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Metal-Free Peralkylation of the *closo*-Hexaborate Anion

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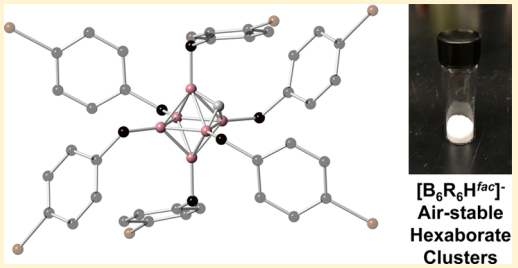
Supporting Information

ABSTRACT: The synthesis of fully alkylated *closo*-hexaborate dianions is reported. The reaction of $[NBu_4][B_6H_6H^{fac}]$, benzyl bromide, and triethylamine under microwave heating conditions affords persubstituted $[NBu_4][B_6(CH_2Ar)_6H^{fac}]$ (Ar = C_6H_5, 4−Br-C_6H_4), which have been isolated and characterized by NMR spectroscopy, mass spectrometry, single-crystal X-ray diffraction, and other spectroscopic techniques. Electrochemical studies of these clusters reveal an irreversible one-electron oxidation, likely indicating degradative cage rupture. The observed metal-free alkylation is proposed to proceed as a consequence of the pronounced *nucleophilic* character of the hexaborate anion. This work represents the first example of a perfunctionalized hexaborate cluster featuring B−C bonds.



INTRODUCTION

Many polyhedral boron clusters have been shown to exhibit enhanced stability relative to more commonly encountered tricoordinate boranes. This stability has been ascribed to the unique bonding arrangement and three-dimensional aromatic character of these polyhedral clusters.[1] For example, the 12-membered, dodecaborate B_{12}-based cluster core exhibits extreme kinetic stability, remaining intact under strongly acidic, oxidizing, and basic conditions, as well as heating in air beyond 600 °C.[2] Partial and exhaustive functionalization of this cluster core can furnish unique molecular scaffolds which are potentially useful for a wide range of applications[3] including, but not limited to, photoactive materials, polymers, electrolytes, catalysts, therapeutics, and diagnostic agents in biomedicine.[4] The ability to design and tune these molecules remains crucial for producing desirable properties and reactivity.

In general, two main approaches to persubstituted group 13 polyhedral clusters exist. The first involves the assembly of prefunctionalized fragments to form the desired cluster-based motif (Figure 1, route A). This approach has frequently been utilized in the context of group 13 clusters—most notably in the seminal work by Schnöckel—and to a lesser degree with small boron-based clusters.[5] The second approach involves first the synthesis of an unsubstituted cluster core precursor, which is then elaborated with functional groups (Figure 1, route B). This latter approach has been applied almost exclusively in boron cluster chemistry,[4] particularly with the icosahedral boron clusters. This is not surprising, given that unfunctionalized icosahedral boranes are significantly more stable than

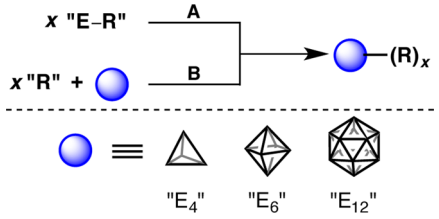


Figure 1. Two general approaches for synthesizing substituted group 13 clusters. Route A involves the combination of substituted fragments "E−R" of one or several types to form the desired molecule. Route B employs a preformed cluster and an external functionality "R" to form the same desired framework.

their heavier group 13 congeners[6] and thus can serve as molecular precursors for the latter method of synthesis.

