programs. For all structure factor calculations, neutral-atom scattering factors and their anomalous dispersion corrections were taken from ref 24. Interatomic distances and angles are given for **1** in Table 2, for **2** in Table 3, for **3** in Table 4, and for **4** in Table 5. ORTEP[25] diagrams showing the solid state conformation and atom-numbering scheme of **1**−**4** are presented in Figures 1−4, respectively.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cl_3B{\cdot}P(SiMe_3)_3$ (**1**) (Standard Deviations in Parentheses)

P(1)−B(1)	2.022(9)	Cl(1)−B(1)	1.857(9)
P(1)−Si(1)	2.297(3)	Cl(2)−B(1)	1.845(9)
P(1)−Si(2)	2.307(3)	Cl(3)−B(1)	1.841(9)
P(1)−Si(3)	2.296(3)		
Si(1)−P(1)−Si(2)	108.79(12)	Cl(1)−B(1)−Cl(2)	109.9(4)
Si(1)−P(1)−Si(3)	108.06(12)	Cl(1)−B(1)−Cl(3)	110.4(5)
Si(2)−P(1)−Si(3)	109.56(10)	Cl(2)−B(1)−Cl(3)	110.1(5)
Si(1)−P(1)−B(1)	110.1(13)	P(1)−B(1)−Cl(1)	108.3(5)
Si(2)−P(1)−B(1)	109.7(3)	P(1)−B(1)−Cl(2)	109.1(4)
Si(3)−P(1)−B(1)	110.6(3)	P(1)−B(1)−Cl(3)	109.0(4)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Br_3B{\cdot}P(SiMe_3)_3$ (**2**) (Standard Deviations in Parentheses)

P(1)−B(1)	1.998(21)	Br(1)−B(1)	2.020(18)
P(1)−Si(1)	2.307(7)	Br(2)−B(1)	2.035(20)
P(1)−Si(2)	2.302(6)	Br(3)−B(1)	1.995(20)
P(1)−Si(3)	2.317(6)		
Si(1)−P(1)−Si(2)	108.42(24)	Br(1)−B(1)−Br(2)	108.3(9)
Si(1)−P(1)−Si(3)	107.46(25)	Br(1)−B(1)−Br(3)	109.7(10)
Si(2)−P(1)−Si(3)	109.02(25)	Br(2)−B(1)−Br(3)	109.5(9)
Si(1)−P(1)−B(1)	110.6(6)	Br(1)−B(1)−P(1)	109.7(9)
Si(2)−P(1)−B(1)	110.5(6)	Br(2)−B(1)−P(1)	109.1(10)
Si(3)−P(1)−B(1)	110.7(6)	Br(3)−B(1)−P(1)	110.4(9)

Decomposition Studies. Thermal gravimetric analyses and differential thermal analyses of **1**−**4** were conducted using a TA Instruments SDT 2960 simultaneous DTA/TGA instrument under a

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(23) For a full system reference of the NRCVAX System, see: Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(24) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(25) Johnson, C. K. ORTEP−A Fortran Thermal Ellipsoid Plot Program. Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

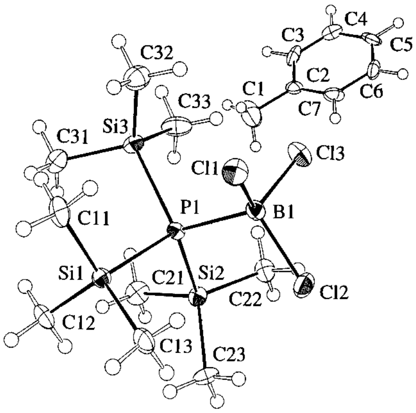

Figure 1. ORTEP diagram (30% probability ellipsoids) of **1**.

Table 4. Bond Distances (Å) and Angles (deg) for $[Br_2BP(SiMe_3)_2]_2$ (**3**) (Standard Deviations in Parentheses)

Br(1)−B(1)	2.007(10)	Si(1)−C(11)	1.852(10)
Br(2)−B(1)	1.991(10)	Si(1)−C(12)	1.858(10)
P(1)−Si(1)	2.312(4)	Si(1)−C(13)	1.857(10)
P(1)−Si(2)	2.313(3)	Si(2)−C(21)	1.862(10)
P(1)−B(1)	2.023(10)	Si(2)−C(22)	1.854(10)
P(1)−B(1a)	2.034(10)	Si(2)−C(23)	1.854(10)
B(1)−P(1a)	2.034(10)		

