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Journal

Zeitschrift für anorganische und allgemeine Chemie, 649(8)

ISSN

0044-2313

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Publication Date

2023-04-14

DOI

10.1002/zaac.202300007

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Peer reviewed

DOI: 10.1002/zaac.202300007

Special
Collection

Facile Synthesis of $(\text{C}_6\text{F}_5)_2\text{BBr}$ and $(\text{C}_6\text{F}_5)_2\text{BX}(\text{OEt}_2)$ ($\text{X} = \text{Cl}, \text{Br}$) using Hydrogen Halides and Piers' Borane

Anthony Wong,^[a] Gustavo Alcántara,^[a] Matthew Avalos,^[a] Guang Wu,^[a] and Gabriel Ménard^{*[a, b]}

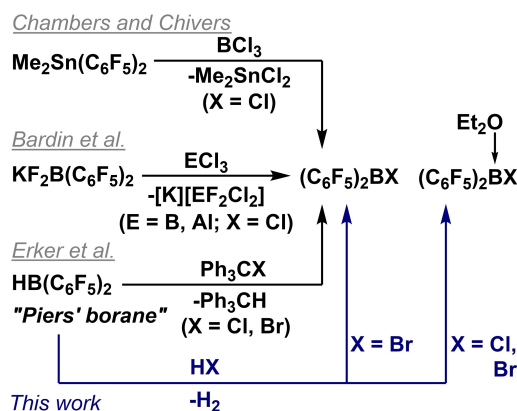
Dedicated to Prof. Doug Stephan on the occasion of his 70th birthday.

We report the facile and efficient synthesis of common electrophilic haloboranes via a protonolysis reaction between Piers' borane, $\text{HB}(\text{C}_6\text{F}_5)_2$, and H-X ($\text{X} = \text{Cl}, \text{Br}$). This route benefits from fast reaction times, easy setup, and minimal workup to yield the

analytically pure etherates, $(\text{C}_6\text{F}_5)_2\text{BCl}(\text{OEt}_2)$ (1) and $(\text{C}_6\text{F}_5)_2\text{BBr}(\text{OEt}_2)$ (2), as well as the ether-free tri-coordinate species, $(\text{C}_6\text{F}_5)_2\text{BBr}$ (3).

Introduction

First synthesized by Chambers and Chivers^[1] and since popularized by many others,^[2–9] $(\text{C}_6\text{F}_5)_2\text{BCl}$ has found widespread usage as a reagent in many transformations, including more recently in frustrated Lewis pair-mediated small molecule activation.^[10–12] Moreover, this chloroborane serves as a synthon to install the highly Lewis acidic $-\text{B}(\text{C}_6\text{F}_5)_2$ fragment^[13–20] into an array of molecules with applications in catalytic hydrogenation,^[10,21–22] transfer hydrocyanation,^[23] and olefin polymerization^[24–25] processes. The original preparation of this compound involved toxic tin-based reagents and harsh reaction conditions.^[1] More recently, Bardin and coworkers reported the synthesis of $(\text{C}_6\text{F}_5)_2\text{BCl}$ from a potassium aryl(fluoro)borate salt in the presence of AlCl_3 or BCl_3 .^[26] Erker and coworkers also obtained $(\text{C}_6\text{F}_5)_2\text{BCl}$ and the heavier $(\text{C}_6\text{F}_5)_2\text{BBr}$ congener in good yield by reacting Piers' borane ($\text{HB}(\text{C}_6\text{F}_5)_2$) with trityl chloride or bromide ($\text{Ph}_3\text{C-X}$; $\text{X} = \text{Cl}, \text{Br}$), respectively (Scheme 1).^[27] Although these reactions successfully generated $(\text{C}_6\text{F}_5)_2\text{BX}$, these syntheses required the use of uncommon reagents (e.g., $\text{KF}_2\text{B}(\text{C}_6\text{F}_5)_2$) or



Scheme 1. Reported synthetic routes to the haloboranes, $(\text{C}_6\text{F}_5)_2\text{BX}$ ($\text{X} = \text{Cl}, \text{Br}$), as well as this work.

the careful selective sublimation of stoichiometric byproducts (e.g., Me_2SnCl_2 , Ph_3CH , etc.). The growing utility of strong Lewis acids in both academic and industrial settings prompted us to seek an alternative synthesis involving the use of less toxic starting materials and a more expedient workup protocol.