Beyond icosahedra, other polyhedral boron clusters are known,[7] and in contrast to the well-established chemistry of the $B_{12}H_{12}^{2-}$ dianion and its derivatives, the chemistry of the *closo*-hexaborate dianion, $B_6H_6^{2-}$—the smallest of the known deltahedral 3D aromatic boron clusters—has received much less attention. Predicted[8] in 1954 and isolated[9] in 1964, the $B_6H_6^{2-}$ dianion, which is stable under ambient conditions in both the solid and solution state, was quickly shown to be rather different from its icosahedral relative. The pioneering work of Preetz[10] revealed the apparent *nucleophilic* character of the hexaborate clusters to be significantly more pronounced than that of the $B_{12}H_{12}^{2-}$ species. This observation led to some

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early examples demonstrating that $B_6H_6^{2-}$ can undergo *partial* substitution with carbon-based electrophiles to form B−C bonds; similar reactions with the dodecaborate scaffold have not been disclosed. To date, *peralkylation* of the hexaborate cluster has never been accomplished. Here we disclose the synthesis and properties of the first peralkylated hexaborate clusters, $B_6(CH_2Ar)_6^{2-}$ (Ar = C_6H_5, 4−Br-C_6H_5), generated as a consequence of the nucleophilic character of the hexaborate dianion.

RESULTS AND DISCUSSION

Preetz and co-workers previously disclosed[11] several examples of alkylated hexaborate clusters of the type $B_6R_nH_{6-n}^{2-}$ (n = 1−3, R = alkyl), and it was ultimately suggested that alkylation would not proceed beyond three substitutions. B−C bond formation is thought to occur with concomitant migration of the terminal H from the B vertex to an adjacent *face* of the hexaborate cluster. This facial proton (H^{fac}) mitigates the nucleophilicity of the cluster and must be removed with base for further substitutions to occur. In the examples reported by Preetz, it was concluded that that removal of H^{fac} was not possible beyond three B−C bond formations.[10] Given our recent report[12] of microwave-assisted functionalization of $B_{12}(OH)_{12}^{2-}$ with alkyl electrophiles, which could afford densely functionalized clusters within minutes, we wondered whether similar reaction conditions might produce fully functionalized $B_6R_6^{2-}$ frameworks, bypassing previously encountered limitations.

Treatment of $[NBu_4][B_6H_6H^{fac}]$ with 30 equiv. of benzyl bromide and Hünig's base in CH_3CN under microwave heating conditions led to the formation of a new species displaying a single, broad resonance at δ −7.6 in the ^{11}B NMR spectrum. Further optimization of the reaction conditions permitted the isolation of $[NBu_4][B_6(CH_2C_6H_5)_6H^{fac}]$ (**1a**) after workup in 65% yield (Figure 2A and the Supporting Information). The facial proton in **1a** can be identified by its characteristic upfield shift at δ −3.8 in the ^{1}H NMR spectrum. This assignment is consistent with previous spectroscopic and structural studies[10,13] of analogous unfunctionalized and partially functionalized B_6-based clusters as well as computational studies in which electron density maxima are found at each face of the B_6 cluster.[14] Complete boron vertex substitution, which occurs in the absence of metal catalysis, is also strongly suggested by the disappearance of characteristic terminal B−H stretching vibrations at ∼2400 cm^{-1} in the infrared (IR) spectrum of purified **1a** (Figure 2B).

X-ray diffraction of crystals of **1a** revealed significant disorder due to "wagging" of the benzyl substituents, which was also observed for $[B_6H_5(CH_2Ph)]^{2-}$.[15] We therefore employed a functionalized benzyl electrophile in an attempt to impart greater order and crystallinity to the desired persubstituted product. Treatment of $[NBu_4][B_6H_6H^{fac}]$ with 4-bromobenzyl bromide under conditions otherwise identical with those used to synthesize **1a** similarly affords a compound that displays a single broad peak in the ^{11}B NMR spectrum at δ −7.6 and an IR spectrum consistent with **1a** (Figure 2). Upon workup, perfuctionalized **1b** is afforded in 48% yield as a white, air-stable solid.