B(1)−P(1)−B(1a)	89.4(4)	P(1)−Si(1)−C(11)	108.0(3)
P(1)−B(1)−P(1a)	90.6(4)	P(1)−Si(1)−C(12)	106.6(3)
Br(1)−B(1)−Br(2)	108.8(5)	P(1)−Si(1)−C(13)	112.6(3)
Si(1)−P(1)−Si(2)	107.00(12)	P(1)−Si(2)−C(21)	106.7(4)
Br(1)−B(1)−P(1)	112.4(5)	P(1)−Si(2)−C(22)	113.4(3)
Br(1)−B(1)−P(1a)	113.4(5)	P(1)−Si(2)−C(23)	109.3(3)
Br(2)−B(1)−P(1)	116.4(5)	C(11)−Si(1)−C(12)	110.3(4)
Br(2)−B(1)−P(1a)	114.4(5)	C(11)−Si(1)−C(13)	108.6(4)
Si(1)−P(1)−B(1)	118.2(3)	C(12)−Si(1)−C(13)	110.8(5)
Si(1)−P(1)−B(1a)	112.2(3)	C(21)−Si(2)−C(22)	108.1(4)
Si(2)−P(1)−B(1)	113.8(3)	C(21)−Si(2)−C(23)	111.4(5)
Si(2)−P(1)−B(1a)	115.8(3)	C(22)−Si(2)−C(23)	108.0(5)

Table 5. Bond Distances (Å) and Angles (deg) for $[Cl_2BP(SiMe_3)_2]_2$ (4) (Standard Deviations in Parentheses)

Cl(1)−B(1)	1.852(3)	Si(1)−C(11)	1.851(3)
Cl(2)−B(1)	1.839(3)	Si(1)−C(12)	1.862(3)
P(1)−Si(1)	2.3071(13)	Si(1)−C(13)	1.862(3)
P(1)−Si(2)	2.3009(15)	Si(2)−C(21)	1.855(3)
P(1)−B(1)	2.025(3)	Si(2)−C(22)	1.858(3)
P(1)−B(1a)	2.024(3)	Si(2)−C(23)	1.861(3)
B(1)−P(1a)	2.024(3)		

B(1)−P(1)−B(1a)	88.80(12)	C(11)−Si(1)−C(12)	108.95(15)
P(1)−B(1)−P(1a)	91.20(12)	C(11)−Si(1)−C(13)	109.11(15)
Cl(1)−B(1)−Cl(2)	109.53(15)	C(12)−Si(1)−C(13)	111.02(15)
Si(1)−P(1)−Si(2)	107.62(5)	C(21)−Si(2)−C(22)	109.79(16)
Cl(1)−B(1)−P(1)	111.84(15)	C(21)−Si(2)−C(23)	109.23(15)
Cl(1)−B(1)−P(1a)	112.85(17)	C(22)−Si(2)−C(23)	110.86(15)
Cl(2)−B(1)−P(1)	115.86(17)	P(1)−Si(1)−C(11)	111.25(10)
Cl(2)−B(1)−P(1a)	114.63(15)	P(1)−Si(1)−C(12)	108.95(11)
Si(1)−P(1)−B(1)	113.27(10)	P(1)−Si(1)−C(13)	107.56(12)
Si(1)−P(1)−B(1a)	115.83(10)	P(1)−Si(2)−C(21)	112.05(11)
Si(2)−P(1)−B(1)	118.48(10)	P(1)−Si(2)−C(22)	107.14(11)
Si(2)−P(1)−B(1a)	112.25(11)	P(1)−Si(2)−C(23)	107.75(11)

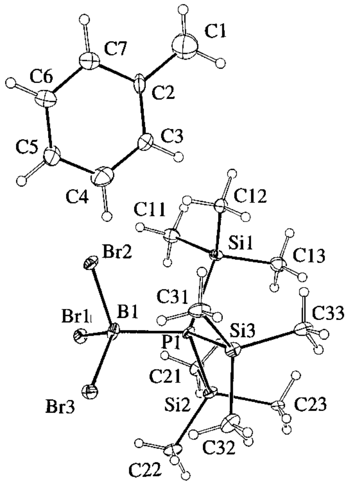

Figure 2. ORTEP diagram (30% probability ellipsoids) of **2**.

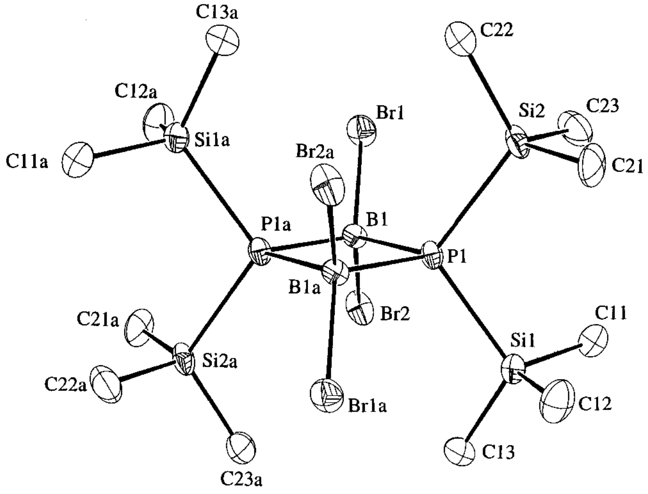

Figure 3. ORTEP diagram (30% probability ellipsoids) of **3**. Hydrogen atoms have been omitted for clarity.

