

## Borole Formation by 1,1-Carbaboration

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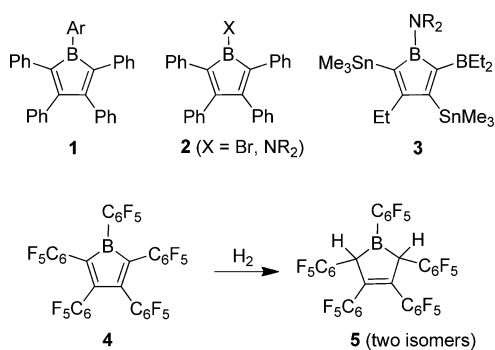
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**S** Supporting Information

**ABSTRACT:** Bis(trimethylsilylethynyl)diphenylamino-borane was reacted with the strong Lewis acid  $B(C_6F_5)_3$  at ambient temperature to give the borole **9** admixed with a small amount of its thermal follow-up product **12**. Compound **9** was subsequently stabilized by adduct formation with pyridine (**10**). Treatment of bis(trimethylsilylethynyl)phenylborane with  $B(C_6F_5)_3$  gave the borole **14**, which reacted with 3-hexyne to give the [4 + 2] cycloaddition product **15**.

Substituted and annulated boroles have found great interest as building blocks in materials science due to their special physical and optical features.<sup>1</sup> The antiaromatic boroles are very reactive.<sup>2</sup> Therefore, isolated borole examples are often highly substituted, often with up to five aromatic substituents or other bulky stabilizing groups. Many borole syntheses make use of nucleophilic reaction pathways involving multiple transmetalation sequences.<sup>3–5</sup> Typical examples (**1**, **2**, **4**) that were prepared in this way are depicted in Scheme 1. The high and

Scheme 1



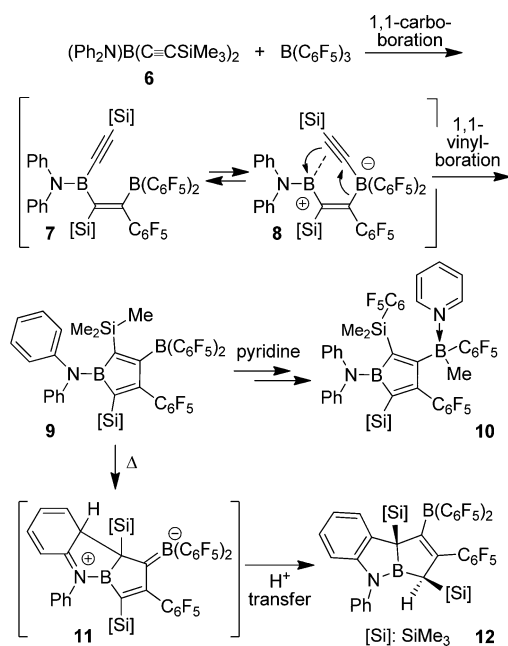
unusual reactivity that boroles may exhibit are illustrated by the reaction of Piers' penta(perfluorophenyl)borole (**4**) that even splits dihydrogen to form **5** (two isomers).<sup>6</sup> Wrackmeyer had reported about the potential use of the unique 1,1-carbaboration reaction<sup>7</sup> of suitably substituted alkynes that in a few instances led to boroles. Compound **3** is a typical example that was generated by 1,1-carbaboration of  $R_2NB(C\equiv C-SnMe_3)_2$  with  $BEt_3$  followed by subsequent rearrangement. Unfortunately, such reaction pathways apparently required the  $SnMe_3$  substituents as migrating groups at the time.<sup>8</sup>

Meanwhile much progress has been achieved in 1,1-carbaboration chemistry especially by using the much stronger Lewis acidic  $R-B(C_6F_5)_2$  boranes. We<sup>9</sup> and others<sup>10</sup> have developed series of 1,1-carbaboration sequences with such

reagents that are easy to perform and, therefore, are finding more and more practical application. This includes not only organometallic examples<sup>11</sup> but also advanced silole,<sup>12</sup> phosphole,<sup>13</sup> and even dihydroborole syntheses.<sup>14</sup> We have now applied the advanced 1,1-carbaboration scheme to borole synthesis and prepared first examples by this route that showed some interesting reaction behavior.

