ORGANOMETALLICS

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The Thioether−Methyleneborane $(PhSCH_2B(C_6F_5)_2)_2$: Synthesis and Reactivity with Donors and Alkynes

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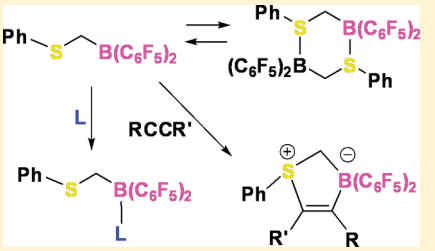
Supporting Information

ABSTRACT: 2-Bromothioanisole, or thioanisole, was lithiated and subsequently reacted with $ClB(C_6F_5)_2$ to yield a new compound with the empirical formulation $PhSCH_2B(C_6F_5)_2$, **1**. NMR data at low temperature as well as X-ray crystallographic data confirmed this species to be the dimer $(PhSCH_2B(C_6F_5)_2)_2$, although an equilibrium governs the interconversion of monomer to dimer at room temperature. Compound **1** reacts with P*t*Bu$_3$ or OPEt$_3$ to form adducts $PhSCH_2B(C_6F_5)_2(L)$ (L = P*t*Bu$_3$ **2**, OPEt$_3$ **3**) in 85% and 87% yield, respectively. Compound **1** also reacts with alkynes, namely, PhCCH, C_4H_9CCH, $PhCCC_4H_9$, $C_2H_5CCC_2H_5$, and PhCCPh, to give the species $(PhSCH_2B(C_6F_5)_2)(R'C{=}CR)$ (R = H, R′ = Ph **4**, C_4H_9 **5**, R = Ph, R′ = C_4H_9 **6**, R = R′ = C_2H_5 **7**, Ph **8**) in yields in the range 70−92%. X-ray crystallographic analysis of **8** confirmed the five-membered zwitterionic heterocyclic formulation.



INTRODUCTION

The reactivity of combinations of Lewis acids and bases in which steric demands preclude or destabilize dative bond formation has been the subject of intense development in recent years.[1−4] While these systems, known as frustrated Lewis pairs (FLPs), react most notably with H_2, such systems also demonstrate broad reactivity with a variety of other small molecules including disulfides,[5] olefins,[6] dienes,[7] acetylenes,[8−12] diynes,[13,14] CO_2,[15,16] azides,[17] and N_2O.[18] In the majority of instances, this chemistry has been explored employing the combination of a borane and a sterically encumbered phosphine. That being said, other systems have been reported that incorporate Al-[11,16] or C-based Lewis acids[19] or amines,[8,20−25] N-heterocycles,[26−28] and carbenes[29−32] as bases. In FLP chemistry, sulfur-based donors have drawn less attention, although the adduct $B(C_6F_5)_3\cdot SMe_2$ in combination with a bulky phosphine has been shown to effect the heterolytic cleavage of H_2. Similarly, thioethers such as Me_2S and $(PhCH_2)_2S$ have been shown to add to terminal alkynes in the presence of $B(C_6F_5)_3$ to yield *trans*-zwitterions of the form $R_2SC(R')=CH(B(C_6F_5)_3)$ (Scheme 1).[9,11] It is also noteworthy that the lability of thioether donors has been exploited by Hoshi et al. in the reaction of $B(C_6F_5)_3$ with $BH_3\cdot SMe_2$ to generate the adduct of Piers' borane $(C_6F_5)_2BH\cdot SMe_2$,[33,34] which was subsequently used in a catalytic fashion for the hydroboration of a terminal alkyne with HB(pin). The weak interaction between B and S has also been employed by Gabbaï and co-workers in the development of aryl-linked boron−sulfur sensors for cyanide and fluoride ions in water.[35,36] Methylene-linked thioether boranes are rare. Some years ago Nöth and co-workers[37] described the dimeric species $(BH_2CH_2SMe)_2$ derived from the thermolysis of the precursor amine adduct $Me_3NBH_2CH_2SMe$. More recently Wagner et al.[38] described the related dimer $(PhBrBCH_2SMe)_2$. Herein, we describe the synthesis of a methylene-linked thioether borane that incorporates a highly electrophilic B center. The subsequent reactivity with a number of small molecules of this species is probed. Although this species also forms a six-membered ring, the B−S bonds are labile, allowing capture of the monomeric species by stronger donors. In addition, this species is shown to react with alkynes to give the previously inaccessible sulfonium-borate cyclopentene derivatives.

RESULTS AND DISCUSSION

2-Bromothioanisole was lithiated initially at −78 °C, allowed to warm to 25 °C for isolation, and subsequently reacted with $ClB(C_6F_5)_2$ at −38 °C to generate compound **1**. A crude off-white precipitate was isolated in near quantitative yield, purified by extraction into toluene, and isolated, affording the pure product in 32% yield. Alternatively, **1** was also derived from the lithiation of thioanisole followed by subsequent reaction with $ClB(C_6F_5)_2$. This species gives rise to a broad signal at 5.1 ppm in the $^{11}B\{^1H\}$ NMR spectrum, while the $^{19}F\{^1H\}$ NMR spectrum displayed signals at −130.7, −153.6, and −163.0 ppm. The corresponding ^1H NMR spectrum for **1** showed the expected resonances for the phenyl protons and a singlet at 2.82 ppm. These data were consistent with the empirical formulation of **1** as $PhSCH_2B(C_6F_5)_2$. X-ray quality crystals of **1** were obtained from a concentrated solution in toluene and bromobenzene at −38 °C. The results showed that **1** is a dimer, in the solid state of the formulation $(PhSCH_2B(C_6F_5)_2)_2$ (Figure 1). In this form, the two boron centers are each four coordinate, resulting from coordination to sulfur. The B−S bond distances were found to be 2.054(4) and 2.071(5) Å. These bond lengths are comparable to those in the adduct $B(C_6F_5)_3\cdot SMe_2$ (2.091(5) Å) reported by