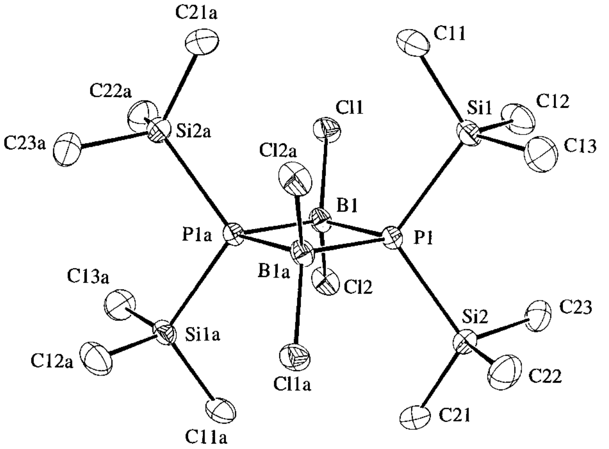

Figure 4. ORTEP diagram (30% probability ellipsoids) of **4**. Hydrogen atoms have been omitted for clarity.

nitrogen flow for **1** and **2** and under dynamic vacuum for **3** and **4**. Bulk decomposition studies were performed using a water-cooled sublimator and tube-style heating mantle with a Glas-Col Digi-Trol II heating controller. The method used for the bulk thermolyses of **1**−**4** was as follows: With the sample under a slight positive pressure of argon, the heating controller was set to 50 °C. Once the mantle reached this temperature, the set point was ramped another 50 °C. This process was repeated up to 200 °C. At 200 °C, the temperature was ramped 30 °C; when the sample had reached 230 °C, the system was placed under vacuum to remove eliminated trimethylsilyl halides. The temperature was then ramped in increments of 30 °C to 290 °C, 10 °C increments from 290 to 310 °C, 30 °C increments from 310 to 400 °C, and then finally a 50 °C increment to 450 °C. The sample was annealed overnight under vacuum at 450 °C.

Thermolysis of 1. A sample of **1** (0.538 g, 1.46 mmol) was loaded into a sublimator and thermolyzed by the method described above. The initially white powder turned yellow, orange, and finally orange/brown as the temperature was increased. Yellow and white sublimates were noted on the cooler glass surfaces of the sublimator. These sublimates were identified by ^{1}H NMR to be both the original compound and decomposition products of **1**. This orange/brown powder was collected to yield 0.066 g of **1A** (1.58 mmol, 108% yield as calculated for BP). Anal. Calcd (found) for BP: C, 0.00 (17.44); H, 0.00 (3.29); B, 25.87

(10.74); P, 74.13 (41.43). B:P = 0.74:1.00. Titration of hydrolyzed volatiles required 21.5 mL of NaOH (0.080 M), corresponding to elimination of 1.72 mmol (39.2%) of Me_3SiCl.

Thermolysis of 2. Compound **2** (0.597 g, 1.19 mmol) was loaded into a sublimator and thermolyzed by the method described above. The initially white powder rapidly turned yellow, orange, and then reddish and melted around 100 °C to a red/brown liquid with a clear liquid refluxing off the sublimator cold finger. When exposed to vacuum at 230 °C, this liquid dried to a orange/red solid. The final product was a deep orange/red powder, yield 0.084 g (2.01 mmol, 169% yield as calculated for BP) of **2A**. Anal. Calcd (found) for BP: C, 0.00 (13.24); H, 0.00 (2.67); B, 25.87 (9.45); Br, 0.00 (26.00); P, 74.13 (30.83). B:P = 0.88:1.00. Titration of hydrolyzed volatiles required 18.2 mL of NaOH (0.080 M), corresponding to elimination of 1.46 mmol (34.8%) of Me_3SiBr.