An X-ray diffraction study was carried out on single crystals of **1b** grown from a cooling solution of **1b** in boiling ethanol. **1b** crystallizes in the $P2_1$ space group with two independent ion pairs in the asymmetric unit (Figure 3). One NBu_4^+ counterion

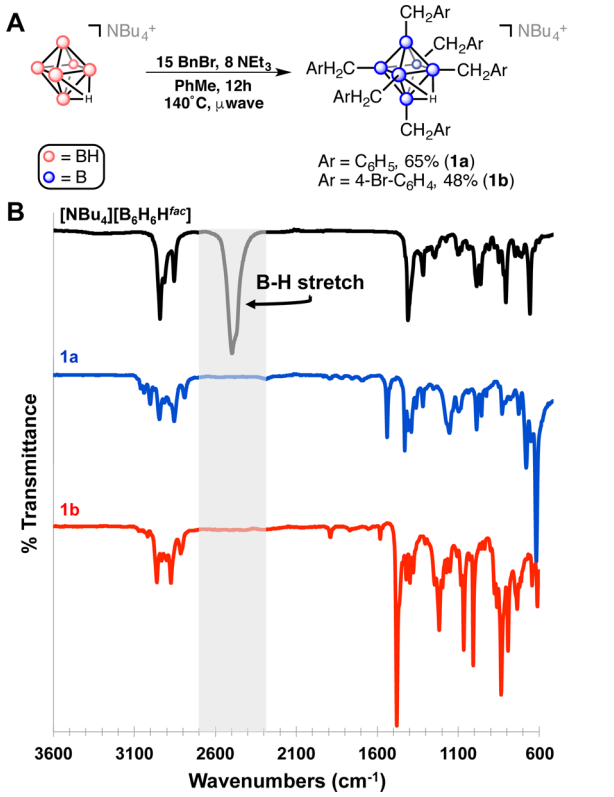

Figure 2. (A) Synthetic scheme for **1a**,**b** from $B_6H_6^{2-}$. (B) IR spectra of $[NBu_4][B_6H_6H^{fac}]$, and **1a**,**b**. The absence of stretching vibrations from ∼2100 to 2600 cm^{-1} for **1a**,**b** suggests a lack of terminal B−H bonds and complete cluster substitution.

is detected per cluster, supporting the proposed facially protonated monoanion and consistent with the ^{1}H NMR data.

While definitive location of the facial proton (H^{fac}) proved difficult, its position can be tentatively assigned on the basis of the bond metrics of the B_6-based core. The B1−B2−B3 face contains three of the four longest B−B distances in the cluster

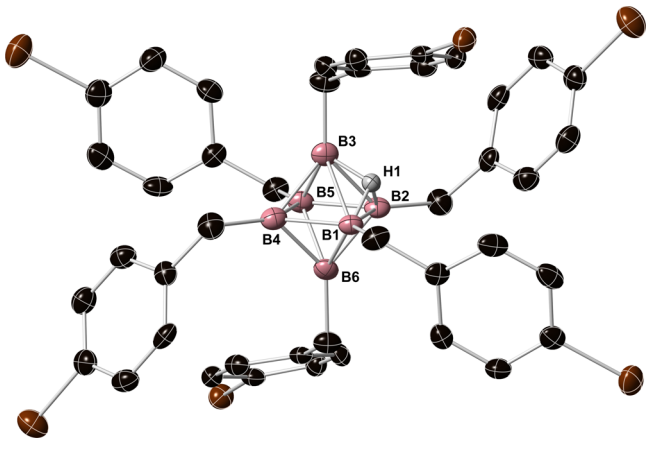

Figure 3. B_6-based component of the single-crystal X-ray structure of **1b**. Benzyl protons and the NBu_4 counterion are omitted for clarity. H1 (H^{fac}) was placed at the B1−B2−B3 face and refined. Selected distances (Å): B1−B2, 1.817(8); B1−B3, 1.818(8); B1−B4, 1.725(9), B1−B6, 1.729(8); B2−B3, 1.788(8); B2−B5, 1.713(9), B2−B6, 1.739(8); B3−B4, 1.779(9); B3−B5, 1.769(8); B4−B5, 1.822(8); B4−B6, 1.746(8); B5−B6, 1.764(8). Thermal ellipsoids (except for H1) are plotted at 50% probability.