Received: April 20, 2011
Published: June 07, 2011

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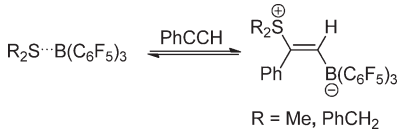
Scheme 1



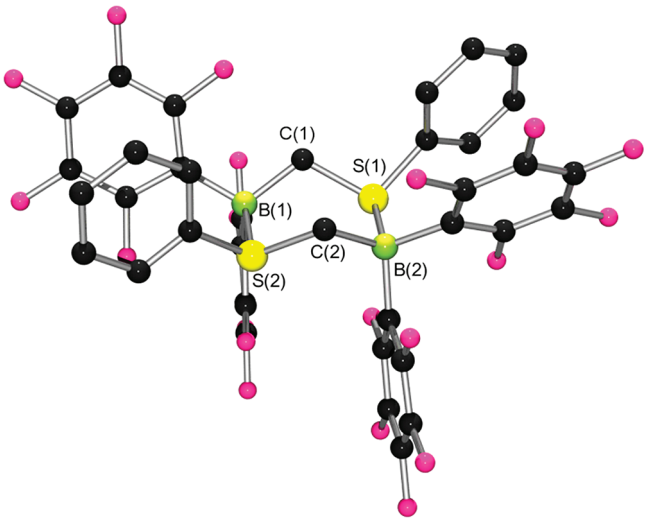


Figure 1. POV-Ray depictions of **1**. C: black, F: pink, B: yellow-green, S: yellow.

Denis et al.[39] and similar to that in the dimer $(PhBrBCH_2SMe)_2$ (2.000(5) Å) described by Wagner and co-workers.[38] The dimer **1** adopts a boat conformation in contrast to the geometry of $(PhBrBCH_2SMe)_2$, which is a chair conformation with the Br atoms occupying axial positions.[38] The geometry of **1** is attributed to π-stacking between the electron-rich S−Ph and the electron-deficient B−C_6F_5 groups. This boat conformation is reminiscent of the bent head-to-tail eight-membered ring reported for the species $(2\text{-}PyCH_2BCy_2)_2$.[40]

Variable-temperature NMR studies of **1** were undertaken. Upon cooling to −60 °C, the $^{19}F\{^1H\}$ NMR spectrum reveals two inequivalent environments for the C_6F_5 rings consistent with a dimeric structure. Upon warming to 55 °C, these resonances are replaced with those corresponding to a single C_6F_5 environment. In an analogous fashion, the ^1H NMR data were temperature dependent. The resonance attributable to the methylene protons observed as a singlet at 2.82 ppm broadens on cooling to about −5 °C with the corresponding growth of a doublet of doublets at 3.51 ppm. Upon further cooling to −60 °C, this quartet coalesces to a single broad peak at 3.47 ppm. (Figure 2). The corresponding information from the ^{11}B spectra was less informative, as a single broad resonance was observed at 0.92 ppm at 55 °C and was not observable at −60 °C. These data suggest complex equilibria, involving monomer−dimer interconversion. The ^1H resonance at 2.82 ppm is attributed to the methylene group of a monomeric form in which rapid inversion at S occurs via dissociation and B−S bond re-formation. On the other hand, the quartet for this methylene group that grows in on cooling is attributable to a dimeric form of **1**. Further cooling slows the exchange between chair and boat forms (Scheme 2). This interpretation is also consistent with the ^{19}F and ^{11}B data.

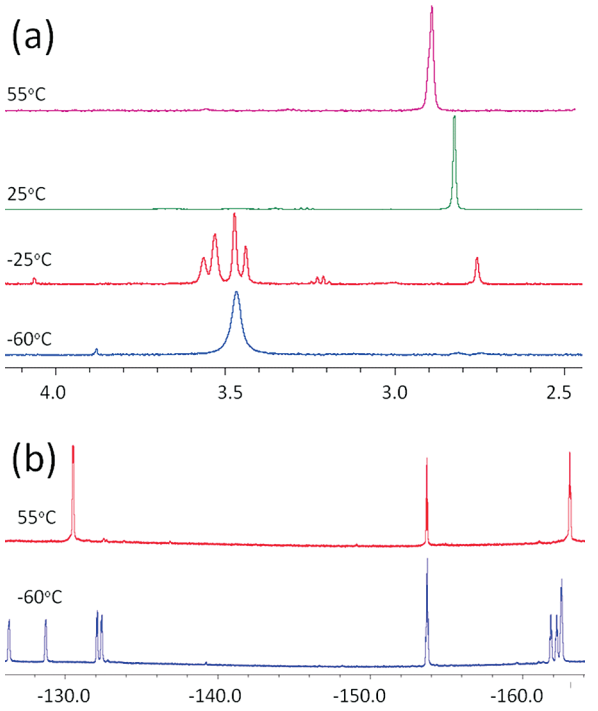
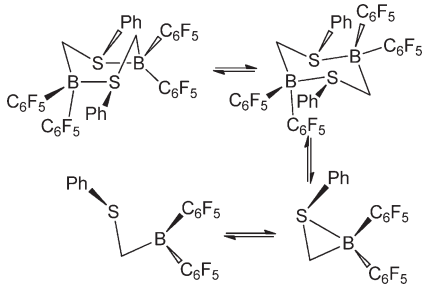


Figure 2. Variable-temperature (a) ^1H and (b) ^{19}F NMR spectra of **1**. Chemical shifts are given in ppm.