We prepared the amidoborane **6** by treatment of  $(Ph_2N)-BCl_2$  with  $Li-C\equiv C-SiMe_3$  (for details see the Supporting Information, SI). The borylacetylene **6** was then treated with  $B(C_6F_5)_3$  in a 1:1 molar ratio at ambient temperature. The reaction went to completion within a few hours to give the borole **9** admixed with a small amount of its thermal follow-up product **12** (see Scheme 2). Removal of the solvent gave **9** as a

Scheme 2

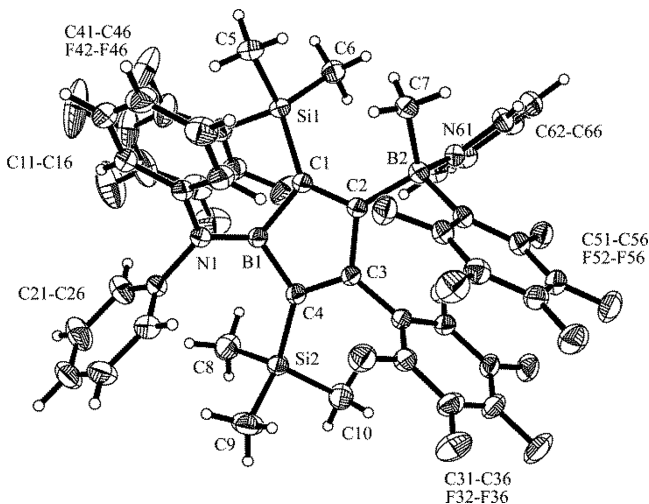


sensitive dark-red oil [ $\lambda_{max}$  ( $CH_2Cl_2$ ) = 360 nm]. Generated in the in situ experiment it was characterized by NMR spectroscopy. It shows a 1:1 intensity pair of  $^{11}B$  NMR resonances at  $\delta$  49.2 (NB) and 58.8 ( $B(C_6F_5)_2$ ) and  $^{19}F$  NMR signals of the carbon-bound  $C_6F_5$  group plus a double intensity set of *o*, *p*, *m*- $C_6F_5$  resonances of the adjacent  $B(C_6F_5)_2$  substituent. The borole core shows  $^{13}C$  NMR resonances at  $\delta$

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180.7, 162.6, 148.8, and 158.8. We have monitored a pair of  $^1\text{H}$  NMR  $\text{SiMe}_3$  signals with corresponding  $^{29}\text{Si}$  NMR resonances at  $\delta -9.0$  (Si2) and  $-9.6$  (Si1) (numbering scheme see Figure 1). The phenyl substituents at nitrogen are inequivalent and, consequently, give rise to two sets of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals (for details see the SI).



**Figure 1.** A projection of the molecular geometry of compound **10** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg.): N1–B1 1.408(3), B1–C1 1.588(3), C1–C2 1.361(3), C2–C3 1.547(3), C3–C4 1.358(3), B1–C4 1.595(3), C2–B2 1.633(3), B2–C7 1.630(3), B2–N61 1.633(3), B2–C51 1.652(3), C1–B1–C4 106.7(2).

