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Ambient temperature isolation of a monoatomic boron(0) complex

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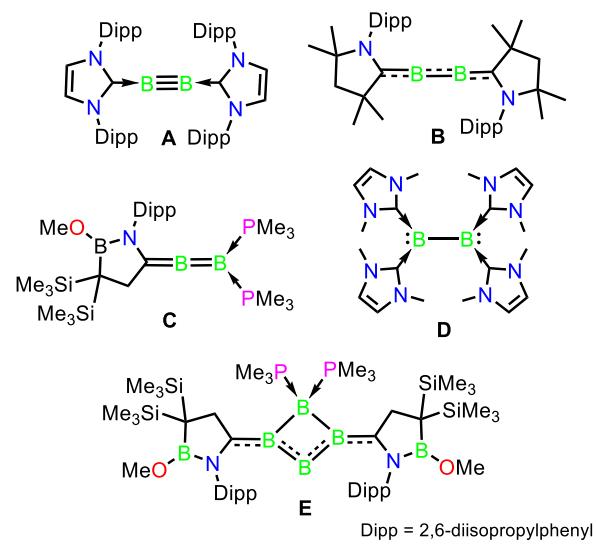
ABSTRACT The first bottleable example of a neutral Group 13 atom bound only by neutral donor ligands (L) has been fully characterized by spectroscopic methods and its structure determined by a single crystal X-ray diffraction study. A two-coordinate paramagnetic L_2B^0 complex can readily be accessed through a facile reduction reaction and is stabilized by π -accepting cyclic (alkyl)(amino)carbene (CAAC) ligands. Further reduction of $(CAAC)_2B$ leads to the isolation of a stable diamagnetic boride anion. In turn, oxidation leads to the putative formation of a transient two-coordinate cationic borylene which has been trapped to form a stable boron(I) complex. Density functional theory calculations support the formulation of $(CAAC)_2B$ as a boron(0) complex stabilized by strong multiple bonding.

Introduction

The isolation of stable, formally zero-valent element complexes has allowed chemists to explore the reactivity of the elements in discrete forms. Within the realm of transition metals, these complexes are often important catalysts for organic reactions that capitalize on the high reactivity of low-valent states toward bond activation.¹⁻³ Within the s- and p-block elements, ligand stabilization of neutral atoms and element clusters has yielded highly-reactive yet bottleable complexes L_nE_m (L = neutral donor ligand) that can participate in atom transfer reactions, inert bond activation, serve as electron-rich ligands for transition metals, and can themselves behave as metal-mimicking catalysts.⁴⁻¹⁴

While the monoatomic complexes L_nE are known for the even-numbered s- and p-element groups, including L_2Be ,¹⁵ L_2C ,¹⁶⁻¹⁸ and the heavier tetrylones,¹⁹⁻²⁷ the paramagnetic Group 13 analogues are unknown outside of matrix isolation studies due to their reactive open-shell electronic structure.²⁸⁻³¹ Accordingly, all known stable complexes containing formal B^0 centers are diamagnetic and feature B-B bonds. Ligand-stabilized B_2 fragments were first accessed in the form of diborynes, which possess a genuine boron-boron triple bond ($L \rightarrow B \equiv B \leftarrow L$) (Figure 1, **A**).³² These and related L_nB_2 complexes (Figure 1, **B-D**) have revealed strongly ambiphilic reactivity in the coordination of unsaturated centers and the activation of inert bonds.³³⁻⁵¹ Kinjo and co-workers have also recently reported the first example of a ligand-stabilized B_4 cluster (Figure 1, **E**).⁵²

Previous work: Ligand-stabilized B_2 and B_4



This work: Ligand-stabilized B

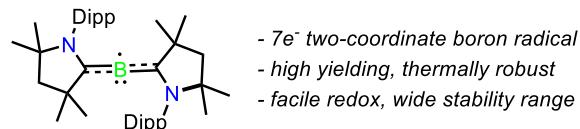


Figure 1. Examples of ligand-stabilized boron(0) fragments.

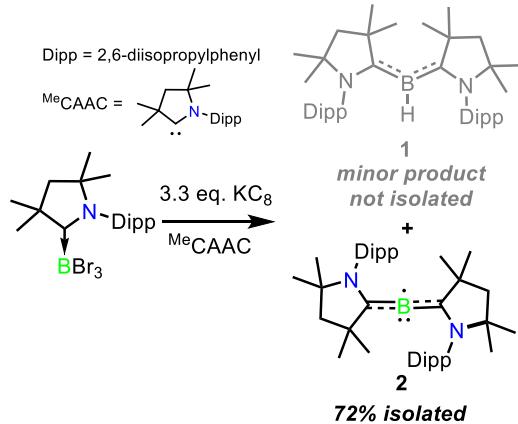
While bottleable examples of L_nB have remained elusive, the seminal discovery of the first stable metal-free B^I compound (L_2BR – termed a *borylene*, R = covalently bound group) by Bertrand and co-workers⁵³ opened a new field of study in the coordination chemistry, reactivity towards small molecule activation, and catalytic properties of low-valent boron.⁵⁴⁻⁵⁸ Notably, the fixation, catenation, and reduction of N_2 to ammonia at a borylene center recently

reported by Braunschweig and co-workers has elevated these molecules from fundamental interest to a new frontier in green catalysis.⁵⁹⁻⁶³ Critical to the isolation of low-valent boron is the use of π -acidic ligands to delocalize and stabilize the boron-centered lone pair. Cyclic (alkyl)(amino)carbenes (CAACs)⁶⁴⁻⁶⁶ have become a popular choice for this purpose due to their stability, crystallinity, steric tuneability, and ability to stabilize elements in multiple oxidation states.⁶⁷⁻⁶⁸ Their significant π -accepting properties have also allowed them to behave as redox non-innocent ligands in some cases.⁶⁹