Scheme 2



Using an external standard as a reference, integration of the ^1H NMR signals attributable to the monomeric and dimeric forms of **1** allowed an evaluation of the enthalpy and entropy associated with the monomer−dimer equilibrium. These values were determined to be 34.9 kJ/mol and 122.6 J/(mol·K), respectively. These energies correspond to a Gibbs free energy of −1.63 kJ/mol and thus a K_{eq} (25 °C) of 1.9. For comparative purposes the corresponding thermodynamic parameters were determined for $B(C_6F_5)_3\cdot SMe_2$. These were found to be an enthalpy of 76.1 kJ/mol and an entropy of 168.1 J/(mol·K). For an additional comparison it is noted that the ΔH and ΔS for the monomer−dimer equilibrium for the species $(2\text{-}PyCH_2BCy_2)_2$ and **2**-$PyCH_2BCy_2$ were determined to be 79.2 kJ/mol and 218 J/(mol·K).[40] The lower values in the present system were attributed to lower Lewis acidity of the boron center in **1** in comparison to $B(C_6F_5)_3$ and the poorer basicity of S in comparison to the Py−N.

Compound **1** reacts with P*t*Bu$_3$ or OPEt$_3$ to form adducts $PhSCH_2B(C_6F_5)_2(L)$ (L = P*t*Bu$_3$ **2**, OPEt$_3$ **3**), which can be isolated in 85% and 87% yield, respectively. The ^{11}B NMR resonances are observed as sharp signals at δ −7.2 and 0.61 ppm,

dx.doi.org/10.1021/om200336t |*Organometallics* 2011, 30, 3652–3657

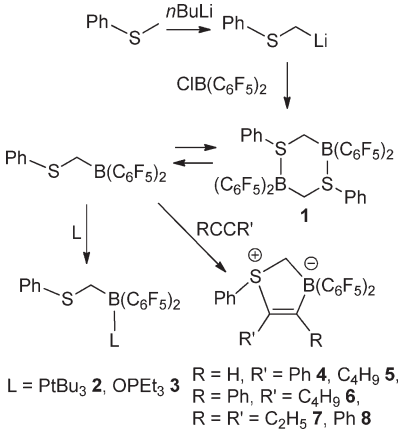
respectively, and the gaps between the *para*- and *meta*-fluorines in the $^{19}F\{^1H\}$ NMR spectra are 4.3 and 5.1 ppm for **2** and **3**, respectively, which is consistent with a four-coordinate B center. The ^{31}P signals for **2** and **3** were observed at 68.4 and 76.9 ppm, respectively. The formations of **2** and **3** demonstrate the stronger donor ability of phosphine and phosphine-oxide in comparison to thioether and are consistent with the accessibility of the monomeric fragment of **1** in solution, despite the electrophilic nature of the B center. These reactions, in which the dimer is cleaved, are reminiscent of the reaction of $(PhBrBCH_2SMe)_2$ with Me_2NSiMe_3 to give the amido-borane $PhB(CH_2SMe)(NMe_2)$ reported by Wagner and co-workers.[38]

As **1** contains donor and acceptor sites in dynamic equilibrium, it is conceivable that this species could react as an FLP. A number of reactions observed with previous FLPs were attempted with **1**. Compound **1** did not form a stoichiometric adduct with PhCH=N*t*Bu, suggesting the steric congestion about the N-donor precluded adduct formation. However, treatment of this possible FLP with H_2 at 60 °C for 12 h led to no reaction, in contrast to the reaction of $B(C_6F_5)_3$ and imine with H_2, where hydrogenation of the imine has been reported.[20] This observation is consistent with the reduced Lewis acidity of the B center in **1** resulting from both the presence of the alkyl substituent and the equilibrium between the monomeric and dimeric form.

As FLPs have been shown to react with olefins[6] and alkynes,[9,11] compound **1** was also tested for possible reactivity with these substrates. **1** was found to be unreactive with 1−hexene. Interestingly, **1** does react with both terminal and internal alkynes. The addition of the alkynes PhCCH, C_4H_9CCH, $PhCCC_4H_9$, $C_2H_5CCC_2H_5$, and PhCCPh led to the formation of the new species $(PhSCH_2B(C_6F_5)_2)(R'C{=}CR)$ (R = H, R′ = Ph **4**, C_4H_9 **5**, R = Ph, R′ = C_4H_9 **6**, R = R′ = C_2H_5 **7**, Ph **8**) in yields in the range 70−92%. The ^1H NMR spectra of these products gave rise to two distinct doublets ranging from 2.39 to 3.73 ppm, corresponding to the inequivalent protons in the CH_2 moiety. In the case of **4** and **5**, proton resonances at 8.33 and 7.61 ppm, respectively, were attributable to the presence of an alkenyl proton. $^{19}F\{^1H\}$ NMR data for **4**−**8** show two sets of resonances derived from the *ortho*-, *meta*-, and *para*-fluorine atoms, consistent with two inequivalent C_6F_5 rings. Sharp ^{11}B NMR resonances were observed in the range −8.3 to −6.1 ppm, inferring the presence of anionic four-coordinate boron centers. Collectively these data suggest cycloadditions of the thioether-borane species **1** with the respective alkynes (Scheme 3). This formulation was confirmed unambiguously by an X-ray crystallographic study of **8** (Figure 3). The five-membered ring is a zwitterion with a formal positive charge on S and an anionic charge on B. Within the S−B cyclopentene ring the S−C bond lengths in **8** are found to be 1.7887(14) and 1.8059(14) Å, while the B−C bonds are 1.634(2) and 1.666(2) Å and the C=C bond is 1.3462(19) Å, consistent with the presence of a double bond. The angles at S and B within the ring are found to be 96.11(7)° and 103.38(11)°. The remaining angles within the ring at C(1), C(2), and (C3) are found to be 107.44(9)°, 116.53(12)°, and 113.62(10)°, respectively.

