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Insertion Reactions of Diazomethanes and Electrophilic Boranes

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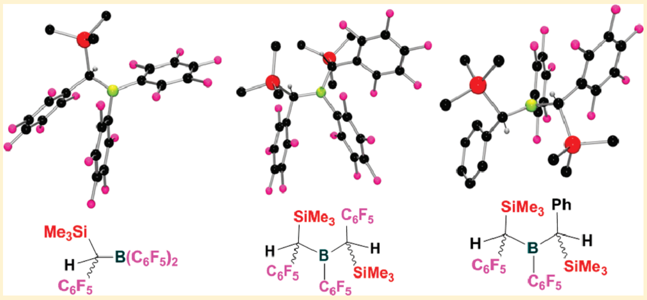
Supporting Information

ABSTRACT: The electrophilic pentafluoroarylboranes $B(C_6F_5)_3$, $PhB(C_6F_5)_2$, and $ClB(C_6F_5)_2$ react with (trimethylsilyl)diazomethane, diphenyldiazomethane, or (pentafluorophenyl)diazomethane, affording insertion into the one or two B−C bonds in a facile and high-yielding route to the boranes $(Me_3SiCH(C_6F_5))B(C_6F_5)_2$, $(Me_3SiCH(C_6F_5))_2B(C_6F_5)$, $(Me_3SiCH(C_6F_5))(Me_3SiCH(Ph))B(C_6F_5)$, $(C_6F_5)ClB(CPh_2(C_6F_5))$, and $(C_6F_5)_2B(CH(C_6F_5)_2)$.



Tris(pentafluorophenyl)borane was first prepared in 1964;[1] however, it was not until 1991 that the pioneering work of Marks[2] and Ewen[3] independently demonstrated the unique ability of $B(C_6F_5)_3$ to effect electrophilic alkyl abstraction from early-metal metallocene derivatives, affording highly effective olefin polymerization catalysts. This remarkable evolution from an intellectual curiosity to these applications has been extensively chronicled by Piers and Chivers.[4] Since that time, a plethora of applications[5] of perfluoroarylboranes have been developed for organometallic[5−10] and main-group chemistry,[11−14] optoelectronic materials,[15−26] frustrated Lewis pair chemistry,[27−31] and sensors for anions and toxic agents.[32−38] In catalysis, $B(C_6F_5)_3$ has been exploited for a variety of Lewis acid mediated processes,[4,39] while more recently it has been used to effect in the catalytic synthesis of silicones[40] as well as in metal-free hydrogenations.[27,41,42]

Despite the general and broad interest in perfluoroarylborane derivatives, the synthesis and purification of electrophilic boranes can be technically challenging. Several authors[43−46] have developed approaches to generating arylboranes from precursors such as BCl_3 and $ClB(C_6F_5)_2$, while Piers and others have exploited hydroboration of alkenes and alkynes with $HB(C_6F_5)_2$ to generate related alkyl- or alkenylboranes. The groups of Marks[47−54] and Piers[55−65] have also developed elegant strategies to bulky and electrophilic boranes, employing methodologies which depend on the use of tin and mercury intermediates.[66,67] While most synthetic routes to perfluoroarylborane derivatives involve reactions of B−halide or B−H bonds, recent reports by the Erker[68−74] and Berke[75] groups have described thermally induced 1,1-carboborations of terminal and internal alkynes by $B(C_6F_5)_3$, affording new electrophilic vinylboranes. In this communication, we describe the facile and high-yielding insertions of diazomethanes into the B−C bonds of electrophilic boranes, providing an avenue to sterically elaborated electrophilic boranes.