Herein, we report a protonolysis route using hydrogen halides (H-X) and Piers' borane to generate the desired haloboranes, $(\text{C}_6\text{F}_5)_2\text{BX}$. We isolated these compounds in both their three-coordinate ($\text{X} = \text{Br}$) or their more stable four-coordinate etherates ($\text{X} = \text{Cl}, \text{Br}$; Scheme 1). Our results provide a new, facile approach to synthesizing these widely-used haloboranes.

Results and Discussion

Given that the hydridic B-H bond in Piers' borane readily undergoes protonolysis in the presence of weak Brønsted acids (H_2O , ROH , etc.),^[2,28] we reasoned that the addition of hydrogen halides (e.g. HCl , HBr) should readily afford the desired haloboranes with H_2 as the only byproduct. Accordingly, the

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202300007>

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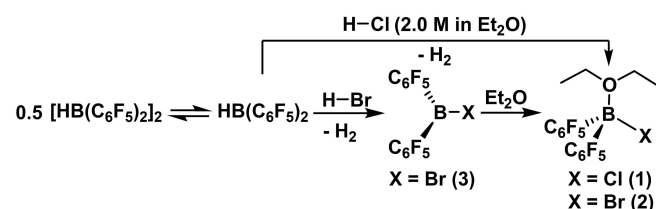
etherate, $(\text{C}_6\text{F}_5)_2\text{BCl}(\text{OEt}_2)$ (**1**), was readily generated through the dropwise addition of commercial stoichiometric HCl (2.0 M in Et_2O) into a thawing suspension of Piers' borane in benzene. Upon addition, we observed the immediate effervescence of H_2 concomitant with the dissolution of the borane, generating a colorless solution. Once gas evolution ceased, all volatiles were removed *in vacuo* and the oily residue was triturated with cold pentane yielding an analytically pure white solid, as evidenced by multinuclear (^1H , ^{11}B , ^{19}F) NMR spectroscopy (Scheme 2).

Analysis of the product by ^{11}B NMR spectroscopy revealed a resonance centered at 23.0 ppm and the corresponding ^{19}F NMR resonances were located at -131.7 , -151.3 , and -162.1 ppm, with the narrow shift difference between the latter two *para* and *meta* resonances being consistent with a four-coordinate boron center. In addition, the ^1H NMR spectrum revealed shifted resonances for Et_2O (3.53, 0.68 ppm) consistent with adduct formation to B (Figures S1–S4).^[29] Single crystals suitable for XRD studies were grown from a saturated solution of the product in an ether/pentane mixture stored at -38°C . The solid-state molecular structure unambiguously confirmed the formation of the chloroborane product **1** (Figure 1a). Inspection of the solid-state metric parameters revealed a longer B–Cl bond length (1.873(2) Å) compared to the known unsaturated compound (1.746(5) Å), which was expected from the formation of four-coordinate boron.^[30] Furthermore, we observed that the ether ligand played a significant role in stabilizing this species relative to the tri-coordinate version. Indeed, there was no evidence of decomposition after storing the solid product at -38°C in an inert atmosphere for

15 months, in contrast to the tri-coordinate $(\text{C}_6\text{F}_5)_2\text{BCl}$ which is well known to have a short shelf life under similar conditions. However, exposure to adventitious water did lead to the generation of the cyclic trimer, $[(\text{C}_6\text{F}_5)_2\text{BOH}(\text{OEt}_2)]_3$, as evidenced by our solid-state molecular structure Figure S13.^[31]