Thermolysis of 3. Compound **3** (0.253 g, 0.363 mmol) was loaded into a sublimator and thermolyzed by the method described above. The initially white powder gradually turned yellow and then orange, with the final product being an orange/yellow powder, yield 0.011 g (0.263 mmol, 72.5% yield as calculated for BP) of **3A**. Anal. Calcd (found) for BP: C, 0.00 (18.12); H, 0.00 (3.52); B, 25.87 (10.99); Br, 0.00 (24.38); P, 74.13 (23.18). B:P = 1.36:1.00. Titration of hydrolyzed volatiles required 10.1 mL of NaOH (0.080 M), corresponding to elimination of 0.808 mmol (74.2%) of Me_3SiBr.

Thermolysis of 4. Compound **4** (0.187 g, 0.355 mmol) was loaded into a sublimator and thermolyzed by the method described above. The initially white powder gradually turned yellow and then orange, with the final product being a fine brown powder, yield 0.017 g (0.407 mmol, 115% yield as calculated for BP) of **4A**. Anal. Calcd (found) for BP: C, 0.00 (16.82); H, 0.00 (2.16); B, 25.87 (17.59); P, 74.13 (23.32). B:P = 2.16:1.00. Titration of hydrolyzed volatiles required 9.2 mL of NaOH (0.080 M), corresponding to elimination of 0.737 mmol (51.9%) of Me_3SiCl.

Results and Discussion

The 1:1 mole ratio reactions of BCl_3 and BBr_3 with $P(SiMe_3)_3$ both produced Lewis acid−base adducts of the reactants, which were consistent with the behavior of aluminum trihalides.[26] Single-crystal X-ray structural determinations of the adducts $Cl_3B{\cdot}P(SiMe_3)_3$ (**1**) and $Br_3B{\cdot}P(SiMe_3)_3$ (**2**) showed these molecules to be solvated with toluene, a feature shared with the analogous aluminum−phosphorus adducts $Cl_3Al{\cdot}P(SiMe_3)_3$ and $Br_3Al{\cdot}P(SiMe_3)_3$.[26] Both **1** and **2** crystallized in a staggered configuration with respect to the substituents on B and P, much like their Al analogs. The B−P bond lengths for **1** and **2** were found to be 2.022(9) and 2.00(2) Å, respectively. By comparison, Schmidbaur and co-workers reported a B−P bond length of 1.913(4) Å for a related B−P adduct, $Cy_3P{\cdot}B(H)_2SiMe_3$ (Cy = cyclohexane).[15] The larger substituents on the boron (Cl or Br vs H) are likely the reason for the longer bond lengths for **1** and **2**.

NMR studies of adducts **1** and **2** revealed some interesting results. For these compounds, the phosphorus atom would be expected to produce a doublet in the ^1H, ^{13}C, and ^{11}B spectra. Also, the ^{31}P spectrum should reveal a 1:1:1:1 quartet from the ^{11}B coupling if the boron atom has a tetrahedral coordination environment. These features are displayed in the corresponding spectra of both **1** and **2**, with a slight downfield shift noted when the peaks of **1** are compared with those of **2** in the ^1H, ^{13}C, and ^{31}P spectra resulting from increased shielding by the larger and less electronegative bromine atoms on **2**. However, spectra of these adducts often display additional features. In the ^1H NMR spectrum of **1**, a weak triplet was observed at δ 0.49, as well as a singlet at 0.19. These peaks correspond to the presence of a dimeric compound $[Cl_2BP(SiMe_3)_2]_2$ and of Me_3SiCl, indicating the possibility of an adduct−dimer interchange in solution. Much stronger signals were observed in the case of **2**. In a repeated preparation of this compound, the ^1H, ^{13}C, and ^{11}B spectra all displayed triplets in addition to the expected doublets from the phosphorus splitting. These triplets would be expected from virtual coupling of two phosphorus atoms in a B−P−B−P ring to these three nuclei. Furthermore, the ^{31}P spectrum of this sample displayed a septet, which would result from two boron nuclei splitting the phosphorus signal. All of these signals are consistent with what would be expected for a dimeric compound: $[Br_2BP(SiMe_3)_2]_2$. In fact, the mass spectrum, elemental analysis, and NMR data all indicate the presence of a compound of this formula, yet repeated crystallizations of the bulk powder from toluene yielded only **2**.

