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## ARTICLE TYPE

Reactions of Iodine-Nitrene Reagents with Boranes<sup>†</sup>Shawn Postle<sup>a</sup> and Douglas W. Stephan<sup>\*a,b</sup>

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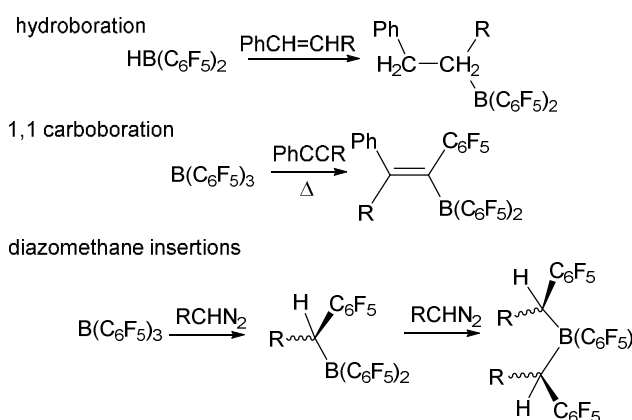
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5 Reactions of the boranes (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BR (R = C<sub>6</sub>F<sub>5</sub>, Ph, H) with the nitrene-iodine reagents XC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N=IPh, X = Me, Cl and MeSO<sub>2</sub>N=IPh effect the insertion of nitrene into the B-C and B-H bonds affording the species (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BN(SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X)R (X = Me, R = C<sub>6</sub>F<sub>5</sub> 1, Ph 3, H, 4, X = Cl, 5, X = NO<sub>2</sub>, 7) and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BN(SO<sub>2</sub>Me)H 6).

The Lewis acid chemistry of electrophilic boranes has been the subject of intense interest over the past two decades. In seminal work Piers and co-workers unveiled the ability of highly Lewis acidic boranes to catalyse hydrosilylations<sup>1-2</sup> while Marks exploited such species as co-catalysts for polymerization catalysis.<sup>3-4</sup> More recently, interest in electrophilic boranes was furthered with the advent of frustrated Lewis pair (FLP) chemistry.<sup>5-7</sup> In this area electrophilic boranes act in concert with sterically encumbered donors to effect the activation of a variety of small molecules.<sup>8</sup> Moreover, electrophilic boranes participate in FLP chemistry of H<sub>2</sub> mediated the metal-free catalytic hydrogenation of imines, enamines, silylenol ethers, olefins, alkynes and ketones.<sup>9-11</sup> Similarly, FLP approaches have led to the development of metal-free approaches to catalytic hydroamination.<sup>12</sup>

In all of these applications, the species B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> has been the principle electrophilic reagent employed for much of this chemistry.<sup>13</sup> This dominant position is largely due to the synthetic challenge associated with the installation of alternative electron withdrawing substituents on borane. Nonetheless, there have been some efforts in this regard. For example, years ago Marks prepared the fluorinated biphenyl derivative B(C<sub>6</sub>F<sub>4</sub>C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>14-15</sup> while more recently Gabbai and co-workers have exploited B(C<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>.<sup>16</sup> Other researchers have prepared a variety of species of the general formula RB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> including a number of chiral derivatives.<sup>17-21</sup> The standard synthetic methods for the preparation of such boranes include the use of nucleophilic aryl reagents in reactions with boron halides or the hydroboration of olefinic derivatives employing "Piers borane" HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>.<sup>22-25</sup> Erker et al. to have extensively exploited the interesting strategy to electrophilic vinyl-borane derivatives provided by 1,1 carboboration of alkynes.<sup>26-29</sup> Seeking new sterically demanding electrophilic boranes we have recently reported the insertion of diazomethanes, into B-C bonds affording a facile synthetic route to species of the form (RR'CH)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and (RR'CH)<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>30</sup> In a recent paper Braunschweig and coworkers have reported the use of azides to effect the insertion of nitrenes into B-C bonds.<sup>31</sup> In this manuscript, we further expand the exploitation of insertion

