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Synthesis of 9-Borafluorene Analogues Featuring a Three-Dimensional 1,1'-Bis(*o*-carborane) Backbone

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Abstract

The synthesis of [1,1'-bis(*o*-carboranyl)]boranes was achieved through the deprotonation of 1,1'-bis(*o*-carborane) reagents followed by salt metathesis with (*i*-Pr)₂NBCl₂. X-ray crystallography confirms planar central BC₄ rings and Gutmann-Beckett studies reveal an increase in Lewis acidity at the boron center in comparison to their biphenyl congener, 9-borafluorene.

Polyhedral carborane clusters are viewed as three-dimensional aromatic analogues to the ubiquitous two-dimensional aromatic arenes (e.g. benzene).¹ These species share high delocalization within the cage and ring resulting in high kinetic stability.² The significant difference is that carboranes exhibit aromaticity while benzene is a classical aromatic molecule. Due to their unique steric profile and electronic structure, *o*-carboranes have been explored as a substitute for phenyl groups in molecules. The lability of the C-H vertices (pK_a = 22 *c.f.* benzene = 43) of *o*-carborane facilitates selective derivatization to incorporate carboranes into molecular architectures.³ 1,1'-Bis(*o*-carborane, **B**) can be viewed as a three-dimensional analogue to a biphenyl unit, a common ligand scaffold in organometallic chemistry (**A**, Figure 1).⁴ The facile manipulation and high stability has resulted in complexes featuring **B** being investigated in medicine and electronic materials.^{2a, 5}

9-Borafluorenes (**1A**) contain a biphenyl backbone linked by a tricoordinate boron center and have been recognized as attractive targets for molecular sensors⁶, reagents for the synthesis of polycyclic aromatic hydrocarbons⁷ as well as components in organic light emitting diodes (OLEDs)⁸ and organic photovoltaics (OPVs).⁹ The vacant p_z orbital on the boron center extends conjugation throughout the three fused rings. We envisioned that 1,1'-

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Conflicts of interest

There are no conflicts to declare.

bis(*o*-carborane) could replace the biphenyl framework in 9-borafluorenes to generate a species with a three-dimensional backbone.

The initial strategies to access the target [1,1'-bis(*o*-carboranyl)]boranes were inspired by effective methods for the synthesis of 9-borafluorenes, specifically transmetalation of a stannole or dilithiated species with RBX_2 .¹⁰ The corresponding [1,1'-bis(*o*-carboranyl)]stannole^{4j} was recently reported and the [1,1'-bis(*o*-carboranyl)]dilithium species¹¹ has been generated and utilized *in situ*. Unfortunately, all attempts to access the [1,1'-bis(*o*-carboranyl)]borane via these reagents were unsuccessful (Tables S-1 and S-2). In addition, the transmetalation reaction with the [1,1'-bis(*o*-carboranyl)]magnesium species did not generate the desired boracycle (Table S-3). Potassium bis(trimethylsilyl)amide [$\text{K}(\text{HMDS})$] is also an effective base for the deprotonation of the C-H vertices and the resultant salt, $\text{K}_2[\text{B}]$, is easier to generate and offers enhanced solubility in comparison to the dilithiated reagent.^{4k,12} After several attempts using a variety of conditions (Table S-4), the room temperature generation of $\text{K}_2[\text{B}]$ in THF followed by addition of $(\text{tPr})_2\text{NBCl}_2$ proved to be an effective method to furnish the desired [1,1'-bis(*o*-carboranyl)]borane **1B**. Acquiring a $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture showed a three-coordinate peak at 32.9 ppm, slightly shifted from $(\text{tPr})_2\text{NBCl}_2$ (31.3 ppm), coupled with the disappearance of one of the diagnostic signals corresponding to **B** (−2.2 ppm) and emergence of a doublet at 1.8 ppm, suggesting restricted rotation about the C-C bond in **B**.¹³ After isolation, the product was dissolved in CDCl_3 and the subsequent ^1H NMR spectrum contained no C-H carborane signal at 3.51 ppm, indicating successful deprotonation of the carboranyl moieties and the product was isolated in 89% yield (Scheme 1). The identity of **1B** was further confirmed based on single crystal X-ray diffraction studies (Figure 2). The synthetic route was compatible with the octa-methylated variant **1BMe₈**¹⁴ featuring a $^{11}\text{B}\{^1\text{H}\}$ NMR resonance at 33.7 ppm corresponding to the $(\text{tPr})_2\text{NB}$ -center, and a singlet at 6.3 ppm resulting from $\kappa^2\text{-C,C'}$ -chelation of the bis(*o*-carborane). X-ray diffraction studies confirmed the structural identity of **1BMe₈**, which was isolated in 67% yield (Figure 2).