Interestingly, these heterocycles proved to be thermally stable even upon heating to 120 °C overnight. Moreover, in contrast to previously observed addition reactions, in which phosphine and borane add to alkynes, addition of phosphine to a mixture of **1** and phenylacetylene resulted only in the isolation of heterocyclc sulfonium-borate **4**. The formation of these thioether-borane heterocycles

Scheme 3



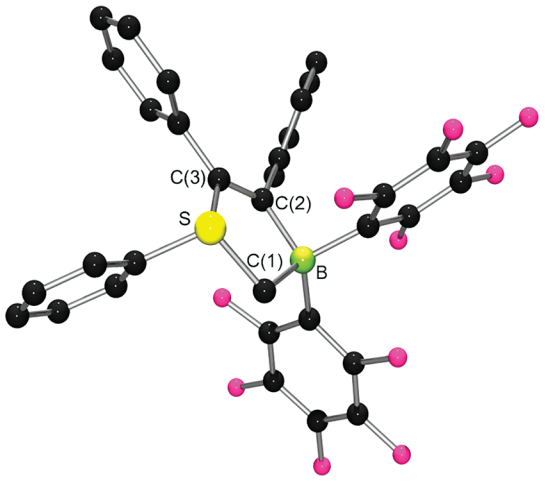


Figure 3. POV-ray depictions of **8**. C: black, F: pink, B: yellow-green, S: yellow.

is thought to proceed via initial interaction of the alkyne with the boron center. Presumably the proximity of the nucleophilic sulfur center to the Lewis acid-activated alkyne prompts the cyclization. It is noteworthy that we have previously demonstrated that thioethers and $B(C_6F_5)_3$ act as FLPs to effect addition to terminal alkynes, affording a *trans*-zwitterionic addition product of the form $R_2SCPh{=}CH(B(C_6F_5)_3$.[9,11] The present systems, however, are shown to give rise to *cis*-addition products **4**−**8**. These systems are reminiscent of the products derived from the thermally induced rearrangement reactions of the zwitterionic species $R_2PHC(=CHR)AlR_2(CCR)$ to give cyclopentene phosphonium aluminates very recently described by Uhl and coworkers.[41] In addition, it is noteworthy that five-membered rings containing B and S have received only very limited attention.[42]

In conclusion, a new linked boron−sulfur species, $PhSCH_2B(C_6F_5)_2$, was shown to be a dimer in the solid state, although it exists in equilibrium with the monomeric species in solution. As a result, it reacts with donors to form classical Lewis acid−base adducts. It has also been demonstrated to react as an FLP with alkynes to effect the formation of novel boron−sulfur heterocyclopentenes. Current efforts are focused on developing new reactivity of FLP systems.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed under dry, oxygen-free atmospheres either in a nitrogen-filled Innovative Technologies glovebox or on a Schlenk line under nitrogen. All solvents used were purchased from Caledon Laboratories and dried through a PureSolve solvent system. All deuterated solvents were purchased from Acros or Cambridge Isotope Laboratories. Deuterated solvents were dried overnight with the corresponding drying agent (CaH_2 for CD_2Cl_2, CaH_2 for C_6D_5Br, Na/Ph_2CO for d_8-toluene), then sonicated for half an hour, and vacuum transferred into a dry 100 mL bomb charged with activated 4 Å molecular sieves. Molecular sieves were activated by storage overnight in an oven at 120 °C. Reagents were purchased from Sigma Aldrich or Strem Chemicals and were stored in the glovebox except for sulfur precursors (thioanisole, 2-bromothioanisole), which were stored over 4 Å molecular sieves and kept inside the fumehood. A 400 MHz Bruker UltraShield spectrometer, a 400 MHz Bruker Avance III automatic sample changer, or a 400 MHz Varian Mercury spectrometer was used to perform ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR spectroscopy. ^{1}H, ^{13}C, ^{11}B{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR resonances were referenced internally to residual protonated solvent, deuterated solvent, $BF_3\cdot Et_2O$, 80% $CFCl_3$, and 85% H_3PO_4, respectively. To aid in the assignment of carbon atoms in the ^{13}C{^{1}H} NMR, ^{1}H−^{13}C HSQC experiments were carried out using conventional pulse sequences. Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz. Elemental analyses were performed by the in-house service in the Department of Chemistry at the University of Toronto.[43]