We then extended this protonolysis strategy to access the bromoborane analog, **2**. Due to the known reaction between HBr and Et_2O ,^[32] we modified our protocol slightly by employing anhydrous HBr gas, conveniently generated *in situ* from the bromination of tetralin.^[33] Accordingly, to a thawing solution of Piers' borane in benzene, we introduced anhydrous HBr gas which resulted in effervescence concomitant with the dissolution of Piers' borane, analogous to the synthesis of **1**. We note that the known tri-coordinate $(\text{C}_6\text{F}_5)_2\text{BBr}$ ^[27] compound (**3**) is formed here in 73% yield and can be isolated (see experimental section). The etherate can also be readily isolated by addition of Et_2O to **3** using an analogous workup procedure to the chloroborane, **1**. The ^{11}B NMR spectrum of **2** revealed a resonance at 10.0 ppm shifted upfield relative to **1**. The ^{19}F NMR spectrum displayed resonances at -131.6 , -153.4 , and -162.7 ppm, with the *para* and *meta* resonances shifted downfield relative to **1** (Figure S8). Single crystals suitable for XRD studies were grown from a saturated solution of the product in ether at -38°C , which revealed the expected isostructural congener, **2** (Figure 1b). The bond metrics and angles are nearly identical to that of **1** – reflected in the compounds growing in the same space group, $\text{P2}_1/\text{n}$ – except for the expected elongated B–Br (2.061(2) Å) and B–O (1.556(2) Å) bond lengths. Similar to **1**, compound **2** is indefinitely stable under inert atmosphere in the freezer (-38°C).

While the ligated ether likely provides kinetic stabilization for long-term storage, the presence of it may also hinder Lewis acid functionality. In line with this, we probed whether we could remove the ligated ether by subliming compounds **1** or **2**. In contrast to $\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{OEt}_2$,^[29] the ether-free analogs, $(\text{C}_6\text{F}_5)_2\text{BCl}$ and $(\text{C}_6\text{F}_5)_2\text{BBr}$, do not form under these conditions. Despite the reluctance of the ligated ether to be removed *in vacuo*, both compounds have been successfully employed as precursors to install the acidic $-\text{B}(\text{C}_6\text{F}_5)_2$ fragment into our reported vanadium imido systems,^[19–20] which suggests partial ligand dissociation occurs in solution.



Scheme 2. Access to the chloroborane $(\text{C}_6\text{F}_5)_2\text{BCl}(\text{OEt}_2)$ (**1**) and the heavier bromoborane (**2**, **3**) congeners through protonolysis of Piers' borane with hydrogen halides.

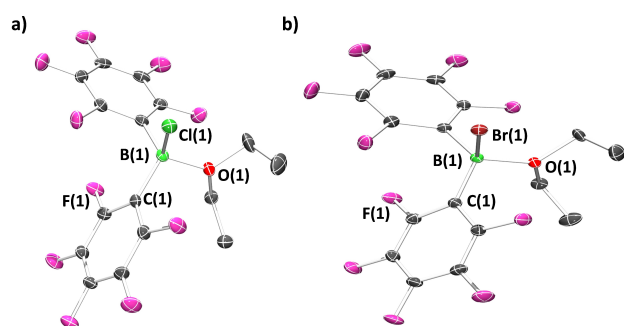


Figure 1. Solid-state molecular structures of the isostructural haloborane series: a) $(\text{C}_6\text{F}_5)_2\text{BCl}(\text{OEt}_2)$ (**1**); b) $(\text{C}_6\text{F}_5)_2\text{BBr}(\text{OEt}_2)$ (**2**).

Conclusions

In conclusion, we synthesized electrophilic haloboranes using a simple acid–base reaction between Piers' borane and hydrogen halides. For the chloroborane (**1**), the etherate is directly prepared, whereas for the heavier bromoborane, both the etherate (**2**) and the tri-coordinate version (**3**) can be isolated directly using anhydrous, ether-free preparations. Our new protocol to access these haloboranes may provide a gateway into more applications in Lewis acid mediated transformations.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of dry, oxygen-free N_2 or Ar through standard Schlenk or glovebox techniques (MBraun UNILab Pro SP Eco equipped with a $-38^\circ C$ freezer). Pentane, diethyl ether, benzene, and toluene were dried using an MBraun solvent purification system. Benzene- d_6 was purchased from Aldrich or Cambridge Isotope Laboratories, degassed by freeze-pump-thaw, and stored on activated 4 Å molecular sieves prior to use. HCl (2.0 M in Et_2O) and Br_2 were purchased from Aldrich, Strem, or other commercial vendors and used as received. $C_{10}H_{12}$ (tetralin) and Et_3SiH was purchased from Aldrich, degassed by freeze-pump-thaw, and stored on activated 4 Å molecular sieves prior to use. Piers' borane, $HB(C_6F_5)_2$, was prepared by a slight modification to the literature procedure as detailed below.^[2] $B(C_6F_5)_3$, was prepared according to a literature procedure and sublimed prior to use.^[34] Elemental analyses (C, N, H) were performed at the University of California, Berkeley, using a PerkinElmer 2400 Series II combustion analyzer.