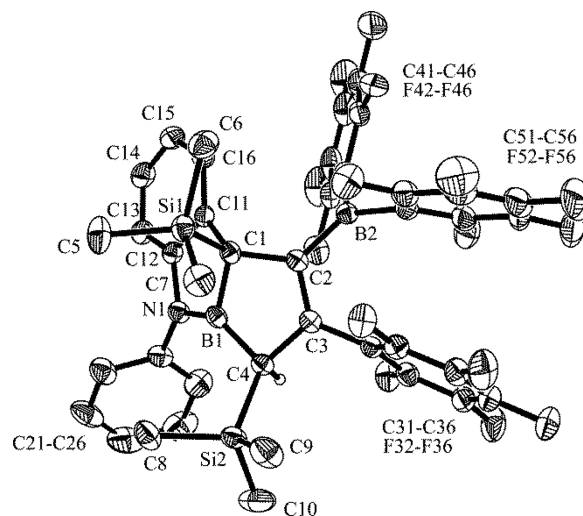
The in situ generated borole was treated with pyridine. Workup gave the product **10** in 46% yield as an orange red solid. The X-ray crystal structure analysis showed a planar five-membered borole framework with a pronounced double–single–double carbon–carbon bond alternation (see Figure 1). The boron atom bears the  $\text{Ph}_2\text{N}$  substituent with a short N1–B1 bond. A trimethylsilyl substituent is bonded to the adjacent borole carbon atom C4, and we find the  $\text{C}_6\text{F}_5$  group attached at C3. The remaining silyl and boryl substituents have undergone an unusual  $\text{CH}_3/\text{C}_6\text{F}_5$  exchange (as it is sometimes observed in silyl/boryl systems).<sup>15</sup> Consequently, we find a  $\text{SiMe}_2(\text{C}_6\text{F}_5)$  substituent attached at the borole carbon atom C1. The resulting  $\text{BCH}_3(\text{C}_6\text{F}_5)$  substituent at C2 has the pyridine donor attached to it ( $\sum\text{B2}^{\text{CCB}} = 331.6^\circ$ ). Both the borole boron atom B1 and its adjacent nitrogen atom N1 exhibit slightly distorted trigonal-planar coordination geometries ( $\sum\text{B1}^{\text{NCC}} = 356.3^\circ$ ,  $\sum\text{N1}^{\text{CCB}} = 359.0^\circ$ ).

In solution the borole **10** shows a UV–vis absorption at  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2) = 389 \text{ nm}$  ( $\epsilon = 3409$ ). We have observed the borole  $\text{Ph}_2\text{N-B}$   $^{10}\text{B}$  NMR feature at  $\delta 47.6$  and the  $^{10}\text{B}$  NMR signal of the tetracoordinate boron center at  $\delta -2.2$ . The  $^{29}\text{Si}$  NMR signals of the silyl substituents occur at  $\delta -11.2$  ( $\text{SiMe}_3$ ) and  $-12.0$  ( $\text{SiMe}_2$ ). Due to the persistent boron B2 chirality, the  $\text{SiMe}_2(\text{C}_6\text{F}_5)$  substituent features a pair of diastereotopic methyl groups [ $^1\text{H}$  NMR:  $\delta -0.27, -0.59$  (each 3H)].

We assume that the borole formation from **6** by the reaction with  $\text{B}(\text{C}_6\text{F}_5)_3$  follows a typical sequential pathway as it had been suggested analogously for silole or phosphole formation.<sup>7,12,13</sup> 1,1-Carboboration of one of the trimethylsilylacetylide moieties could then lead to the intermediate **7** (see Scheme 2). This would then react by means of (reversible) alkynyl shift

between the boron atoms to generate **8**. Subsequent 1,1-vinylboration would then directly lead to the borole system **9**.

Boroles are very reactive heterocycles,<sup>2,6</sup> and compound **9** is no exception. Upon heating ( $100^\circ\text{C}$ , overnight) it readily attacked the phenyl group at nitrogen in the proximal position to the  $\text{B}(\text{C}_6\text{F}_5)_2$  substituent. From the reaction mixture, we isolated the annulated dihydroborole product **12** as a pale yellow solid in 60% yield (Figure 2).