Synthesis of $(PhSCH_2B(C_6F_5)_2)_2$, 1. In a preweighed 50 mL Schlenk flask with a stir bar, ca. 25 mL of Et_2O was added via cannula. To the reaction vessel was added via a needle 0.30 mL of 2-bromothioanisole (2.25 mmol) (alternatively thioanisole can be used) under a constant flow of N_2 gas. The flask was then submerged in an acetone/dry ice bath, and the contents were stirred for a few minutes to allow for the temperature to equilibrate to −78 °C. *n*BuLi (1.55 mL of 1.6 M in hexanes, 2.47 mmol) was added dropwise to the cold solution using a needle and syringe. The reaction was allowed to stir for 2 h, during which the clear, colorless solution turned milky. The volatiles were evacuated, and the contents were dried under vacuum. To this lithiated species (0.241 g, 1.85 mmol) was added cold pentane (ca. 2 mL), and the mixture was stirred. In a separate scintillation vial, $ClB(C_6F_5)_2$[33] (0.704 g, 1.85 mmol) was weighed out and dissolved in cold pentane (ca. 10 mL). The chloroborane solution was transferred to the vial with the lithiated compound and stirred overnight while warming gradually to room temperature. The reaction mixture was filtered and the precipitate extracted into toluene. Removal of the solvent afforded a fine white powder (**1**) in 32% yield. ^{1}H NMR (d_8-toluene, 400 MHz, 25 °C): δ 6.72 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, *o*-H), 6.59−6.55 (m, 3H, *m*-H, *p*-H), 2.82 (s, 2H, CH_2). ^{1}H NMR (d_8-toluene, 400 MHz, −60 °C): δ 6.80 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, *o*-H), 6.52 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, *p*-H), 6.36 (t, 2H, $^3J_{H-H}$ = 7.2 Hz, *m*-H), 3.47 (s, 2H, CH_2). ^{1}H NMR (d_8-toluene, 400 MHz, 55 °C): δ 6.78−6.77 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, *o*-H), 6.64−6.59 (m, 3H, *m*-H, *p*-H), 2.87 (s, 2H, CH_2). ^{19}F{^{1}H} NMR (d_8-toluene, 377 MHz, 25 °C): δ −130.7 (m, 4F, *o*-F), −153.6 (t, 2H, $^3J_{F-F}$ = 20.4 Hz, *p*-F), −163.0 (m, 4F, *m*-F). ^{19}F{^{1}H} NMR (d_8-toluene, 377 MHz, −60 °C): δ −126.3 (m, 1F, *o*-F), −128.7 (m, 1F, *o*-F), −132.1 (d, 1F, $^3J_{F-F}$ = 24.3 Hz, *o*-F), −132.4 (d, 1F, $^3J_{F-F}$ = 24.3 Hz, *o*-F), −153.7 (t, 1F, $^3J_{F-F}$ = 21.7 Hz, *p*-F), −153.8 (t, 1F, $^3J_{F-F}$ = 21.7 Hz, *p*-F), −161.8 (m, 1F, *m*-F), −162.2 (m, 1F, *m*-F), −162.5 (m, 1F, *m*-F), −162.6 (m, 1F, *m*-F). ^{19}F{^{1}H} NMR (d_8-toluene, 377 MHz, 55 °C): δ −130.5 (m, 4F, *o*-F), −153.7 (t, 2H, $^3J_{F-F}$ = 20.4 Hz, *p*-F), −163.1 (m, 4F, *m*-F). ^{11}B{^{1}H} NMR (d_8-toluene, 128 MHz, 25 °C): δ 5.1 (s). ^{11}B{^{1}H} NMR (d_8-toluene, 128 MHz, 55 °C): δ 0.92 (br s). ^{11}B{^{1}H} NMR (d_8-toluene, 128 MHz, −60 °C): not observed. ^{13}C{^{1}H} NMR partial (CD_2Cl_2, 100 MHz, 25 °C): δ 130.7 (s, *p*-C), 129.9 (s, *o*-C), 129.8 (s, *m*-C), 33.3 (s, CH_2). Anal. Calcd for $C_{19}H_7BF_{10}S$: C 48.75, H 1.51. Found: C 49.22, H 1.65. X-ray quality crystals of the dimer were obtained from a concentrated solution of product in toluene and bromobenzene at −38 °C. X-ray data: monoclinic $P2_1/n$, a = 8.1411(7) Å, b = 18.587(2) Å, c = 23.881(3) Å, β = 96.257(4)°, V = 3594.0(6) Å^3, Z = 4, data (>2σ) = 4011, variables = 559, R_1 = 0.0546, wR_2 = 0.1373, GOF = 1.015.

Synthesis of $(PhSCH_2B(C_6F_5)_2(L)$ (L = P*t*Bu$_3$ 2, OPEt$_3$ 3). These compounds were prepared in an analogous manner, and thus only one preparation is detailed. In a 20 mL scintillation vial with a stirbar in a cold brass ring (−38 °C) 74.8 μmol of compound **1** and 74.8 μmol of P*t*Bu$_3$ were weighed out. These compounds were dissolved in ca. 4 mL of cold toluene (−38 °C) and stirred overnight. Subsequent evacuation of solvent resulted in clear, colorless oils. Addition of cold pentane and placement of the vial in the glovebox freezer overnight resulted in a white precipitate.

2: ^{1}H NMR (d_8-toluene, 400 MHz): δ 7.37 (d, 2H, $^3J_{H-H}$ = 7.4 Hz, *o*-H), 6.89−6.85 (m, 2H, *m*-H), 6.83−6.81 (m, 1H, *p*-H), 2.38 (d, 2H, $^3J_{P-H}$ = 16.4 Hz, CH_2), 0.93 (d, $^3J_{H-H}$ = 13.3 Hz, 27 Hz, *t*Bu). ^{19}F{^{1}H} NMR (d_8-toluene, 377 MHz): δ −129.6 (br m, 4F, *o*-F), −160.6 (t, 2F, $^3J_{F-F}$ = 20.6 Hz, *p*-F), −164.9 (m, 4F, *m*-F). ^{11}B{^{1}H} NMR (d_8-toluene, 128 MHz): δ −7.2 (s). ^{31}P{^{1}H} NMR (d_8-toluene, 162 MHz): δ 68.4 (s). ^{13}C{^{1}H} NMR partial (CD_2Cl_2, 100 MHz): δ 134.2 (s, *m*-C), 128.2 (s, *o*-C), 125.4 (s, *p*-C), 40.0 (d, $^2J_{P-C}$ = 31.2 Hz, $C(CH_3)_3$), 30.9 (br s, CH_2, $C(CH_3)_3$). Yield: 85%. Anal. Calcd for $C_{31}H_{34}BF_{10}PS$: C 55.54, H 5.11. Found: C 54.92, H 5.70.