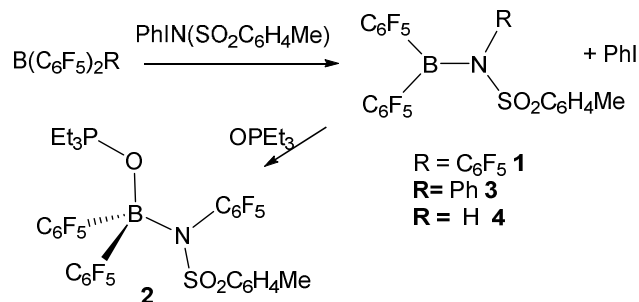
reactions, demonstrating that electron-deficient amino-boranes can be readily prepared via the insertion of nitrenes into B-C and B-H bonds using nitrene-iodide reagents.



Scheme 1 Synthetic routes to electrophilic borane derivatives

The borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was reacted with MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N=IPh<sup>32</sup> in pentane yielding a white slurry. Subsequent workup and isolation afforded **1** as clear and colorless crystals in 74% yield. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **1** was seen as a broad singlet at 43.6 ppm, while the <sup>1</sup>H NMR data were consistent with the incorporation of the tosylate fragment and the <sup>19</sup>F NMR spectrum showed three sets of resonances attributable to three distinct fluoroarene rings. Collectively these data inferred the formulation of **1** as (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BN(SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me)(C<sub>6</sub>F<sub>5</sub>) (Scheme 2). This notion was further supported by the high resolution mass spectral data which showed a [M]<sup>+</sup> ion of mass of 681.0068 while the computed value for the formula is 681.0085. Efforts to crystallize **1** for X-ray diffraction studies were unsuccessful. Combination of **1** with OPET<sub>3</sub> in toluene and standing at room temperature overnight afforded large rectangular crystals of **2** in 88% yield. The <sup>11</sup>B{<sup>1</sup>H} NMR signal for **2** at 1.41 ppm is consistent with the a quaternary B center. The corresponding <sup>19</sup>F spectrum was simplified to 6 resonances with a significant reduction of the meta-para gap, also consistent with a four coordinate B center. The <sup>1</sup>H NMR spectrum showed the signals consistent with the presence of the phosphine oxide residue and the tosylate fragment in a ratio of 1: 1. Collectively these data are consistent with the formulation of **2** as the phosphine-oxide borane adduct (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BN(SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me)(C<sub>6</sub>F<sub>5</sub>)•OPET<sub>3</sub> (Scheme 2). <sup>31</sup>P{<sup>1</sup>H} NMR peak at 80.74 ppm is 2.68 ppm downfield from the corresponding

resonance of  $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OPEt}_3$  inferring that **1** offers an increased Lewis acidity relative to the precursor borane  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>33</sup> This formulation of **2** was confirmed crystallographically (Figure 1). The X-ray data affirmed the pseudo-tetrahedral geometry about B and revealed B-N and B-O bond distances of 1.584(2) and 1.503(2) Å.



Scheme 2 Synthesis of 1-4

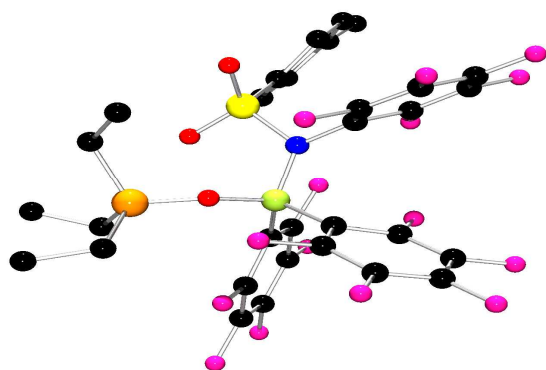


Figure 1. POV-ray depiction of **2**; C: black, B: yellow-green, O: red, S: yellow, N: blue, P: orange, F: pink, Hydrogen atoms have been omitted for clarity.