The reaction of $B(C_6F_5)_3$ with a slight stoichiometric excess of $Me_3SiCH(N_2)$ proceeds smoothly and rapidly at −78 °C to generate the new borane **1**. Following purification by recrystallization, **1** was isolated in 65% yield. The ^{11}B NMR signal of **1** was not discernible between −60 and 85 °C. The ^{19}F NMR spectrum of **1** showed resonances at −130.9, −149.8 and −161.3 ppm attributable to the *o*-, *p*-, and *m*-fluorine atoms of the two equivalent C_6F_5 groups bound to boron. In addition, resonances in the ^{19}F NMR spectrum attributable to the *o*-, *p*-, and *m*-fluorine atoms of a C_6F_5 ring bound to carbon were observable at −140.8, −158.9 and −162.9 ppm, respectively. Integration of these peaks confirmed that the two C_6F_5 environments in **1** were present in a 2:1 ratio. The corresponding ^1H NMR spectrum displayed resonances at 4.38 and 0.16 ppm attributable to CH and $SiMe_3$ fragments in a 1:9 ratio. The latter fragment also gives rise to a broadened ^{29}Si resonance at −111.0 ppm. These data support the formulation of **1** as $(Me_3SiCH(C_6F_5))B(C_6F_5)_2$ (Scheme 1). This formulation was later confirmed crystallographically (Figure 1). The B−C bond lengths for the fluoroarene groups were found to be 1.593(2) and 1.577(2) Å, while the B−C bond length for the tertiary carbon atom was determined to be 1.545(2) Å. The anticipated pseudo-trigonal-planar geometry about B is evident from the C−B−C angles of 122.3(1), 117.8(2) and 119.6(1)°. The tertiary carbon derived from formal insertion of the diazomethane fragment into the B−C bond is found to be chiral. Interestingly, the BC_2 plane of the $B(C_6F_5)_2$ fragment is oriented away from the $SiMe_3$ group. Indeed, the $SiMe_3$ fragment is oriented so as to block one face of the B plane with the closest C−H···B approach being a methyl group of the $SiMe_3$ fragment at 3.10 Å from the electron-deficient boron. It is noteworthy that there was no evidence of this interaction in solution by ^1H NMR spectroscopy, even down to −85 °C.

In an analogous manner, reaction of $B(C_6F_5)_3$ with 2 equiv of $Me_3SiCH(N_2)$ proceeds smoothly and rapidly at −78 °C to

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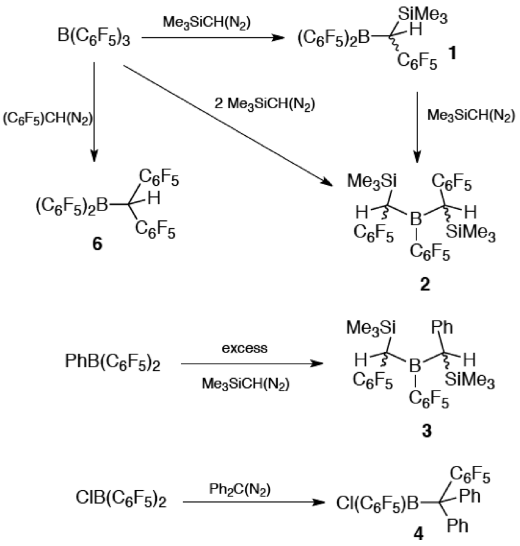
Scheme 1. Synthesis of Compounds 1−4 and 6



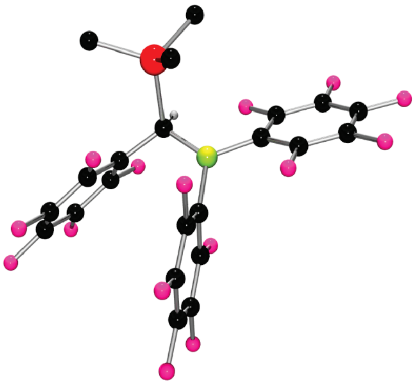


Figure 1. Pov-ray depiction of **1**: C, black; B, yellow-green; F, pink; Si, red.

generate the new borane **2**. Following recrystallization from pentane at −35 °C, **2** was isolated as colorless crystals in 67% yield. This species exhibits a broad ^{11}B NMR resonance at 75.4 ppm. The corresponding ^{19}F and ^{1}H NMR spectral data show signals attributable to two products in a ratio of 72:28. The major product gives rise to 8 ^{19}F resonances corresponding to 3 distinct C_6F_5 rings in a 1:1:1 ratio, while the minor product gave rise to 15 distinct resonances at −85 °C. The corresponding ^{1}H NMR data for the methine and methyl protons were observed at 3.79 and 0.22 ppm for the major isomer and 3.58 and −0.17 ppm for the minor isomer. These data were consistent with the formulation of the product **2** as the *RR*/*SS* and *RS*/*SR* diastereomers of **2** $(Me_3SiCH(C_6F_5))_2B(C_6F_5)$ (Scheme 1). Crystals of the racemic diastereomer of **2** were characterized crystallographically, thereby confirming the proposed "double insertion" of the diazomethane into two B−C bonds of $B(C_6F_5)_3$ (Figure 2). The B−C bonds of the fluoroarene and tertiary carbons at 1.600(3), 1.556(3) and 1.566(3) Å are slightly longer than those noted for compound **1**. The geometry about B in **2** is similar to that in **1**, although the steric crowding resulting from the adjacent tertiary C centers gives rise to a cog-wheel type meshing of the substituents. The impact of this steric congestion is also demonstrated as addition of further equivalents of $Me_3SiCH(N_2)$ (2, 5, and 10 equiv) to **2** resulted in no further reaction.