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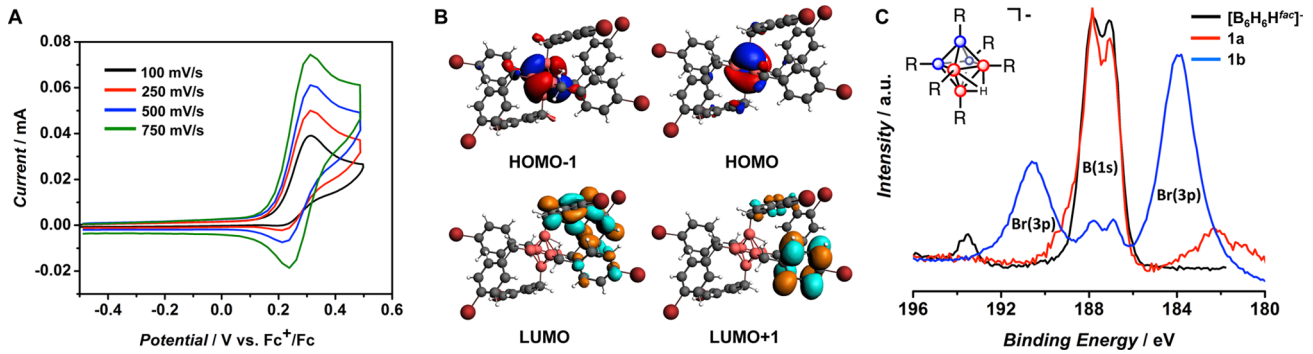

Figure 4. (A) Cyclic voltammogram of **1a** in CH_3CN. Faster scan rates reveal the pseudoreversibility of the 1−/0 redox couple. (B) Kohn−Sham representations derived from the DFT analysis of the frontier molecular orbitals of the anionic component of **1b**, $[B_6(CH_2\text{-}4\text{-}Br\text{-}C_6H_4)_6]^-$. (C) Normalized X-ray photoelectron spectra of $[NBu_4][B_6H_6H^{fac}]$ and **1a,b**. The B(1s) region shows two different boron environments: those in which bonding interactions to H^{fac} are present (red spheres) and absent (blue spheres).

(1.818, 1.818, and 1.789 Å), which are large in comparison to the average of all other B−B distances, 1.725 Å (range 1.713−1.824 Å). We therefore suggest that H^{fac} is bound to this face of the cage in the solid state. This assignment is consistent with previous reports.[13,16] All B−C bonds range from 1.592 to 1.601 Å, which are consistent with the B−C bond distances in previously reported monobenzylated clusters.[15]

While the homo- and heteroleptic perhalogenation (Cl, Br, I) of $B_6H_6^{2-}$ has been reported,[17] **1a,b** are the first molecules of their type in which *carbon*-based substituents are bound to each vertex of the hexaborate cage. Indeed, the only other reports of perfunctionalized hexaborate clusters are the charge-neutral $B_6(NR_2)_6$ species (R = Me, Et).[18] In contrast to **1a,b**, the $B_6(NR_2)_6$ clusters irreversibly open into cyclic constitutional isomers on heating. We suggest that the formation of **1a,b** proceeds via a simple S_N2 mechanism: $B_6H_6^{2-}$, which contains electron density maxima at each face of the octahedron and is generated by deprotonation of the $B_6H_7^-$ anion under the reaction conditions, is proposed to behave as the nucleophile, displacing the primary halide of the benzyl electrophile, forming a B−C bond. The hydride bound to the boron vertex undergoing substitution shifts to an adjacent face (see H^{fac} in Figure 3) in concert with this B−C bond formation and must be deprotonated by base in order for further substitutions to occur. At this point, however, single-electron pathways cannot be ruled out.

Perhalogentated clusters $B_6X_6^{2-}$ (X = Cl, Br, I), mixed halogen clusters $B_6X_nX'_{6-n}{}^{2-}$ (X = F, Cl, Br, I; for X = F, n = 1), and $B_6X_5R^{2-}$ (R = alkyl) were previously shown to exhibit redox behavior.[19] To determine the electrochemical behavior of **1a,b**, cyclic voltammetry (CV) studies were conducted. Solutions of **1a,b** in anhydrous CH_3CN display apparent irreversible one-electron-oxidation waves at 0.32 and 0.46 V vs Fc/Fc^+, respectively (see Figure 4A and the Supporting Information). The observed redox irreversibility is consistent with previous reports of hexaborate cluster decomposition under oxidizing conditions (*vide infra*).[10,20] The anodic shift in the oxidative peak potential between **1a** and **1b** is likely due to the slightly more electron withdrawing nature of the benzyl substituents in **1b**; similar substituent effects have been observed in hexaborate[19] and dodecaborate systems.[12]