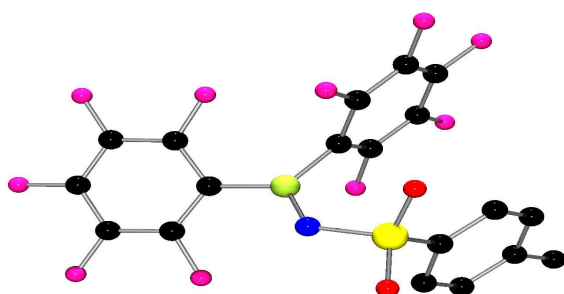
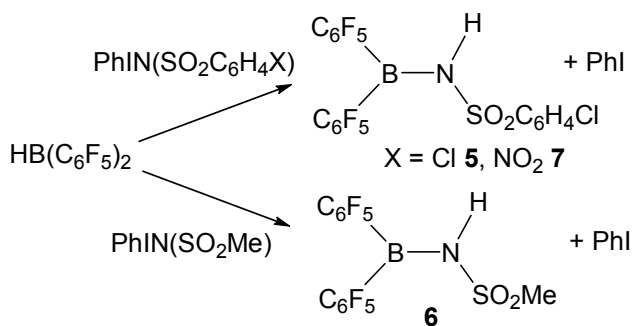


Figure 2. POV-ray depiction of **4**; C: black, B: yellow-green, O: red, S: yellow, N: blue, F: pink, Hydrogen atoms have been omitted for clarity.

The analogous reaction of  $\text{PhB}(\text{C}_6\text{F}_5)_2$  with  $\text{MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{IPh}$  proceeded in a similar fashion affording **3** precipitating from pentane. Recrystallization from  $\text{CH}_2\text{Cl}_2$  resulted in crystalline **3** in an isolated yield of 76%.  $^1\text{H}$  NMR data confirmed the incorporation of the tosylate fragment while the  $^{11}\text{B}\{^1\text{H}\}$  resonance at 42.00 ppm and the  $^{19}\text{F}$  signals at  $-131.42$ ,  $-131.62$ ,  $-150.95$ ,  $-151.59$ ,  $-161.06$ ,  $-131.42$  ppm were consistent with

three coordinate boron and inequivalent  $\text{C}_6\text{F}_5$  rings. These data together with mass of the molecular ion from high resolution MS (Calc, 591.0522, Found 591.0529) were consistent with the formulation of **3** as  $(\text{C}_6\text{F}_5)_2\text{BN}(\text{SO}_2\text{C}_6\text{H}_4\text{Me})\text{Ph}$ . Similarly, reaction of  $\text{HB}(\text{C}_6\text{F}_5)_2$  with  $\text{MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{IPh}$ , results in the formation of  $(\text{C}_6\text{F}_5)_2\text{BN}(\text{SO}_2\text{C}_6\text{H}_4\text{Me})\text{H}$  **4**. The  $^1\text{H}$  NMR resonance at 7.88 ppm is consistent with the NH fragment, while the  $^{11}\text{B}\{^1\text{H}\}$  NMR shift at 34.4 reflects a diminished Lewis acidity at B. While  $^{19}\text{F}$  NMR and HRMS data were also consistent with the formulation of **4**, X-ray crystallographic data confirmed it unambiguously (Figure 2). The B-N bond length in **4** was found to be 1.408(3) Å, significantly shorter than that seen in **2**. This reflects the strong  $\pi$ -bonding between the three coordinate B center and N.