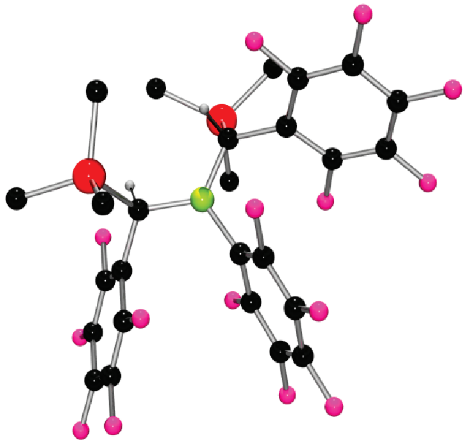


Figure 2. Pov-ray depiction of **2**: C, black; B, yellow-green; F, pink; Si, red.

Indeed, **2** is easily and cleanly prepared *via* addition of excess $Me_3SiCH(N_2)$ to $B(C_6F_5)_3$ with simple separation from the unreacted $Me_3SiCH(N_2)$ *via* product recrystallization from cold pentane.

The analogous reaction of $Me_3SiCH(N_2)$ and $PhB(C_6F_5)_2$ in a 1:1 ratio was undertaken. Preliminary ^{19}F NMR spectroscopy of the reaction mixture was consistent with the formation of two products, resulting from single and double insertions of $Me_3SiCH(N_2)$ into B−C bonds. While these species could not be separated, a single product formulated as $(Me_3SiCH(C_6F_5))(Me_3SiCH(Ph))B(C_6F_5)$ (**3**) was prepared in a clean fashion *via* addition of 2 equiv of $Me_3SiCH(N_2)$ at −78 °C to $PhB(C_6F_5)_2$. The crude product, obtained as a clear and colorless oil, was recovered in 64% isolated yield. Recrystallization from pentane over a number of days at −35 °C resulted in large rectangular crystals which were crystallographically analyzed, confirming the proposed formulation of **3** (Figure 3). The structure of **3** is in fact very similar to that of **2**, bearing the similar cog-wheel type arrangement of the substituents. The product is pseudoplanar at boron, as demonstrated by the C−B−C angles 121.0(1), 121.6(1) and 117.3(1)°, which add up to nearly 360°. The crowding about the boron center presumably accounts for the inability to effect further insertion. The presence of the trimethylsilyl groups gave rise to a broad signal in the ^{29}Si NMR at −111.5 ppm, while the ^{11}B NMR displayed a broadened signal at 76.3 ppm significantly downfield as

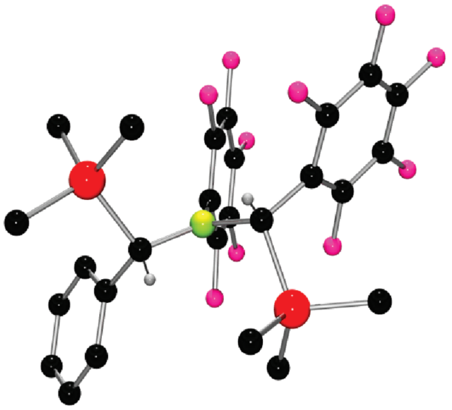


Figure 3. Pov-ray depiction of **3**: C, black; B, yellow-green; F, pink; Si, red.

compared to the chemical shift of the parent borane, $PhB(C_6F_5)_2$. Only two methine and two methyl signals at 3.7 and 3.5 ppm and at 0.2 and 0.7 ppm were observed in the ^1H NMR spectrum. The ^{19}F NMR spectrum of **3** was pristinely clean, showing nine resonances attributable to the three C_6F_5 environments. These ^{19}F and ^1H data are consistent with the presence of only the *RR*/*SS* diastereomers. The diastereoselectivities seen for the "double insertion" into $PhB(C_6F_5)_2$ and $B(C_6F_5)_3$ suggests that the chirality of the initial insertion influences the chirality of the second insertion. It is also interesting to note that the resulting dissymmetric substitution about the planar borane center of **3** makes this species prochiral at boron.