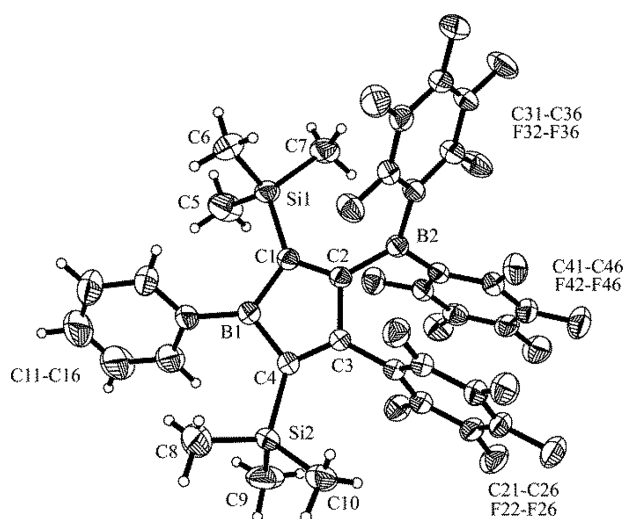
**Figure 2.** Molecular geometry of compound **12** [thermal ellipsoids are shown with 30% probability; hydrogen are omitted due to clarity (except C4)]. Selected bond lengths (Å) and angles (deg.): B1–N1 1.416(4), B1–C1 1.565(5), B1–C4 1.557(5), C1–C2 1.539(4), C2–C3 1.373(4), C3–C4 1.522(4), B2–C2 1.527(5), N1–B1–C4 135.8(3), B1–N1–C11 108.6(3), C1–B1–C4 112.1(3).

The X-ray crystal structure analysis revealed the formation of the new benzannulated heterobicyclo[3.3.0]octadiene framework with a planar-tricoordinate bridgehead boron atom ( $\sum\text{B1}^{\text{NCC}} = 356.9^\circ$ ). The B1–N1 bond is short, and the nitrogen atom also shows a planar-tricoordinate geometry ( $\sum\text{N1}^{\text{CCB}} = 358.9^\circ$ ). The substituted dihydroborole subunit<sup>16</sup> contains a pair of B–C( $\text{sp}^3$ ) single bonds, a pair of C( $\text{sp}^3$ )–C( $\text{sp}^2$ ) single bonds and the C2=C3 double bond to which the  $\text{C}_6\text{F}_5$  and the  $\text{B}(\text{C}_6\text{F}_5)_2$  substituents are bonded. The boron atom B2 features a planar-tricoordinate bonding geometry ( $\sum\text{B2}^{\text{CCB}} = 359.7^\circ$ ). The boryl plane is markedly rotated out of conjugation with the adjacent C2=C3 double bond [ $\angle \text{C3–C2–B2–C51} = -124.5(3)$ ] (see the SI for the spectroscopic characterization of compound **12**).

In Scheme 2 a possible pathway of the formation of the product **12** is depicted. One might assume that the reactive electron-deficient borole heterocycle is intramolecularly attacked by the electron-rich amino-arene to give a zwitterionic intermediate **11** that contains a borata-diene moiety (which is just a  $\pi$ -resonance form of a stabilized  $\alpha$ -boryl carbanion).<sup>17</sup> Proton transfer then would complete this electrophilic aromatic substitution sequence with formation of the observed product **12**.

The formation of a borole by the 1,1-carboboration route is not limited to the example of compounds **9** and **10** described above. We treated  $\text{PhBCl}_2$  with 2 equiv of lithium trimethylsilylacetylide. The in situ generated bis(alkynyl)borane **13** was then reacted with  $\text{B}(\text{C}_6\text{F}_5)_3$  to give the borole **14** formed by an 1,1-carboboration sequence [red crystalline

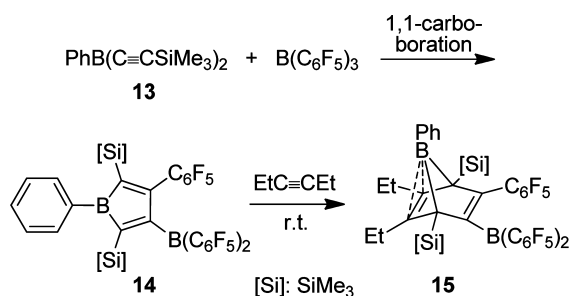
solid, 43% isolated,  $^{11}\text{B}$  NMR:  $\delta$  74.0, 65.3]. Compound **14** was characterized by X-ray diffraction (see Figure 3).



