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Synthesis of 9-borafluorene analogues featuring a three-dimensional 1,1′-bis(*o*-carborane) backbone†

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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 $(^{i}Pr)_2NBCl_2$. X-ray crystallography confirms planar central BC_4 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 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 three-dimensional aromaticity while benzene is a classical π 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 *cf.* 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**, Fig. 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 sensors,[6] reagents for the synthesis of polycyclic aromatic hydrocarbons[7] 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′-bis(*o*-carborane) could replace the biphenyl framework in 9-borafluorenes to generate a species with a three-dimensional backbone.

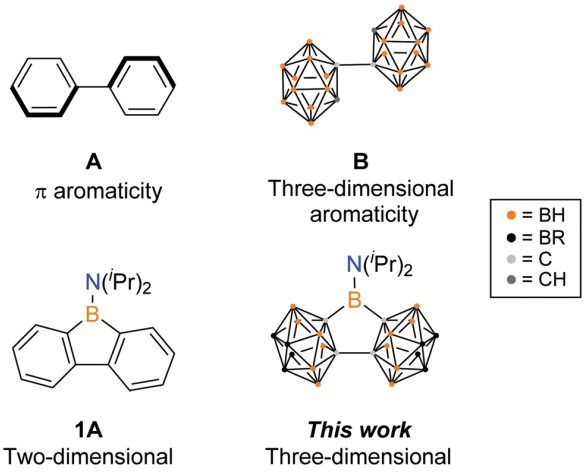

Fig. 1 Relationship of biphenyl (**A**) to 1,1′-bis(*o*-carborane) (**B**) and the corresponding chelated boranes investigated in this work.

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 transmetallation 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 species[11] 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, ESI†). In addition, the transmetallation reaction with the [1,1′-bis(*o*-carboranyl)]magnesium species did not generate the desired boracycle (Table S-3, ESI†). Potassium bis(trimethylsilyl)amide [K(HMDS)] is also an effective base for the deprotonation

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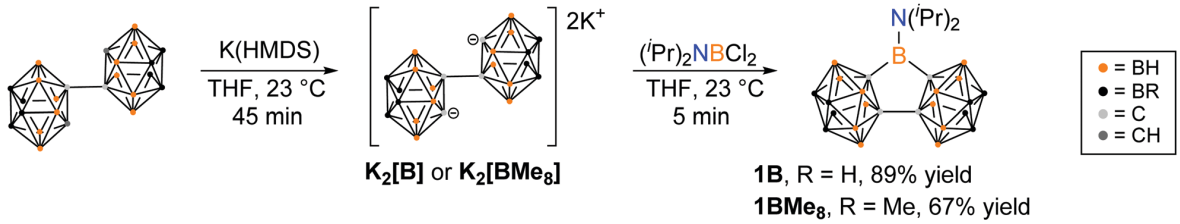
of the C–H vertices and the resultant salt, **K_2[B]**, is easier to generate and offers enhanced solubility in comparison to the dilithiated reagent.[4k,12] After several attempts using a variety of conditions (Table S-4, ESI†), the room temperature generation of **K_2[B]** in THF followed by addition of $(^iPr)_2NBCl_2$ proved to be an effective method to furnish the desired [1,1′-bis(*o*-carboranyl)]borane **1B**. Acquiring a $^{11}B\{^1H\}$ NMR spectrum of the crude reaction mixture showed a three-coordinate peak at 32.9 ppm, slightly shifted from $(^iPr)_2NBCl_2$ (31.3 ppm), coupled with the disappearance of one of the diagnostic signals corresponding to **B** (−2.2 ppm) and emergence of a singlet at 1.7 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 (Fig. 2). The synthetic route was compatible with the octa-methylated variant **$1BMe_8$**[14] featuring a $^{11}B\{^1H\}$ NMR resonance at 33.7 ppm corresponding to the $(^iPr)_2NB$-center, and a singlet at 6.0 ppm resulting from κ^2-C,C′-chelation of the bis(*o*-carborane). X-ray diffraction studies confirmed the structural identity of **$1BMe_8$**, which was isolated in 67% yield (Fig. 2).