As the scan rate is incrementally raised from 100 mV/s to 750 mV/s for **1a**, a reverse reductive wave becomes more pronounced (Figure 4A). These data suggest that the benzyl substituents of **1a** stabilize the transient neutral $B_6(CH_2C_6H_5)_6H^{fac}$ toward decomposition relative to $[NBu_4][B_6H_6H^{fac}]$ (see the Supporting Information). One possible explanation lies in the peripheral benzyl substituents: the steric bulk of these groups likely prevents oxidative dimerization, which is known to occur with $B_6H_6^{2-}$.[19c,21] Similar stabilizing effects by boron cluster substitution have been suggested by Michl in the context of icosahedral carba-*closo*-dodecaborates.[22] Therefore, the irreversibility of this redox couple must originate from some other mode of decomposition, likely cage degradation (*vide infra*).[23] We attribute the absence of redox reversibility at higher scan rates in the case of **1b** to electronic differences in the benzyl substituents in comparison to **1a**, which may destabilize the cluster to a greater degree upon oxidation. Identification of the decomposition products of these oxidative processes is currently ongoing.

The electronic structure of **1b** was probed using density functional theory (DFT) at the BP86-D3/TZP level of theory, and the frontier molecular orbital diagrams obtained from this study are presented in Figure 4B. In agreement with previous computational studies of $[B_6H_6]^{2-}$,[14] the highest occupied molecular orbital (HOMO) and the HOMO-1 are found to be delocalized across the eight faces of the octahedron. In contrast, the lowest unoccupied molecular orbital (LUMO) and the LUMO+1 are primarily located on the benzyl moieties. The observed decomposition of **1a,b** under anodic electrochemical potentials (*vide supra*) is consistent with removal of an electron from the cluster-based HOMO, resulting in kinetic destabilization due to an overall reduction in cage bonding character and 3D aromaticity.[24]

Intrigued by the unique bonding structure of **1a,b**, we performed X-ray photoelectron spectroscopy (XPS) measurements to further probe the electronic landscape of the B_6-based core (Figure 4C). The B(1s) binding energy for **1a,b** and unfunctionalized cluster $[NBu_4][B_6H_6H^{fac}]$ is observed to be ∼187 eV, which is consistent with B(1s) binding energies previously measured for substituted icosahedral dodecaborate clusters[12] and with the B(1s) binding energy of boron species in general.[25] The degree and type of substitution (H vs alkyl; benzyl vs 4-bromobenzyl) do not seem to strongly affect the binding energy. Interestingly, we find two maxima in the 187 eV region for all compounds at 187.1 and 187.9 eV (Figure 4C). We attribute this observation to the existence of two distinct boron environments in $[NBu_4][B_6H_6H^{fac}]$ and **1a,b**: one triangular face contains three boron atoms which share bonding interactions to H^{fac}; the other three atoms of the octahedron do not contain a B···H^{fac} interaction. Since higher binding energies roughly correlate with degree of oxidation, we

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suggest that, given the reduction in electron density from one face of the octahedron by H^+ in the form of a covalent bonding interaction relative to B−H units which do not contain this interaction, the peak of higher binding energy corresponds to the set of boron atoms binding B···H^{fac}. To our knowledge, this is the first XPS study of a hexaborate species.