A notable structural feature of **1B** and **1BMe₈** are highly planar central BC_4 rings (maximum deviation from planarity = 0.029 Å and 0.011 Å, respectively), which is comparable to their borafluorene counterpart **1A** (0.020 Å). The boron atom of the central ring and adjacent nitrogen atom of **1B** are trigonal planar [Σ_{angles} : $\text{B}(1) = 360.0(18)^\circ$ and $\text{N}(1) = 360.0(17)^\circ$, Table 1]. Positional disorder of the isopropyl groups on the nitrogen atom of **1BMe₈** prevents an in-depth analysis of the metrical parameters of the substituents. The endocyclic carbon-carbon bonds of **1B** and **1BMe₈** are longer than **1A**^{10b} [**1B**: C(1)-C(2) 1.649(3) Å, C(2)-C(3) 1.528(3) Å, and C(3)-C(4) 1.649(3) Å, **1BMe₈**: C(1)-C(2) 1.652(3) Å, C(2)-C(3) 1.524(3) Å, and C(3)-C(4) 1.646(3) Å, **1A**: C(1)-C(2) 1.418(3) Å, C(2)-C(3) 1.474(3) Å, and C(3)-C(4) 1.413(3) Å] but contracted from the parent **B^{3j}** [C(1)-C(2) 1.630(3) Å, C(2)-C(3) 1.528(3) Å, and C(3)-C(4) 1.649(3) Å]. The B-N bond lengths of **1B** and **1BMe₈** are slightly shorter compared to previously reported B-N length of **1A** [1.371(3) Å and 1.384(4) Å *c.f.* 1.396(3) Å]^{10b, 15}, indicating strong π -donation from the nitrogen lone pair to boron.¹⁶

The UV-Vis spectra of **1B** and **1BMe₈** in CH_2Cl_2 (Figure 3A) exhibit absorption maxima at 232 and 233 nm, respectively, blueshifted from **1A** (248 nm).^{10b} Cyclic voltammetry (CV)

measurements conducted on **1B** show a quasi-reversible one-electron reduction wave at -0.93 V and a second irreversible one-electron reduction at -1.86 V versus the ferrocenium/ferrocene couple (Fc^+/Fc). In comparison, **1BMe₈** exhibits only an irreversible reduction at -2.09 V whereas **1A** showed only a reversible reduction at -2.95 V, indicating that the bis(*o*-carboranyl) backbone imparts an electron-withdrawing effect facilitating reduction (Figure 3B).^{10b}

In order to understand the electronic effects of the bis(*o*-carboranyl) ligand scaffold, density functional theory (DFT) calculations were carried out. The geometries of **1A**, **1B**, and **1BMe₈** were optimized based on the X-ray structure of **1B** at the PBE-D3(BJ):TZP level, and single-point calculations were carried out at the B3LYP-D3(BJ):TZ2P level of theory (Figure S-13). The frontier orbital diagrams for **1B** and **1BMe₈** are similar, where the highest occupied molecular orbital (HOMO) is predominantly of π -character with respect to the B-N fragment, and the lowest occupied molecular orbital (LUMO) primarily resides on the bis(*o*-carboranyl) borane fragment. In contrast to the HOMO for **1A** is entirely on the biphenyl fragment with no contribution from the amine, and the LUMO for **1A** is localized on the biphenyl borane fragment. The HOMO-LUMO gaps for **1B** and **1BMe₈** are comparable (5.99 eV and 6.03 eV, respectively), and significantly larger than **1A** (4.17 eV). These data corroborate similar absorption maxima for **1B** and **1BMe₈** as well as a bathochromic shift relative to the absorption maximum of **1A** (Figure 3A). The calculated higher-lying LUMO for **1BMe₈** (-1.74 eV) relative to that of **1B** (-2.05 eV) is consistent with the observed more negative reduction potential for **1BMe₈** (-2.09 V and -1.86 V, respectively; Figure 3B).

