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Borole Formation by 1,1-Carboboration

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Supporting Information Placeholder

ABSTRACT: Bis(trimethylsilylethynyl)diphenylaminoborane 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.¹ The anti-aromatic boroles are very reactive.² 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 transmetallation sequences.^{3,4,5} Typical examples (1, 2, 4) that were prepared in this way are depicted in Scheme 1. The high and 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).⁶ Wrackmeyer had reported about the potential use of the unique 1,1-carboboration reaction7 of suitably substituted alkynes that in a few instances led to boroles. Compound 3 is a typical example that was generated by 1,1-carboboration of $R_2NB(C \equiv C-SnMe_3)_2$ with BEt₃ followed by subsequent rearrangement. Unfortunately, such reaction pathways apparently required the SnMe₃ substituents as migrating groups at the time.⁸

Scheme 1



Meanwhile much progress has been achieved in 1,1carboboration chemistry especially by using the much

stronger *Lewis* acidic R-B(C_6F_5)₂ boranes. We⁹ and others¹⁰ have developed a large series of 1,1–carboboration sequences with such reagents that are easy to perform and, therefore, are finding more and more practical application. This includes¹¹ organometallic examples, but also advanced silole¹², phosphole¹³ and even dihydroborole syntheses¹⁴. We have now applied the advanced 1,1–carboboration scheme to borole synthesis and prepared first examples by this route that showed some interesting reaction behavior.

Scheme 2



We prepared the amidoborane **6** by treatment of $(Ph_2N)BCl_2$ with Li-C=CSiMe₃ (for details see the Supporting Information). 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 sensitive dark red oil [λ_{max} (CH₂Cl₂) = 360 nm]. Generated in the in situ experiment it was characterized by NMR spectroscopy. It shows a 1 : 1 intensity pair of ¹¹B NMR resonances at δ **49.2** (NB) and 58.8 (B(C₆F₅)₂) and ¹⁹F NMR signals of the

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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 ¹³C NMR resonances at δ 180.7, 162.6, 148.4, and 158.8. We have monitored a pair of ¹H NMR SiMe₃ signals with corresponding ²⁹Si NMR resonances at δ -9.0 (Si) and -9.6 (Si2)(numbering scheme see Figure 1). The phenyl substituents at nitrogen are inequivalent and, consequently, give rise to two sets of ¹H and ¹³C NMR signals (for details see the Supporting Information).

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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 Ph₂N substituent with a short N1-B1 bond. A trimethylsilyl substituent is bonded to the adjacent borole carbon atom C₄ and we find the C_6F_5 group attached at C3. The remaining silyl and boryl substituents have undergone an unusual CH_3/C_6F_5 exchange (as it is sometimes observed in silyl/boryl systems).¹⁵ Consequently, we find a $SiMe_2(C_6F_5)$ substituent attached at the borole carbon atom C1. The resulting $BCH_3(C_6F_5)$ substituent at C2 has the pyridine donor attached to it ($\sum B_2^{CCC}$ 331.6°). Both the borole boron atom B1 and its adjacent nitrogen atom N1 exhibit slightly distorted trigonal-planar coordination geometries $(\Sigma B_1^{NCC} = 356.3^\circ, \Sigma N_1^{CCB} = 359.0^\circ).$



Figure 1. A projection of the molecular geometry of compound **10** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (grad.): 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).

In solution the borole **10** shows a UV/Vis absorption at $\lambda_{max}(CH_2CI_2) = 389$ nm ($\epsilon = 3400$). We have observed the borole Ph₂N–B ¹⁰B NMR feature at δ 47.6 and the ¹⁰B NMR signal of the tetracoordinate boron center at δ -2.2. The ²⁹Si NMR signals of the silyl substituents occur at δ -11.2 (SiMe₃) and -12.0 (SiMe₂). Due to the persistent boron B2 chirality the SiMe₂(C₆F₅) substituent features a pair of diastereotopic methyl groups [¹H NMR: δ -0.27, -0.59 (each 3H)].

We assume that the borole formation from 6 by the reaction with $B(C_6F_5)_3$ follows a typical sequential pathway as it had been suggested analogously for silole or phosphole for-2

mation.^{7,12,13} 1,1–Carboboration of one of the trimethylacetylide 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^{2,6} and compound **9** is no exception. Upon heating (100 °C, overnight) it readily attacked the phenyl group at nitrogen in the proximal position to the $B(C_6F_5)_2$ substituent. From the reaction mixture, we isolated the annulated dihydroborole product **12** as a pale yellow solid in 60% yield.

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 ($\sum B1^{NCC} = 356.9^{\circ}$). The B1-N1 bond is short and the nitrogen atom also shows a planar-tricoordinate geometry ($\sum N1^{CCB} = 358.9^{\circ}$). The substituted dihydroborole subunit¹⁶ contains a pair of typical B-C(sp³) single bonds, a pair of C(sp³)-C(sp²) single bonds and the C2=C3 double bond to which the C₆F₅ and the B(C₆F₅)₂ substituents are bonded. The boron atom B2 features a planar-tricoordinate bonding geometry ($\sum B2^{CCC} = 359.7^{\circ}$). The boryl plane is markedly rotated out of conjugation with the adjacent C2=C3 double bond [Θ C3-C2-B2-C51 -124.5(3)] (see the Supporting Information for the spectroscopic characterization of compound 12).



Figure 2. Molecular geometry of compound 12 [thermal ellipsoids are shown with 30% probability; hydrogen are omitted due to clarity (exept C4)]. Selected bond lengths (Å) and angles (grad.): 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).

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 π -resonance form of a stabilized α -boryl cabanion¹⁷). Proton transfer then would complete this electrophilic aromatic substitution sequence with formation of the observed product 12.

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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 PhBCl₂ with two equivalents of lithium trimethylsilyacetylide. The in situ generated bis(alkynyl)borane **13** was then reacted with $B(C_6F_5)_3$ to give the borole **14** formed by an 1,1-carboboration sequence [red crystalline solid, 43% isolated, ¹¹B NMR: δ 74.0, 63.0]. Compound **14** was characterized by X-ray diffraction (see Figure 3).

Scheme 3



Figure 3. Molecular geometry of compound 14 [thermal ellipsoids are shown with 30% probability]. Selected bond lengths (Å) and angles (grad.): 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), Σ B1^{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-hexyne¹⁸ in a 1:1 molar ratio to finally isolate the [4+2] cycloadditon product 15 as an yellow crystaline solid [50% yield, ¹¹B NMR: δ 61.6 (B(C₆F₅)₂), -9.9 (BPh)]. The X-ray crystal structure analysis showed a trigonal-planar boron atom inside the bicyclic framework (Σ B1^{CCC} = 359.4°) that is, however, markedly leaning over to the C5=C6 double bond [respective pairs of bond lenths: 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 transmetallation reactions under carefully controlled reaction conditions, often making use of the respective tin and/or zirconium derivatives. Carbonfunctionalized borole derivatives are difficult to obtain by these established routes. The 1,1-carboboration sequence seems to provide a useful synthetic alternative, especially by using the strongly electrophilic $RB(C_6F_5)_2$ reagents as we have shown in our study. Using these current advanced developments of the "Wrackmeyer-reaction"^{7,9} seems to provide an easy and convenient new entry to interesting boryl-functionalized isolable borole derivatives with a possible potential of further derivatization or functionalization of the anti-aromatic borole nucleus.



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 (grad.): 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), $\Sigma B1^{C21C1C4}$ 359.4, $\Sigma B2^{CCC}$ 359.7.

ASSOCIATED CONTENT

Supporting Information

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

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SYNOPSIS TOC