In order to reproducibly synthesize $[X_2BP(SiMe_3)_2]_2$ compounds, a salt elimination route was employed. To this end, BBr_3 was reacted in a 1:1 mole ratio with $LiP(SiMe_3)_2$, and a light-orange powder was isolated. From this powder, crystals were grown from toluene and found to have a dimeric structure: $[Br_2BP(SiMe_3)_2]_2$ (**3**). The mass spectrum showed the expected parent ion peak at *m*/*z* 695.9. Multinuclear NMR studies of this sample showed the aforementioned features attributed to **3**; however, evidence for **2** was observed in the form of doublets in the ^1H and ^{11}B spectra as well as a weak quartet in the ^{31}P spectrum. These data indicate two possible solution-phase behaviors: (1) a monomer−dimer equilibrium; (2) an adduct−dimer equilibrium. The analogous dimeric gallium−phosphorus systems were shown to exhibit monomer−dimer equilibria in NMR solutions by the presence of both sets of peaks in the spectra.[9,10] Peaks have been identified in the spectra of **2** corresponding to **3**, and vice versa. Furthermore, a singlet observed in the ^1H spectra of **2** and **3** at δ 0.28 indicates the presence of Me_3SiBr, an expected byproduct of interconversion between the adduct **2** and the dimer **3**. From these data, it would seem likely that a transmutation between the adduct and dimeric compounds occurred in solution. Variable-temperature ^1H NMR studies of these compounds showed an irreversible conversion of **2** to **3** at elevated temperatures. The doublet at δ 0.36 identified as **2** diminished in intensity relative to the triplet at δ 0.56 corresponding to **3** as the temperature was increased over 70 °C. The singlet at δ 0.28 assigned to Me_3SiBr also increased in intensity as the temperature rose, indicating elimination of this moiety from **2** to form **3**. This is further supported by the appearance of a doublet at δ 0.29 ppm ($^3J_{P-H} = 4.4$ Hz) which can be assigned to the monomeric unit $Br_2BP(SiMe_3)_2$, an expected intermediate in the formation of **3** from **2**. As the sample was cooled from 90 to 25 °C, the intensity of the triplet remained the same, and no reappearance of the adduct doublet was observed, evidence that the conversion of **2** to **3** at higher temperatures was not reversible once the sample was returned to room temperature. The isolation of crystalline **2** from method a of the preparation of **3** was due to either to preferential crystallization of the adduct from the toluene solution or to selection of crystals of the adduct for characterization when both **2** and **3** were present in the sample.

In an analogous lithium halide elimination reaction using BCl_3 and $LiP(SiMe_3)_2$, a yellow/white powder was isolated. Upon crystallization from toluene, this compound was also found to have a dimeric structure: $[Cl_2BP(SiMe_3)_2]_2$ (**4**). Both **3** and **4** possess planar four-membered central rings and distorted tetrahedral geometries around the group 13 and group 15 centers, features shared with their gallium−phosphorus analogs $[Cl_2GaP(SiMe_3)_2]_2$[9] and $[Br_2GaP(SiMe_3)_2]_2$.[10] The average B−P bond lengths in **3** and **4** are 2.030 and 2.024 Å, respectively, which are both significantly shorter than the 2.081 Å reported

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[26] Wells, R. L.; McPhail, A. T.; Laske, J. A.; White, P. S. *Polyhedron* **1994**, *13*, 2737.

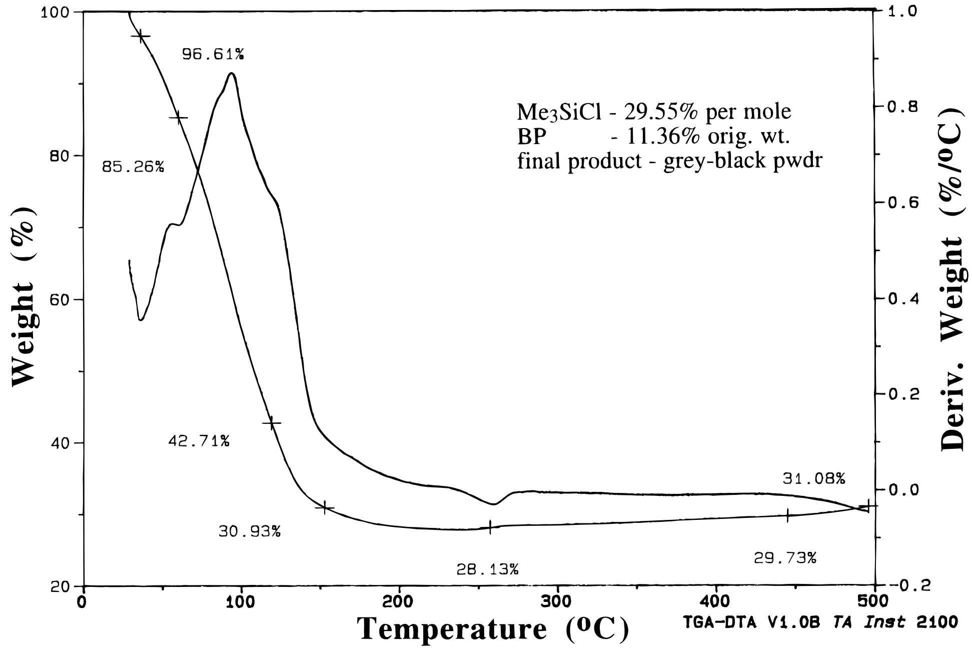

Figure 5. TGA/DTA analysis of **1** (sample run under nitrogen purge).