Spectroscopic Analyses. NMR spectra were obtained on a Varian Unity Inova 600 MHz, Varian Unity Inova 500 MHz, Bruker Avance NEO 500 MHz, Bruker Avance III HD 400 MHz, or Agilent Technologies 400 MHz spectrometers, and referenced to the residual solvent of benzene- d_6 (7.16 ppm), or externally ($^{11}B:BF_3 \cdot Et_2O$; $^{19}F:CFCl_3$). Chemical shifts (δ) are recorded in ppm and the coupling constants are in Hz.

X-ray crystallography. Data were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo $K\alpha$ X-ray source ($\alpha = 0.71073 \text{ \AA}$). The crystals were mounted on a cryoloop with Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.5° frame widths. Data collection and cell parameter determination were conducted using the SMART program. Integration of the data frames and final cell parameter refinement were performed using SAINT software. Absorption correction of the data was carried out using SADABS. Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL or OLEX². All POV-Ray depictions of the solid-state molecular structures are shown at the 50% probability ellipsoid level unless otherwise noted.

Synthesis of $HB(C_6F_5)_2$ (Piers' borane): Under an N_2 atmosphere, using a 250 mL thick-walled cajon flask, $B(C_6F_5)_3$ (4.91 g, 9.70 mmol) was suspended in benzene (100 mL). Et_3SiH (1.23 g, 10.56 mmol, 1.1 equiv.) was added. The container was sealed and the solution was stirred at $85^\circ C$ for 4 days. The reaction was tracked by NMR spectroscopy and Et_3SiH was added if needed after 4 days of stirring. The solution was next concentrated *in vacuo* to ~ 30 mL resulting in the precipitation of the product. The product was isolated via filtration, washed with pentanes, and dried. It was characterized by NMR spectroscopy (1H , ^{11}B , ^{19}F) which matched the reported compound.^[2]

Synthesis of $(C_6F_5)_2BCl(OEt_2)$ (1): In a 20 mL vial, $HB(C_6F_5)_2$ (0.500 g, 1.45 mmol) was suspended in benzene (4 mL) and the solution was frozen. A stir bar was subsequently placed on top of this frozen mixture. HCl (2.0 M in Et_2O , 1.33 mL, 2.65 mmol) was added dropwise to this stirring slurry. Effervescence of H_2 was immediately observed concomitant with the dissolution of all solid material, yielding a colorless solution. The reaction mixture was allowed to stir until gas evolution ceased (~ 5 mins). All volatiles were subsequently removed *in vacuo*, yielding an oily residue. Repeated

trituration with pentane yielded a white solid precipitate. The resulting solid was collected and washed with a minimal amount of cold ($-38^\circ C$) pentane (5×0.25 mL) to give an analytically pure white solid after drying (0.531 g, 1.168 mmol, 80.8% yield). Single crystals suitable for XRD studies were grown from a saturated solution of the product in an ether/pentane mixture stored at $-38^\circ C$. 1H NMR (400 MHz, C_6D_6 , $25^\circ C$): $\delta = 3.53$ (q, $^3J_{HH} = 7.1$ Hz, 4H; CH_2), 0.68 (t, $^3J_{HH} = 7.1$ Hz, 6H; CH_3). ^{13}C NMR (126 MHz, C_6D_6 , $25^\circ C$): $\delta = 148.1$, 141.7, 137.7, 115.3, 74.1 (CH_2), 14.4 (CH_3). ^{11}B NMR (128 MHz, C_6D_6 , $25^\circ C$): $\delta = 23.0$ (br). ^{19}F NMR (376 MHz, C_6D_6 , $25^\circ C$): $\delta = -131.7$ (d, $^3J_{FF} = 22.6$ Hz, 4F; *o*- C_6F_5), -151.3 (br, 2F; *p*- C_6F_5), -162.1 (td, $J = 22.9$, 8.8 Hz, 4F; *m*- C_6F_5). **Elemental analysis (%)** Calcd for $C_{16}H_{10}BClF_{10}O$: C, 42.28; H, 2.22. Found: C, 41.92; H, 1.99.