To experimentally gauge Lewis acidity, the Gutmann-Beckett method was utilized.¹⁷ This method involves the addition of an excess of Et_3PO to a solution of the borane and monitoring the change in chemical shift of the $^{31}\text{P}\{^1\text{H}\}$ NMR signal ($\delta_{31\text{Psample}} - 41.0$). Multiplying this value by 2.21 gives the acceptor number (AN), where a greater AN signifies stronger Lewis acidity. The AN of **1A** is 13.5 in C_6D_6 ^{10b} and performing the analogous study with **1B** gave an AN value of 15.3. Methyl substitution at the peripheral boron vertices have an inductive effect, in this case acting as electron-withdrawing groups.^{3k, 18} Subsequent Gutmann-Beckett studies of **1BMe₈** corroborated this hypothesis with an AN of 20.3, aligning with an increase of Lewis acidity at the boron center.

In summary, we have taken advantage of the lability of the C-H bonds of 1,1'-bis(*o*-carborane) to access 9-borafluorene analogues with a three-dimensional backbone. These species represent the first examples of 1,1'-bis(carboranyl)boranes and feature a highly planar central ring with enhanced Lewis acidity in comparison to 9-borafluorenes. Methyl substitution at the 8,9,10,12-B-vertices results in an increase of the overall Lewis acidity of the molecule. The results demonstrate the potential of utilizing bis(*o*-carboranes) as biphenyl analogues to create unique boracyclic architectures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig 1. Relationship of biphenyl (**A**) to 1,1'-bis(*o*-carborane) (**B**) and the corresponding chelated boranes investigated in this work.

Fig 2. Solid-state structures of **1B** and **1BMe₈**. Thermal ellipsoids are depicted at 50% probability and hydrogen atoms are removed for clarity. The diisopropyl group in **1BMe₈** is positionally disordered and only the major component is shown.

Fig 3.

A) UV-Vis absorption emission spectra for **1B** and **1BMe₈** obtained from solutions of CH₂Cl₂ ($\lambda = 232$ and 233 nm respectively). **B)** Cyclic voltammograms of **1B** and **1BMe₈** recorded in anhydrous tetrahydrofuran with 0.1 M [NⁿBu₄] [PF₆] and referenced to the ferrocenium/ferrocene redox couple (Fc⁺/Fc; scan rate = 0.1 V/s).

Scheme 1.
Synthesis of **1B** and **1BMe₈**.

Table 1.Salient bond lengths (Å) and angles [°] in compounds **1B**, **1BMe₈**, and **1A**.

	1B	1BMe₈	1A
B(1)-C(1)	1.631(3)	1.622(4)	1.593(3)
C(1)-C(2)	1.649(3)	1.652(3)	1.418(3)
C(2)-C(3)	1.528(3)	1.524(3)	1.474(3)
C(3)-C(4)	1.649(3)	1.646(3)	1.413(3)
C(4)-B(1)	1.630(3)	1.626(4)	1.601(3)
B(1)-N(1)	1.371(3)	1.384(4)	1.396(3)
N(1)-B(1)-C(4)	126.06(19)	125.50(2)	128.97(13)
C(1)-B(1)-N(1)	125.61(18)	125.40(2)	127.51(19)
C(1)-B(1)-C(4)	108.33(16)	109.00(2)	103.44(17)
B(1)-N(1)-C(5)	119.94(17)		120.90(2)
B(1)-N(1)-C(8)	120.09(18)		119.76(18)
C(5)-N(1)-C(8)	119.96(16)		119.35(19)