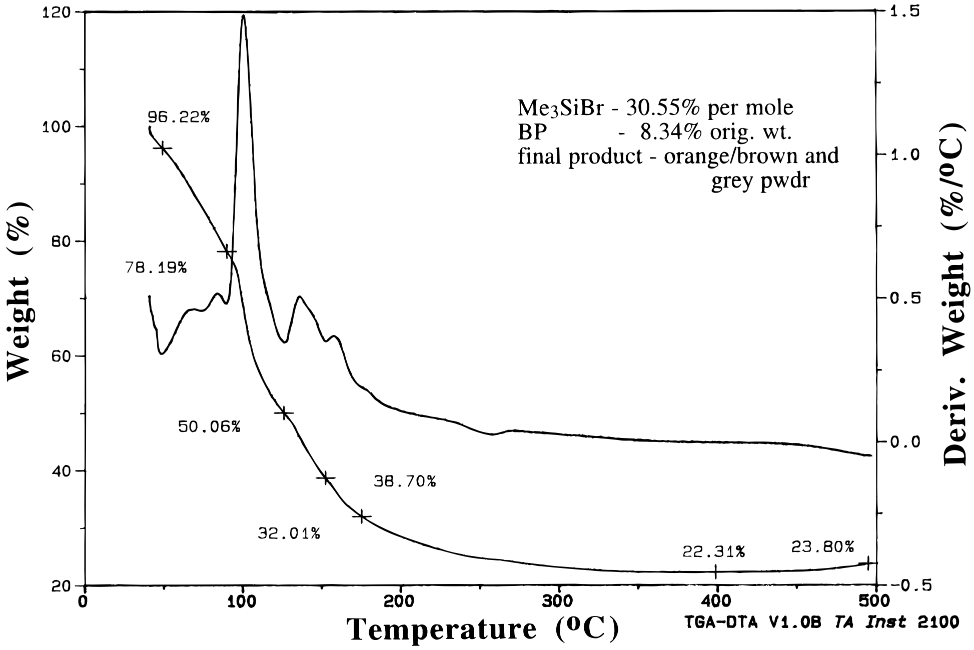

Figure 6. TGA/DTA analysis of **2** (sample run under nitrogen purge).

by Groshens *et al.* for $[Me_2BP(t\text{-}Bu)_2]_2$.[14] This difference is likely a result of the size difference of the substituents on the boron atoms, as the larger halogens force the central B—P—B—P ring into a more planar configuration (B—P—B angles 89.4 and 88.8° and P—B—P angles 90.6 and 91.2° for **3** and **4**, respectively) than would the smaller methyl and *tert*-butyl groups on $[Me_2BP(t\text{-}Bu)_2]_2$ (B—P—B angle 92.2°, P—B—P angle 87.8°). A closer approximation to the ideal square planar geometry would reduce the distance between the boron and phosphorus centers in the ring and result in a shorter bond length, as observed for **3** and **4**. NMR studies of **4** display the expected features of a boron—phosphorus dimeric complex as discussed above in the case of **3**. Peak patterns in the ^{11}B (doublet) and ^{31}P (equal quartet) spectra of **4** indicate that this compound, like **3**, rearranges to the analogous adduct (**1**) in solution. The presence of both a singlet at δ 0.19 (corresponding to Me_3SiCl) and a weak doublet at δ 0.34 (corresponding to **1**) in the ^1H NMR spectrum supports this hypothesis, as well as the evidence for the presence of **4** in the ^1H NMR spectrum of **1** discussed above. There are also additional sets of peaks arranged in multiplets in the ^{11}B and ^{31}P spectra which could indicate a higher-order oligomerization of the $[Cl_2BP(SiMe_3)_2]$ monomeric unit; however, the coupling constants of these multiplets are very nearly the same as those seen for the dimeric complex. Variable-temperature ^1H NMR studies of **1** and **4** showed no conversion of the adduct to the dimer as seen above in the cases of **2** and **3**. Weak peaks corresponding to the dimer in the spectrum of **1** and the adduct in the spectrum of **4** did not increase in intensity as the temperature was increased, nor was there a strengthening of a weak Me_3SiCl singlet observed around δ 0.20. The presence of these peaks likely indicates the presence of a trace amount of the complementary compound in each sample as a minor product; however, the very low intensity of these peaks suggests very little of the dimer is