A notable structural feature of **1B** and **$1BMe_8$** 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}: B(1) = 360.0(18)° and N(1) = 360.0(17)°, Table 1]. Positional disorder of the isopropyl groups on the nitrogen atom of **$1BMe_8$** prevents an in-depth analysis of the metrical parameters of the substituents. The endocyclic carbon–carbon bonds of **1B** and **$1BMe_8$** 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, **$1BMe_8$**: 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 **$1BMe_8$** are slightly shorter compared to the previously reported B–N length of **1A** [1.371(3) Å and 1.384(4) Å *cf.* 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 **$1BMe_8$** in CH_2Cl_2 (Fig. 3A) exhibit absorption maxima at 232 and 233 nm, respectively, blue-shifted from **1A** (248 nm).[10b] Cyclic voltammetry (CV) measurements conducted on **1B** show an irreversible one-electron reduction at −1.86 V *versus* the ferrocenium/ferrocene couple (Fc^+/Fc). In comparison, **$1BMe_8$** exhibits 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 (Fig. 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 **$1BMe_8$** 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 (Fig. S-19, ESI†). The frontier orbital diagrams for **1B** and **$1BMe_8$** are similar,



Scheme 1 Synthesis of **1B** and **$1BMe_8$**.

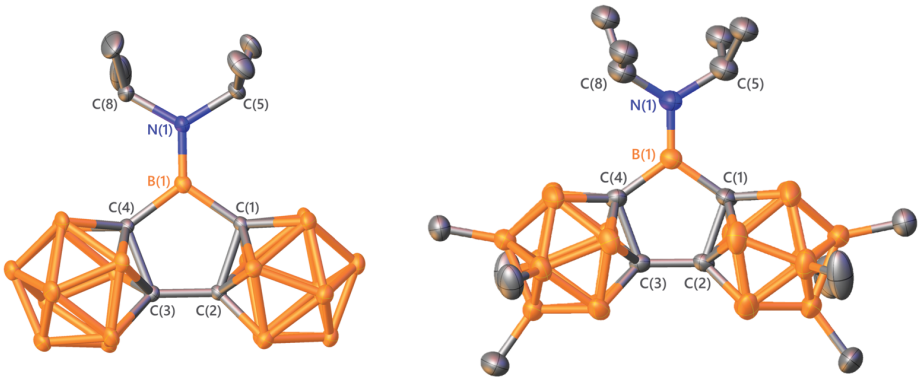


Fig. 2 Solid-state structures of **1B** and **$1BMe_8$**. Thermal ellipsoids are depicted at 50% probability and hydrogen atoms are removed for clarity. The diisopropyl group in **$1BMe_8$** is positionally disordered and only the major component is shown.

Table 1 Salient bond lengths (Å) and angles [°] in compounds **1B**, **1BMe$_8$**, and **1A**

	1B	1BMe$_8$	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)

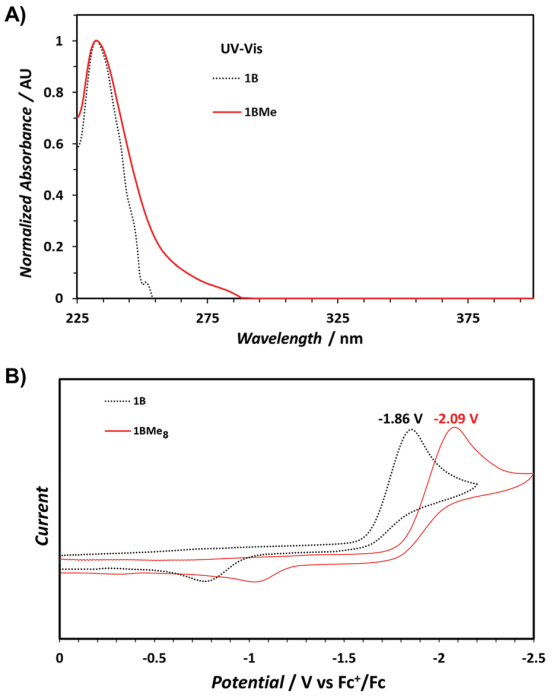


Fig. 3 (A) UV-Vis absorption emission spectra for **1B** and **1BMe$_8$** obtained from solutions of CH_2Cl_2 (λ = 232 and 233 nm respectively). (B) Cyclic voltammograms of **1B** and **1BMe$_8$** recorded in anhydrous tetrahydrofuran with 0.1 M $[N^nBu_4][PF_6]$ and referenced to the ferrocenium/ferrocene redox couple (Fc^+/Fc; scan rate = 0.1 V s^{-1}).

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, 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 **1BMe$_8$** 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 **1BMe$_8$** as well as a bathochromic shift relative to the absorption maximum of **1A** (Fig. 3A). The calculated higher-lying LUMO for **1BMe$_8$** (−1.74 eV) relative to that of **1B** (−2.05 eV) is consistent with the observed more negative reduction potential for **1BMe$_8$** (−2.09 V and −1.86 V, respectively; Fig. 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 Lewis acid and monitoring the change in chemical shift of the $^{31}P\{^1H\}$ NMR signal ($\delta_{^{31}P\text{sample}} - 41.0$). 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 **1BMe$_8$** 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.

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Conflicts of interest

There are no conflicts to declare.

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