3: ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.28−7.25 (m, 2H, *o*-H), 7.25−7.21 (m, 2H, *m*-H), 7.07−7.03 (m, 1H, *p*-H), 2.74 (s, 2H, CH_2), 2.07−1.98 (m, 6H, CH_2), 1.21−1.08 (m, 9H, CH_3). ^{19}F{^{1}H} NMR (CD_2Cl_2, 377 MHz): δ −134.7 (m, 4F, *m*-F), −160.1 (t, 2F, $^3J_{F-F}$ = 20.1 Hz, *p*-F), −165.2 (m, 4F, *m*-F). ^{11}B{^{1}H} NMR (CD_2Cl_2, 128 MHz): δ 0.61 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 76.9 (s). ^{13}C{^{1}H} NMR partial (CD_2Cl_2, 100 MHz): δ 141.9 (s, *ipso* C), 129.1 (s, *m*-C), 126.4 (s, *o*-C), 124.5 (s, *p*-C), 28.2 (s, CH_2), 18.3 (d, $^1J_{P-C}$ = 65.7 Hz, CH_2), 5.8 (d, $^2J_{P-C}$ = 4.7 Hz, CH_3). Yield: 87%. Anal. Calcd for $C_{25}H_{22}BF_{10}OPS$: C 49.86, H 3.68. Found: C 51.01, H 4.14.

Synthesis of $(PhSCH_2B(C_6F_5)_2(R'C{=}CR)$ (R = H, R′ = Ph 4, C_4H_9 5, R = Ph, R′ = C_4H_9 6, R = R′ = C_2H_5 7, Ph 8). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. In a 20 mL scintillation vial with a stir bar in a cold brass ring (−38 °C) compound **1** (64.1 μmol) was weighed out and dissolved in cold toluene (ca. 4 mL, −38 °C). Alkyne (64.1 μmol) was added to the vial via a 0.50 cm^3 syringe. The solution was stirred overnight, and subsequent evacuation of solvent resulted in clear, colorless oils. Addition of cold pentane and placement of the vial in the glovebox freezer overnight resulted in a white to off-white precipitate.

4: ^{1}H NMR (d_8-toluene, 400 MHz): δ 8.33 (s, 1H, CH), 7.08−7.06 (m, 2H, *o*-H), 6.88 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, *o*-H), 6.84−6.79 (m, 3H, *m*-H, *p*-H), 6.64−6.60 (m, 1H, *p*-H), 6.56−6.52 (m, 2H, *m*-H), 3.46 (d, 1H, $^2J_{H-H}$ = 13.6 Hz, CH_2), 2.60 (d, 1H, $^2J_{H-H}$ = 13.6 Hz, CH_2). ^{19}F{^{1}H} NMR (d_8-toluene, 377 MHz): δ −132.6 (d, 2F, $^3J_{F-F}$ = 24.2 Hz, *o*-F), −133.5 (d, 2F, $^3J_{F-F}$ = 24.2 Hz, *o*-F), −159.3 (t, 1F, $^3J_{F-F}$ = 20.2 Hz, *p*-F), −159.5 (t, 1F, $^3J_{F-F}$ = 20.2 Hz, *p*-F), −163.7 (m, 2F, *m*-F), −164.0 (m, 2F, *m*-F). ^{11}B{^{1}H} NMR (d_8-toluene, 128 MHz): δ −7.8 (s). ^{13}C{^{1}H} NMR partial (CD_2Cl_2, 100 MHz): δ 133.7 (s, *p*-C), 131.5 (s, *ipso* C), 131.2 (s, *m*-C), 129.9 (s, *o*-C), 129.5 (s, *m*-C, *p*-C), 129.3 (s, *ipso* C), 127.2 (s, *o*-C), 39.4 (s, CH_2). Yield: 88%. Anal. Calcd for $C_{27}H_{13}BF_{10}S$: C 56.87, H 2.30. Found: C 56.03, H 2.71.

5: ^{1}H NMR (d_8-toluene, 400 MHz): δ 7.61 (s, 1H, CH), 6.96 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, *o*-H), 6.85 (t, 1H, $^3J_{H-H}$ = 7.6 Hz, *p*-H), 6.76 (t, 2H, $^3J_{H-H}$ = 7.6 Hz, *m*-H), 3.57 (d, 1H, $^2J_{H-H}$ = 11.8 Hz, CH_2), 2.49 (d, 1H, $^2J_{H-H}$ = 11.8 Hz, CH_2), 1.87−1.79 (m, 1H, CCH_2CH_2), 1.63−1.55 (m, 1H,, CCH_2CH_2), 1.24−1.16 (m, 2H,, CCH_2CH_2), 1.06−0.89 (m, 2H, CH_2CH_3), 0.65 (t, 3H, $^3J_{H-H}$ = 7.2 Hz, CH_3). ^{19}F{^{1}H}