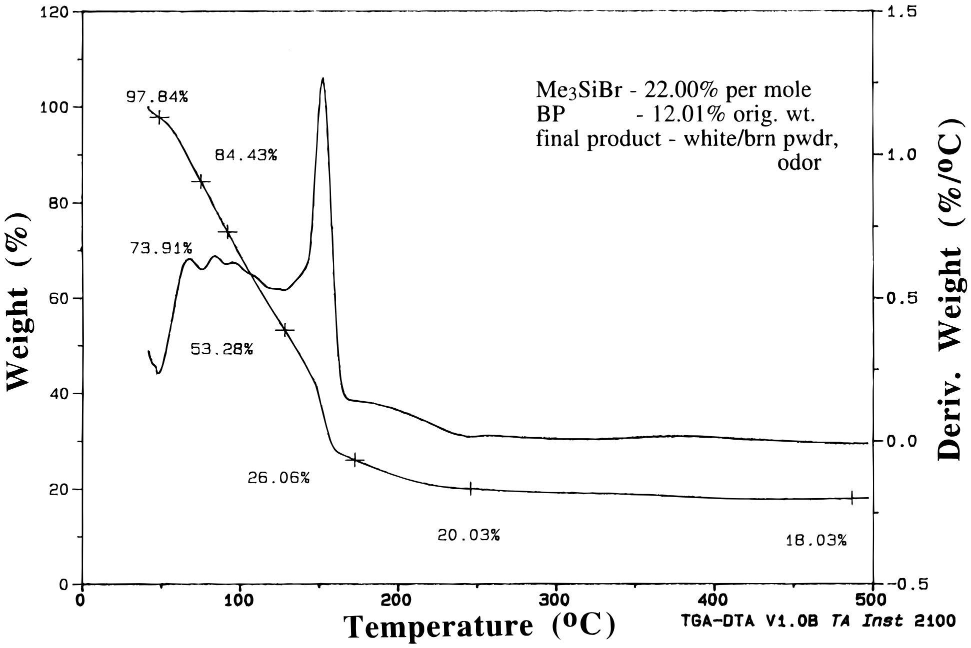

Figure 7. TGA/DTA analysis of **3** (sample run under vacuum).

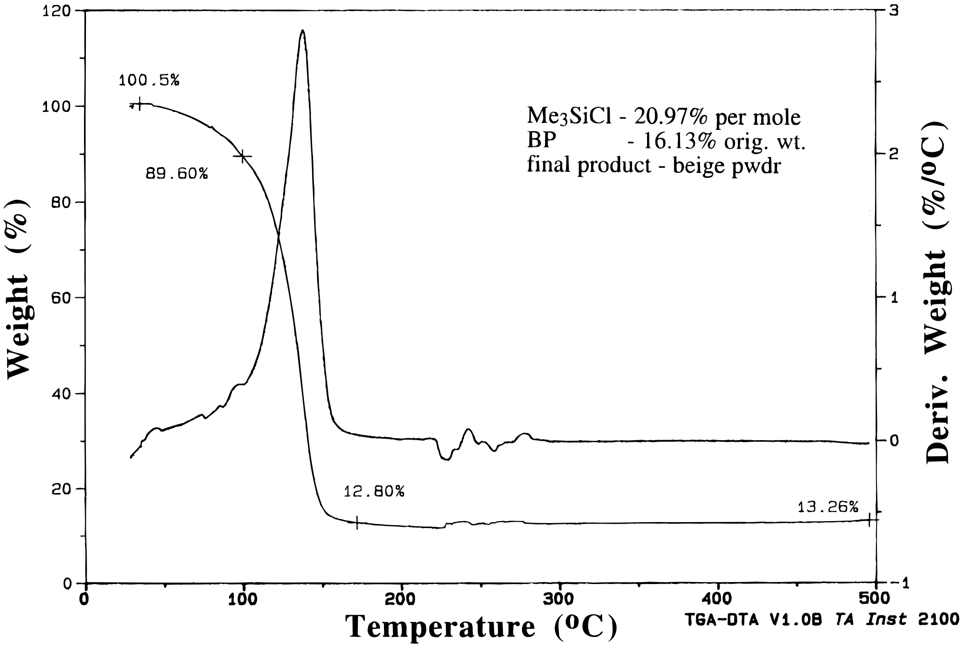

Figure 8. TGA/DTA analysis of **4** (sample run under vacuum).

present in the bulk sample of **1**, as well as very little of the adduct in the bulk sample of **4**. Due to the light-sensitive nature of boron trihalides,[27] exposure to light was likely responsible for the additional features seen in the ^{11}B and ^{31}P peaks of **4**. These peaks can be assigned to light-decomposition products as they were not seen in the spectra of fresh light-protected samples of **4**. It should also be noted that compounds **1**−**5** all began to decompose upon standing in solution or solid form under fluorescent lighting, as evidenced by a yellowing or darkening of their original colors.