Scheme 3 Synthesis of 5-7

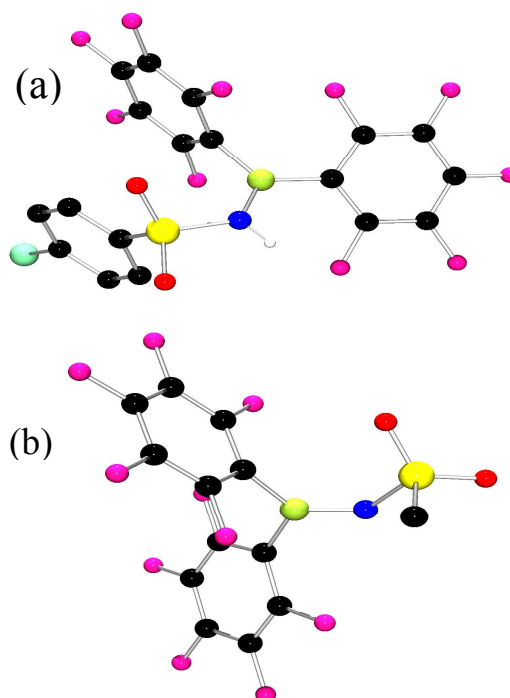


Figure 3. POV-ray depiction of (a) **5**, (b) **6**; C: black, B: yellow-green, O: red, S: yellow, N: blue, Cl: green, F: pink, Hydrogen atoms have been omitted for clarity.

In a similar manner reaction of  $\text{HB}(\text{C}_6\text{F}_5)_2$  with  $\text{ClC}_6\text{H}_4\text{SO}_2\text{N}=\text{IPh}$ ,  $\text{MeSO}_2\text{N}=\text{IPh}$  or  $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{IPh}$  proceed in a similar fashion to afford  $(\text{C}_6\text{F}_5)_2\text{BN}(\text{SO}_2\text{C}_6\text{H}_4\text{Cl})\text{H}$  **5**,  $(\text{C}_6\text{F}_5)_2\text{BN}(\text{SO}_2\text{Me})\text{H}$  **6** and  $(\text{C}_6\text{F}_5)_2\text{BN}(\text{SO}_2\text{C}_6\text{H}_4\text{NO}_2)\text{H}$  **7**,

respectively. NMR and mass spectral data (Figure 3) were consistent with the formulation of these products. The formulations of **5** and **6** were confirmed by X-ray crystallography. The B-N bond distances in **5** and **6** were found to be 1.407(2) and 1.396(4) Å. These data clearly demonstrate the impact on the  $\pi$ -donor character at N resulting from the electron withdrawing and electron donating character of the  $\text{ClC}_6\text{H}_4\text{SO}_2$  and  $\text{MeSO}_2$  substituents on N respectively. The preferential migration of the phenyl and H substituents to N affording **3-6** respectively, is consistent with bond strength arguments and analogous to that seen for related reactions of diazomethane derivatives with various boranes as well as with the migratory behaviour of borane substituents seen for 1,1 carborations of alkynes.

Performing the Gutmann-Beckett method on **4-7** yields  $^{31}\text{P}$  chemical shifts of 80.16, 80.52, 79.79 and 80.66 ppm respectively. While the resulting acceptor numbers correlate with the increasingly electron withdrawing sulfonyl substituents, the range of variability in the Lewis acidity is small.

Interestingly attempts to effect the analogous insertions employing  $\text{ClB}(\text{C}_6\text{F}_5)_2$  was found to provide **4-7** as products. While these reactions are thought to proceed via initial insertion into the B-Cl bond generating transient species of the form  $(\text{C}_6\text{F}_5)_2\text{BN}(\text{SO}_2\text{R})\text{Cl}$ , these species could neither be observed nor isolated. It is thought the N-Cl is highly reactive, scavenging H from either solvent or adventitious water. This is consistent with the general observation of the high sensitivity of the species **1-7** that presumably results from the presence of the electron withdrawing amide fragment.

## Conclusions

In summary, reactions of boranes with iodine-nitrene provides a new and convenient approach to the derivatization of electrophilic boranes providing unique amino-boranes. The utility of this strategy for modification of boron centers and the utility of these species in Lewis acid chemistry and catalysis is the subject of on-going study.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic and spectroscopic details are deposited Crystallographic data have been deposited in the Cambridge database. see DOI: 10.1039/b000000x/. CCDC 1041085-1041088 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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