NMR (d_8-toluene, 377 MHz): δ −132.9 (d, 2F, $^3J_{F-F}$ = 19.3 Hz, *o*-F), −133.6 (d, 2F, $^3J_{F-F}$ = 19.3 Hz, *o*-F), −159.6 (t, 1F, $^3J_{F-F}$ = 20.4 Hz, *p*-F), −159.7 (t, 1F, $^3J_{F-F}$ = 20.4 Hz, *p*-F), −163.9 (m, 2F, *m*-F), −164.0 (m, 2F, *m*-F). $^{11}B\{^1H\}$ NMR (d_8-toluene, 128 MHz): δ −8.3 (s). $^{13}C\{^1H\}$ NMR partial (CD_2Cl_2, 100 MHz): δ 135.6 (s, *ipso* C), 134.0 (s, *p*-C), 131.3 (s, *m*-C), 130.4 (s, *o*-C), 129.9 (s, *ipso* C), 42.9 (s, CH_2), 30.8 (s, CCH_2CH_2), 30.7 (s, CCH_2CH_2), 22.4 (s, CH_2CH_3), 14.0 (s, CH_3). Yield: 91%. Anal. Calcd for $C_{25}H_{17}BF_{10}S$: C 54.57, H 3.11. Found: C 52.79, H 3.37.

6: ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.63−7.61 (m, 2H, *o*-H), 7.53−7.49 (m, 1H, *p*-H), 7.48−7.44 (m, 2H, *m*-H), 7.31−7.28 (m, 2H, *o*-H), 7.28−7.26 (m, 2H, *m*-H), 7.24−7.20 (m, 1H, *p*-H), 3.73 (d, 1H, $^2J_{H-H}$ = 13.2 Hz, CH_2), 2.68−2.62 (m, 1H, CCH_2CH_2), 2.45 (d, 1H, $^2J_{H-H}$ = 13.2 Hz, CH_2), 2.41−2.34 (m, 1H, CCH_2CH_2), 0.92−0.86 (m, 2H, CCH_2CH_2), 0.84−0.74 (m, 1H, CH_2CH_3), 0.51 (t, 3H, CH_3), 0.41−0.40 (m, 1H, CH_2CH_3). $^{19}F\{^1H\}$ NMR (d_8-toluene, 377 MHz): δ −132.6 (m, 2F, *o*-F), −133.0 (m, 2F, *o*-F), −159.5 (t, 1F, $^3J_{F-F}$ = 20.3 Hz, *p*-F), −159.6 (t, 1F, $^3J_{F-F}$ = 20.3 Hz, *p*-F), −163.8 (m, 2F, *m*-F), −163.9 (m, 2F, *m*-F). $^{11}B\{^1H\}$ NMR (d_8-toluene, 128 MHz): δ −6.1 (s). $^{13}C\{^1H\}$ NMR partial (CD_2Cl_2, 100 MHz): δ 133.6 (s, *p*-C), 133.5 (s, *ipso* C), 132.0 (s, *ipso* C), 131.6 (s, *ipso* C), 131.1 (s, *m*-C), 130.3 (s, *o*-C), 129.7 (s, *o*-C), 129.4 (s, *p*-C), 129.0 (s, *m*-C), 128.8 (s, *ipso* C), 127.1 (s, *ipso* C), 43.6 (s, CH_2), 32.3 (s, CCH_2), 31.3 (s, CH_2CH_3), 23.5 (s, $CH_2CH_2CH_2$), 13.6 (s, CH_3). Yield: 92%. Anal. Calcd for $C_{31}H_{21}BF_{10}S$: C 59.44, H 3.38. Found: C 57.72, H 3.65.

7: ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.67−7.64 (m, 2H, *o*-H), 7.64−7.62 (m, 1H, *p*-H), 7.60−7.55 (m, 2H, *m*-H), 3.55 (d, 1H, $^2J_{H-H}$ = 12.9 Hz, CH_2), 2.62 (sextet, 1H, $^3J_{H-H}$ = 7.7 Hz, CCH_2), 2.52−2.47 (m, 2H, CCH_2), 2.39 (d, 1H, $^2J_{H-H}$ = 12.9 Hz, CH_2), 1.83 (sextet, 1H, $^3J_{H-H}$ = 7.7 Hz, CCH_2), 1.03 (t, 3H, $^3J_{H-H}$ = 7.7 Hz, CH_2CH_3), 0.64 (t, 3H, $^3J_{H-H}$ = 7.7 Hz, CH_2CH_3). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 377 MHz): δ −132.6 (m, 2F, *o*-F), −133.2 (m, 2F, *o*-F), −159.7 (t, 1F, $^3J_{F-F}$ = 20.2 Hz, *p*-F), −159.8 (t, 1F, $^3J_{F-F}$ = 20.2 Hz, *p*-F), −164.0 (m, 2F, *m*-F), −164.1 (m, 2F, *m*-F). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 128 MHz): δ −7.0 (s). $^{13}C\{^1H\}$ NMR partial (CD_2Cl_2, 100 MHz): δ 133.8 (s, *p*-C), 131.3 (s, *m*-C), 130.4 (s, *o*-C), 43.3 (s, CH_2), 25.5 (s, CH_2CH_3), 21.3 (s, CH_2CH_3), 14.5 (s, CH_2CH_3), 13.1 (s, CH_2CH_3). Yield: 80%. Anal. Calcd for $C_{25}H_{17}BF_{10}S$: C 54.57, H 3.11. Found: C 53.28, H 3.28.