Considerable difficulties were encountered when solution reactions of BI_3 were attempted. Upon dissolution, these white/light pink crystals immediately turned the solution dark orange. After reaction with tris(trimethylsilyl)phosphine and removal of solvents, an insoluble orange powder or intractable orange oil was frequently the product. Therefore, to circumvent this problem, a pentane solution of $P(SiMe_3)_3$ was added *via* pipet to solid BI_3. This method led to the reproducible isolation of a 1:1 Lewis acid−base adduct of these reactants; $I_3B{\cdot}P(SiMe_3)_3$ (**5**). Multinuclear NMR of **5** displayed the expected signals for this adduct: ^1H, δ 0.46, doublet from P splitting Me protons; ^{13}C, δ 2.53, doublet from P splitting Me carbons; ^{11}B, δ −83.69, doublet from P splitting B; ^{31}P, δ −155.17, equal quartet from B splitting P. Locations of these peaks and coupling constants were comparable with the analogous structurally confirmed adducts **1** and **2** (see above). A peak corresponding to the parent ion less an iodine (*m*/*z* 515.0, $(M - I)^+$) was observed in the mass spectrum of **5**, as well as peaks indicative of the loss of one Me_3SiI group from the adduct (*m*/*z* 441.9, $(I_2BP(SiMe_3)_2)^+$), and adduct fragmentation peaks (*m*/*z* 264.8, BI_2^+; *m*/*z* 250.1, $P(SiMe_3)_3^+$). These data, as well as accurate C, H, B, P, and I

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[27] Brotherton, R. J. Boron: Inorganic Chemistry. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley and Sons: Chichester, U.K., 1994; Vol. 1, p 372.

elemental analyses, support the proposed Lewis acid–base adduct structure of **5**.

An analogous reaction of BI_3 (neat) with a toluene solution of $LiP(SiMe_3)_2$ was conducted, and a small yield (0.011 g) of an orange powder was obtained. However, upon analysis by NMR and EIMS, this powder was not found to correspond to any molecular structure, including the expected $[I_2BP(SiMe_3)_2]_2$. The aforementioned sensitivity of BI_3 to solvents may have contributed to this result; further investigations into this system are continuing.

Decomposition studies of **1**–**4** have also been performed. Compounds **1** and **2** readily sublime when heated under vacuum, so **1** and **2** were heated under a slight positive pressure of inert gas, either nitrogen or argon. Compounds **3** and **4** were decomposed under vacuum conditions, as no significant sublimation was noted. TGA decomposition studies of the adducts **1** (Figure 5) and **2** (Figure 6) showed incomplete elimination of trimethylsilyl halides, with the final ceramic yield of the thermolyzed products significantly greater than that expected for boron phosphide (BP). TGA studies of the dimeric complexes **3** (Figure 7) and **4** (Figure 8) showed final ceramic yields within 3–6% of that expected for BP, much closer to the desired material than their corresponding adducts.

Bulk decomposition of **1** by the aforementioned method yielded a dark orange/brown powder (**1A**). Elemental analysis of this powder showed it to have a B:P ratio of 0.74:1.00, with significant carbon and hydrogen contamination. This powder also displayed a remarkable sensitivity to air, turning bright yellow and giving off a foul odor when exposed for even a short time. When **2** was thermolyzed by this method, the powder decomposed and melted to a brown/red liquid around 100 °C, with a clear liquid refluxing off the cold finger. The final product was an orange/red powder (**2A**), which by elemental analysis had a B:P ratio of 0.88:1.00, again with significant carbon, hydrogen, and silicon (by mass balance) contamination. This powder also showed air sensitivity in the same manner as **1A**, turning yellow and producing a stench when exposed. Decomposition of **3** resulted in an orange/yellow powder (**3A**) with a B:P ratio of 1.36:1.00 by elemental analysis, also with significant carbon, hydrogen, silicon (by mass balance), and bromine contamination. Product **3A** showed air sensitivity similar to that of **1A** and **2A**, producing a yellow powder and stench when exposed to air. Thermolysis of **4** produced a fine brown powder (**4A**), in contrast to the orange/red and orange/yellow products obtained from the other compounds. The B:P ratio of **4A** was found to be 2.16:1.00, again with significant carbon, hydrogen, chlorine (mass balance), and silicon (mass balance) contamination. Air sensitivity was also noted in the case of **4A** by the yellowing of the powder once exposed to air and a stench much like that observed for **1A**, **2A**, and **3A**.

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Supporting Information Available: Tables of all atomic fractional coordinates, interatomic distances, angles, and torsional angles, and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

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