The generality of diazomethane insertion reactions with electrophilic boranes was further probed. While the analogous reaction of $Me_3SiCH(N_2)$ with $ClB(C_6F_5)_2$ at −78 °C gave a complex mixture of products, the reaction of $Ph_2C(N_2)$ and $ClB(C_6F_5)_2$ resulted in a very fast and clean reaction. Examination of the ^{19}F NMR spectra revealed the presence of six distinct resonances, in keeping with two chemically distinct perfluoroaryl groups, where one C_6F_5 group has migrated from the boron center to the adjacent carbon. On the basis of NMR data this product borane was formulated as $(C_6F_5)ClB(CPh_2(C_6F_5))$ (**4**) and was isolated as an oil in 97% yield. Confirmation of the structure of **4** was obtained from a crystallographic study of the pyridine adduct $(C_6F_5)ClB(CPh_2(C_6F_5))(py)$ (**5**) (Figure 4). It should be noted that that no further reaction was observed upon reaction of **4** with further equivalents of $Ph_2C(N_2)$ (1, 2, and 5 equiv).

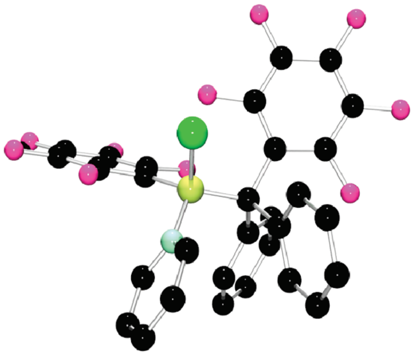


Figure 4. Pov-ray depiction of **5**: C, black; B, yellow-green; F, pink; N, blue.

The diazomethane $(C_6F_5)CH(N_2)$ was prepared from the corresponding hydrazone with decomposition to the diazomethane by Swern oxidation.[76] Stoichiometric reaction of the neat diazomethane with $B(C_6F_5)_3$ at −78 °C resulted in immediate consumption of the diazomethane, as evidenced by the disappearance of the diagnostic yellow color, resulting in the generation of a slightly beige solution. The resulting product was isolated as a beige solid in 60% yield that gave rise to two sets of ^{19}F NMR resonances attributable to two C_6F_5 environments present in a 1:1 ratio, with a single resonance in the ^1H NMR corresponding to the methane proton. These data are consistent with the formation of $((C_6F_5)_2CH)B(C_6F_5)_2$ (**6**). This formulation was later confirmed crystallographically (Figure 5). It is noted that the B−C bond lengths of the perfluoroarenes at 1.553(4) and 1.568(4) Å are shorter than those observed in the related compound **1** at 1.577(2) and 1.593(2) Å, which is in keeping with the increased Lewis acidity of the boron center. The B−C bond length of the boron center in **6** bound to the tertiary carbon is, however, markedly lengthened at 1.573(3) Å as compared to **1** with a B−C bond length of 1.545(2) Å. The C−B−C bond angles at boron were found to be 120.8(2), 119.3(2) and 119.9(2)°, in keeping with a pseudo-trigonal-planar geometry about the boron center.

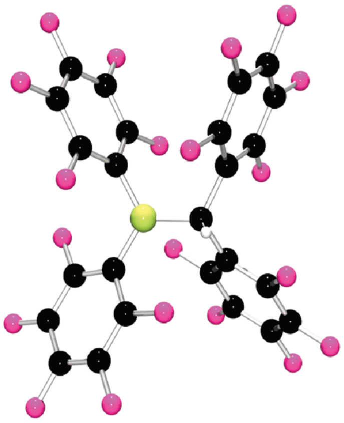


Figure 5. Pov-ray depiction of **6**: C, black; B, yellow-green; F, pink.

While Jie and Shea[77] and Soderquist et al.[78] have exploited diazomethanes to prepare trialkylborane derivatives, the only related precedent for perfluoroarylboranes involves the rather slow transformation of the silylene adduct $(HCNtBu)_2SiB(C_6F_5)_3$ to $(HCNtBu)_2Si(C_6F_5)B(C_6F_5)_2$ upon standing at 20 °C for 3 months.[79] The present work establishes that electrophilic boranes react readily with a series of electronically diverse diazomethanes to provide a facile route to new sterically encumbered yet electrophilic borane derivatives. In this fashion a range of electrophilic boranes can easily be designed for specific applications in Lewis acid catalysis or chemistry. Indeed, we are currently exploring the applications of such boranes in "frustrated Lewis pair" chemistry and catalysis. The results of these studies will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and CIF files giving experimental and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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