**Figure 3.** Molecular geometry of compound **14** [thermal ellipsoids are shown with 30% probability]. Selected bond lengths (Å) and angles (deg.): B1–C11 1.545(5), B1–C1 1.606(4), B1–C4 1.587(5), C1–C2 1.359(4), C2–C3 1.532(4), C3–C4 1.345(4), B2–C2 1.562(4),  $\sum\text{B1}^{\text{CCC}}$  360.0, B1–C1–C2–C3  $-2.3(3)$ , C1–C2–C3–C4 1.0(4).

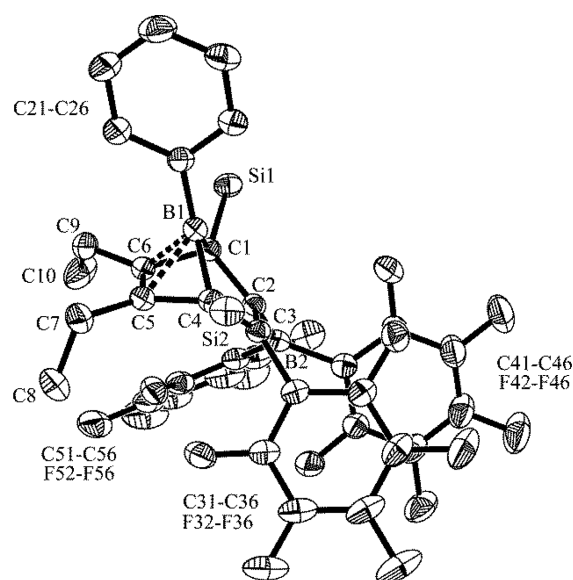
For further chemical characterization compound **14** was reacted with 3-hexyne<sup>18</sup> in a 1:1 molar ratio to finally isolate the [4 + 2] cycloaddition product **15** as a yellow crystalline solid [62% yield,  $^{11}\text{B}$  NMR:  $\delta$  61.6 ( $\text{B}(\text{C}_6\text{F}_5)_2$ ),  $-9.8$  (BPh)] (Scheme 3). The X-ray crystal structure analysis showed a

Scheme 3



trigonal-planar boron atom inside the bicyclic framework ( $\sum\text{B1}^{\text{CCC}} = 359.4^\circ$ ) that is, however, markedly leaning over to the C5=C6 double bond [respective pairs of bond lengths: B1–C1/C4 1.645(3)/1.644(3) Å, B1–C5/C6 1.782(3)/1.777(3) Å, B1–C2/C3 2.533/2.488 Å, see Figure 4].

Due to their antiaromatic character, boroles are very reactive heterocycles and consequently tedious to make. Many syntheses involve transmetalation reactions under carefully controlled reaction conditions, often making use of the respective tin and/or zirconium derivatives. Carbon-functionalized borole derivatives are difficult to obtain by these established routes. The 1,1-carboration sequence seems to provide a useful synthetic alternative, especially by using the strongly electrophilic  $\text{RB}(\text{C}_6\text{F}_5)_2$  reagents as we have shown in our study. Using these current advanced developments of the “Wrackmeyer reaction”<sup>7,9</sup> seems to provide an easy and convenient new entry to interesting boryl-functionalized



**Figure 4.** Molecular geometry of compound **15** [thermal ellipsoids are shown with 30% probability; hydrogens and Me substituents at Si1 and Si2, respectively, are omitted for clarity]. Selected bond lengths (Å) and angles (deg.): B1–C21 1.577(3), B2–C2 1.543(3), C2–C3 1.354(3), C5–C6 1.392(3), C1–C2 1.528(3), C1–C6 1.512(3), B1–C1–C6 68.4(1), B1–C4–C5 68.4(1), B1–C1–C2 105.9(2),  $\sum\text{B1}^{\text{C21C1C4}}$  359.4,  $\sum\text{B2}^{\text{CCC}}$  359.7.

isolable borole derivatives with a possible potential of further derivatization or functionalization of the antiaromatic borole nucleus.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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