8: ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.75−7.73 (m, 2H, Ar−H), 7.57−7.52 (m, 1H, Ar−H), 7.52−7.48 (m, 2H, Ar−H), 7.39−7.36 (m, 1H, Ar−H), 7.15−7.12 (m, 2H, Ar−H), 7.12−7.09 (m, 3H, Ar−H), 7.06−7.00 (m, 2H, Ar−H), 6.89−6.87 (m, 2H, Ar−H), 3.81 (d, 1H, $^2J_{H-H}$ = 12.2 Hz, CH_2), 2.76 (d, 1H, $^2J_{H-H}$ = 12.2 Hz, CH_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 377 MHz): δ −131.9 (d, 2F, $^3J_{F-F}$ = 24.2 Hz, *o*-F), −133.1 (d, 2F, $^3J_{F-F}$ = 24.2 Hz, *o*-F), −160.9 (t, 1F, $^3J_{F-F}$ = 20.0 Hz, F-13), −161.3 (t, 1F, $^3J_{F-F}$ = 20.0 Hz, *p*-F), −165.3 (m, 2F, *p*-F), −165.8 (m, 2F, *m*-F). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 128 MHz): δ −6.3 (s). $^{13}C\{^1H\}$ NMR partial (CD_2Cl_2, 100 MHz): δ 133.8 (s, Ar−C), 133.4 (s, *ipso* C), 132.1 (s, Ar−C), 131.2 (s, Ar−C), 130.7 (s, *ipso* C), 130.6 (s, Ar−C), 130.2 (s, Ar−C), 129.1 (s, Ar−C), 129.0 (s, Ar−C), 128.9 (s, Ar−C), 128.1 (s, Ar−C), 127.3 (s, Ar−C), 43.0 (s, CH_2). Yield: 70%. Anal. Calcd for $C_{33}H_{17}BF_{10}S$: C 61.32, H 2.65. Found: C 60.95, H 3.10. X-ray quality clear colorless cubic crystals were grown from a solution of pentane at −38 °C. X-ray data: monoclinic *C*2/*c*, a = 31.0478(12) Å, b = 11.4951(4) Å, c = 18.9964(7) Å, β = 122.759(2)°, V = 5701.5(4) Å^3, Z = 8, data (>2σ) = 6376, variables = 406, R_1 = 0.0436, wR_2 = 0.1200, GOF = 1.030.

X-ray Crystallography. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer employing Mo Kα radiation (λ = 0.71073 Å). Data collection strategies were determined using Bruker Apex software and optimized to provide >99.5% complete data to a 2θ value of at least 55°. The data were collected at 150(±2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[44] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(F_o - F_c)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

■ ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

Financial support of NSERC of Canada is gratefully acknowledged. D.W.S. is grateful for the award of a Canada Research Chair and a Killiam Research Fellowship for 2009−2011.

■ REFERENCES

(1) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46.
(2) Stephan, D. W. *Chem. Commun.* **2010**, *46*, 8526.
(3) Stephan, D. W. *Dalton Trans.* **2009**, 3129.
(4) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
(5) Dureen, M. A.; Welch, G. C.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 9910.
(6) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968.
(7) Ullrich, M.; Seto, K. S. H.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 2335.
(8) Dureen, M. A.; Stephan, D. W. *Organometallics* **2010**, *29*, 6622.
(9) Dureen, M. A.; Stephan, D. W. *Organometallics* **2010**, *29*, 6594.
(10) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 13559.
(11) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396.
(12) Geier, S. J.; Dureen, M. A.; Ouyang, E. Y.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 988.
(13) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 2414.
(14) Chen, C.; Frohlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2010**, *46*, 3580.
(15) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643.

(16) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796.
(17) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2010**, *39*, 7556.
(18) Otten, E.; Neu, R. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 9918.
(19) Alcarazo, M.; Gomez, C.; Holle, S.; Goddard, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 5788.
(20) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701.
(21) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskela, M.; Repo, T.; Pyykko, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117.
(22) Sumerin, V.; Schulz, F.; Nieger, M.; Leskela, M.; Repo, T.; Rieger, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 6001.
(23) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839.
(24) Jiang, C. F.; Blacque, O.; Berke, H. *Organometallics* **2009**, *28*, 5233.
(25) Birkmann, B.; Voss, T.; Geier, S. J.; Ullrich, M.; Kehr, G.; Erker, G.; Stephan, D. W. *Organometallics* **2010**, *29*, 5310.
(26) Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Commun.* **2010**, *46*, 4884.
(27) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476.
(28) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 10466.
(29) Chase, P. A.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Dalton Trans.* **2009**, 7179.
(30) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433.
(31) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.
(32) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433.
(33) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.
(34) Hoshi, M.; Shirakawa, K.; Okimoto, M. *Tetrahedron Lett.* **2007**, *48*, 8475.
(35) Kim, Y.; Zhao, H.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 4957.
(36) Zhao, H.; Gabbaï, F. P. *Nat. Chem.* **2010**, *2*, 984.
(37) Nöth, H.; Sedlak, D. *Chem. Ber.* **1983**, *116*, 1479.
(38) Ruth, K.; Tüllmann, S.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Chem.—Eur. J.* **2008**, *14*, 6754.
(39) Denis, J.-M.; Forintos, H.; Szelke, H.; Toupet, L.; Pham, T.-N.; Madec, P.-J.; Gaumont, A.-C. *Chem. Commun.* **2003**, 54.
(40) Vergnaud, J.; Ayed, T.; Hussein, K.; Vendier, L.; Grellier, M.; Bouhadir, G.; Barthelat, J.-C.; Sabo-Etienne, S.; Bourissou, D. *Dalton Trans.* **2007**, 2370.
(41) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem., Int. Ed.* **2011**, DOI: 10.1002/anie.201006901.
(42) Ashe, A. J.; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 1821.
(43) On occasion, repeated attempts to obtain C, H analyses gave consistently low C values. This was attributed to the formation of boron carbide during combustion.
(44) Cromer, D. T.; Waber, J. T. *Int. Tables X-Ray Crystallogr.* **1974**, *4*, 71.