CONCLUSION

In summary, we have found that the perfunctionalization of the hexaborate dianion is achievable via treatment with benzyl halides, resulting in the formation of six B−C bonds per cluster. These results suggest that the hexaborate cluster may be potentially (per)functionalized with other electrophiles to form B−R bonds of varying types without the need for metal-based catalysis. The newly reported compounds, which are stable solids under ambient conditions, exhibit irreversible electrochemical oxidations, likely the result of cage degradation, ultimately suggesting a differing reactivity from the peralkylated dodecaborate ($B_{12}R_{12}^{2-/-}$) species.[4b−d]

EXPERIMENTAL SECTION

General Considerations. All experiments were set up in a nitrogen-filled glovebox unless otherwise noted. Toluene (C_7H_8) used for reactions set up in a glovebox to form **1a,b** and acetonitrile (CH_3CN) used for cyclic voltammetry were sparged with argon and passed through activated alumina prior to use. All other solvents were used as received. "Ambient conditions" for this paper refer to room temperature (20−25 °C) and uncontrolled laboratory air.

Materials. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were stored over 3 Å molecular sieves under ambient conditions. Hexanes, toluene (C_7H_8), ethanol (EtOH), and methylene chloride (CH_2Cl_2) were purchased from Sigma-Aldrich. Celite and silica gel (Grade 60, 230−400 mesh) were purchased from Fisher Scientific. 4-Bromobenzyl bromide, tetrabutylammonium hexafluorophosphate, tetrabutylammonium hydroxide (40 wt % in H_2O), tetrabutylammonium bromide (NBu_4Br), potassium phosphate (tribasic; K_3PO_4), and ferrocene were purchased from Sigma-Aldrich and used as received. Benzyl bromide was purchased from Sigma-Aldrich and was filtered through a silica plug and stored over 3 Å molecular sieves; for experiments conducted in the glovebox, the silica-treated benzyl bromide was carried through two freeze−pump−thaw cycles before it was brought into the glovebox. Triethylamine was purchased from Sigma-Aldrich and used as received; for experiments conducted in the glovebox, the triethylamine was carried through two freeze−pump−thaw cycles before it was brought into the glovebox. $[NBu_4][B_6H_7]$ was obtained according to the procedure by Kabbani.[26] Note: use of fresh $NaBH_4$ and $BF_3{\cdot}Et_2O$ is essential for good yields of $[NBu_4][B_6H_6H^{fac}]$. In our hands, we obtain $[NBu_4][B_6H_6H^{fac}]$ instead of the reported $[(NBu_4)_2][B_6H_6]$; the $B_6H_6^{2-}$ anion is strongly basic and acquires protons under ambient conditions or even from solvent with trace water. Preetz has also remarked on this property.[10] However, we find $[NBu_4][B_6H_6H^{fac}]$ to be an acceptable starting material for the synthesis of the compounds outlined below.

Synthetic Procedures. Note: due to the acid sensitivity of the hexaborate clusters, trace acid occasionally found in $CDCl_3$ must be neutralized to ensure product stability in solution. The reported reactions may be set up outside the glovebox and likewise furnish **1a,b** with only slightly diminished yields.

*$[NBu_4][B_6(CH_2C_6H_5)_6H^{fac}]$ (**1a**).* In a nitrogen-filled glovebox, $[NBu_4][B_6H_6H^{fac}]$ (50 mg, 0.140 mmol) was charged in a 10 mL microwave reactor vial followed by 1 mL of C_7H_8. Note: the mixture is poorly soluble in C_7H_8 at room temperature. Then, trimethylamine (142 μL, 1.40 mmol) was added, followed by benzyl bromide (250 μL, 2.10 mmol). The Teflon cap was affixed, and the vial was brought out of the box and set to heat in the microwave for 12 h at 140 °C. After 12 h, a translucent slurry was observed that had a slight blue tint. The slurry was diluted with hexanes (∼6 mL), and the mixture was manually stirred to further precipitate a white solid. The solid was filtered over Celite and washed thoroughly with hexanes. The solid was then washed through the Celite pad into a separate receiving flask with CH_2Cl_2. This filtrate was charged to a separatory funnel containing ∼25 mL of a 0.15 M NBu_4OH (40 wt % in H_2O) aqueous solution. The organic layer was washed twice with this solution, isolated, dried over Na_2SO_4, and filtered through Celite. The filtrate was dried in vacuo. The residue (which may be slightly blue) was then charged with ∼5 mL of EtOH to precipitate a white solid. The mixture was stirred vigorously for ∼20 min and was subsequently set in a −15 °C freezer for 3−4 h. The solid was then isolated on a fritted funnel and washed with cold (−15 °C) EtOH. The white solid product was dried under vacuum (78 mg, 65%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.04 (t, 12H, Ar), 6.88 (t, 6H, Ar), 6.78 (d, 12H, Ar), 2.46 (m, 8H, $[N(CH_2(CH_2)_2CH_3)_4]^+$), 1.80 (s, 12H, CH_2Ar), 1.26 (m, 16H, $[N(CH_2(CH_2)_2CH_3)_4]^+$), 1.18 (t, 12H, $[N(CH_2(CH_2)_2CH_3)_4]^+$), −3.54 (br s, 1H, H^{fac}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.65, 128.99, 127.31, 122.05, 58.29, 23.70, 21.33, 19.71, 13.83. ^{11}B NMR ($CDCl_3$, 160 MHz): δ −6.19. Mass spectrometry (ES$^-$): expected monoisotopic peak (*m*/*z*) for $[B_6C_{42}H_{43}]^-$ 609.3960, found 609.3954.