Synthesis of $(C_6F_5)_2BBr$ (3): In a 25 mL flask equipped with a ground glass joint was added $HB(C_6F_5)_2$ (0.340 g, 0.983 mmol) suspended in benzene (10 mL) and the mixture was frozen. A second 25 mL flask also equipped with a ground glass joint was charged with liquid Br_2 (0.236 g, 1.474 mmol, 1.5 equiv.) in benzene (3 mL). The red solution was frozen and subsequently layered with benzene (2 mL), and this was subsequently frozen. Tetralin (0.049 g, 0.369 mmol) in benzene (2 mL) was added on top and frozen, yielding three distinct layers to prevent the bromination reaction from evolving HBr prior to sealing the system. A stir bar was subsequently added into both flasks before the flasks were connected through a glass bridge. The atmosphere was evacuated and the system was sealed and kept under static vacuum. The system was allowed to thaw at room temperature with constant stirring. The *in situ* generated anhydrous HBr gas that evolved reacted with Piers' borane. Effervescence of H_2 was observed concomitant with the dissolution of all solid material, yielding a light yellow solution. We note that the reaction can tolerate an excess (9 equiv.) of HBr without loss in yield. The reaction mixture was allowed to stir until gas evolution ceased and the reddish color of the Br_2 had faded (~ 1 hour). All volatiles were subsequently removed *in vacuo* yielding an oily residue. Repeated trituration with pentane yielded a solid precipitate. The resulting solid was collected and washed with a minimal amount of cold ($-38^\circ C$) pentane (3×0.25 mL) to give a light yellow solid after drying (0.305 g, 0.718 mmol, 73.0% yield). The product was characterized by NMR spectroscopy (^{11}B , ^{19}F) which matched the reported compound.^[27]

Synthesis of $(C_6F_5)_2BBr(OEt_2)$ (2): In a 20 mL vial, $(C_6F_5)_2BBr$ (3) was dissolved into minimal diethyl ether. Single crystals suitable for XRD studies were grown from this solution at $-38^\circ C$. 1H NMR (400 MHz, C_6D_6 , $25^\circ C$): $\delta = 3.56$ (q, $^3J_{HH} = 7.1$ Hz, 4H; CH_2), 0.67 (t, $^3J_{HH} = 7.1$ Hz, 6H; CH_3). ^{13}C NMR (126 MHz, C_6D_6 , $25^\circ C$): $\delta = 147.8$, 141.5, 137.7, 115.9, 76.0 (CH_2), 14.4 (CH_3). ^{11}B NMR (128 MHz, C_6D_6 , $25^\circ C$): $\delta = 10.0$ (br). ^{19}F NMR (376 MHz, C_6D_6 , $25^\circ C$): $\delta = -131.6$ (dd, $J = 24.0$, 8.5 Hz, 4F; *o*- C_6F_5), -153.4 (br, 2F; *p*- C_6F_5), -162.7 (td, $J = 23.0$, 8.6 Hz, 4F; *m*- C_6F_5). **Elemental analysis (%)** Calcd for $C_{16}H_{10}BBrF_{10}O$: C, 38.52; H, 2.02. Found: C, 38.17; H, 2.02.

Acknowledgements

We thank the National Science Foundation (CHE-2155239) and the UC National Laboratory Fees Research Program (L22CR4468) for financial support.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

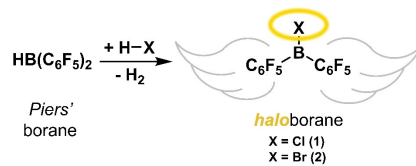
The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Haloboranes · Lewis acids · Piers' borane · hydrogen halides

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Manuscript received: January 13, 2023

Revised manuscript received: February 16, 2023



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1 – 5

Facile Synthesis of $(\text{C}_6\text{F}_5)_2\text{BBR}$ and $(\text{C}_6\text{F}_5)_2\text{BX}(\text{OEt}_2)$ (X = Cl, Br) using Hydrogen Halides and Piers' Borane