*$[NBu_4][B_6(CH_2\text{-}4\text{-}Br\text{-}C_6H_4)_6H^{fac}]$ (**1b**).* In a nitrogen-filled glovebox, $[NBu_4][B_6H_6H^{fac}]$ (100 mg, 0.281 mmol) was charged in a 10 mL microwave reactor vial followed by 2 mL of C_7H_8. Note: the mixture is poorly soluble in C_7H_8 at room temperature. Then, trimethylamine (313 μL, 2.24 mmol) was added, followed by 4-bromobenzyl bromide (1.05 g, 4.21 mmol). The Teflon cap was affixed, and the vial was brought out of the box and set to heat in the microwave for 12 h at 140 °C. After 12 h, a white slurry was observed. The slurry was diluted with hexanes (∼6 mL), and the mixture was manually stirred to further precipitate a white solid. The solid was filtered over Celite and washed thoroughly with hexanes. The solid was then washed through the Celite pad into a separate receiving flask with CH_2Cl_2. This filtrate was charged to a separatory funnel containing ∼25 mL of a 0.02 M NBu_4Br/0.09 M K_3PO_4 aqueous solution (500 mg of NBu_4Br and 2 g of K_3PO_4 in 100 mL of deionized H_2O). The organic layer was washed twice with this solution, isolated, dried over Na_2SO_4, and filtered through Celite. The filtrate was dried in vacuo. The residue (which may be slightly yellow) was then charged with ∼5 mL of EtOH to precipitate a white solid. The mixture was stirred vigorously for ∼20 min and was subsequently set in a −15 °C freezer for 3−4 h. The solid was then isolated on a fritted funnel and washed with cold (−15 °C) EtOH. The white solid product was dissolved in boiling ethanol and allowed to recrystallize. The crystalline product was dried under vacuum (179 mg, 48%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.17 (d, 12H, Ar), 6.57 (d, 12H, Ar), 2.64 (m, 8H, $[N(CH_2(CH_2)_2CH_3)_4]^+$), 1.75 (s, 12H, CH_2Ar), 1.31 (m, 16H, $[N(CH_2(CH_2)_2CH_3)_4]^+$), 1.03 (t, 12H, $[N(CH_2(CH_2)_2CH_3)_4]^+$), −3.75 (br s, 1H, H^{fac}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.32, 130.62, 130.28, 115.56, 58.68, 23.74, 20.49, 19.78, 13.82. ^{11}B NMR ($CDCl_3$, 160 MHz): δ −7.62. Mass spectrometry (ES$^-$): expected monoisotopic peak (*m*/*z*) for $[B_6C_{42}H_{37}Br_6]^-$ 1078.8551, found 1078.8588.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00078.

Experimental and instrumentation details and NMR spectra for **1a,b** as well as supplementary electrochemical, DFT, and XPS data (PDF)

Crystallographic data (CIF)

Cartesian coordinates for the calculated structure (XYZ)

Cartesian coordinates for the calculated structure (XYZ)

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Notes

The authors declare no competing financial interest.

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