The first reported synthesis of a metal-free borylene involved the reduction of (CAAC)BBr₃ adduct with KC₈, which afforded (CAAC)₂BH in a 33% yield.⁵³ The origin of the boron-bound hydrogen atom in this and related reduction reactions has remained speculative,⁷⁰⁻⁷¹ although H-atom abstraction from the reaction solvent or a CAAC-containing moiety have both been experimentally excluded as potential sources. As CAAC ligands have been known to stabilize spin density in main group complexes,⁷²⁻⁷³ we became intrigued at the possibility of a persistent L₂B radical intermediate in the formation of (CAAC)₂BH.

Results and Discussion

In an initial experiment, the reduction of (^{Me}CAAC)BBr₃ with KC₈ in the presence of additional ^{Me}CAAC yielded 38% of the known hydridoborylene (^{Me}CAAC)₂BH **1**.^{53, 70} However, an electron paramagnetic resonance (EPR) spectrum of the crude reaction mixture indicated the presence of a persistent radical species with discernable hyperfine coupling to one ¹¹B and two ¹⁴N nuclei. Through careful optimization of the reaction conditions and work-up procedure, it was subsequently found that the formation of **1** can be minimized, permitting the ambient temperature isolation of the two-coordinate radical (^{Me}CAAC)₂B **2** as a burgundy solid in a 72% yield (Scheme 1). The differences in the two reaction procedures are subtle. We have found that higher concentrations, shorter reaction times, and rigorous solvent purification favors the formation of **2**. Whereas lower concentrations, longer reaction times, and excess equivalents of KC₈ in the reaction mixture were found to favor the formation of **1** (see Supporting Information for experimental details). Nevertheless, our optimized conditions have provided a reliable (>30 preparations) and high-yielding procedure for the selective isolation of **2**.



Scheme 1. Optimized conditions for the synthesis of (^{Me}CAAC)₂B (2).

Orange-brown single crystals of **2** were readily grown from pentane solution, and its molecular structure was determined by an X-ray diffraction study (Figure 2a). The structure revealed a quasi-linear environment at boron (C-B-C = 176.03(12) $^{\circ}$) with B-C bond lengths of 1.4464(16) and 1.4471(16) \AA , slightly longer than a typical B=C double bond,⁷⁴ and slightly shorter than the bond length of 1.457(3) \AA reported by Chiu and co-workers in a two-coordinate boron radical cation.⁷⁵ In the solid state, the facial planes of the two CAAC ligands are canted at an angle of 59.62(14) $^{\circ}$ with respect to each other. Unrestricted DFT calculations (UPBE0-D3(BJ)/def2-TZVP) indicate that the singly occupied molecular orbital (SOMO) and the highest doubly occupied molecular orbital (HOMO) are highly twisted π -bonding orbitals delocalized through the N-C-B-C-N linkage (Figure 2b). The calculated identical Mayer bond orders of 1.65 for both B-C bonds further indicate significant π -interactions between boron and the CAAC ligands. Despite this, it has also been calculated that the B-C bonds possess a very high degree of rotational flexibility at ambient temperature. The angle between the two CAAC ligand planes (as defined by the NC_{CAAC}-C_{CAAC}N dihedral angle) may be rotated through a full 180 $^{\circ}$ while incurring a maximum energetic barrier of 15.1 kcal/mol (Figure S44 in the Supporting Information). Additionally, the C-B-C angle may be bent to 130 $^{\circ}$ at an energetic cost of just 13.8 kcal/mol (Figure S45).

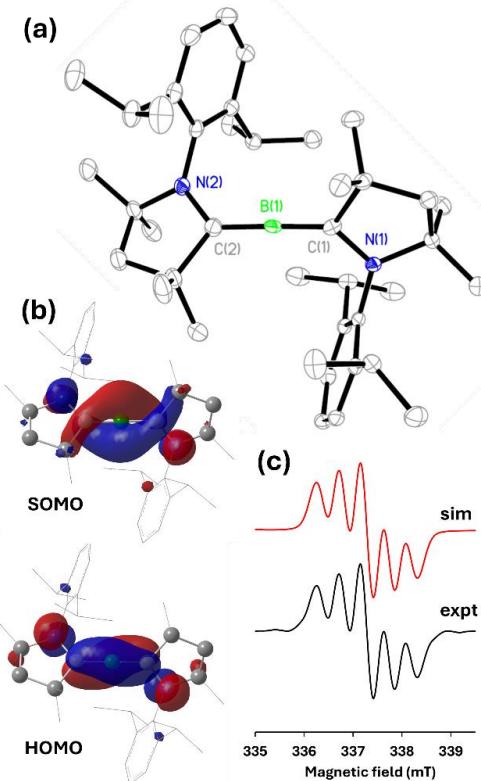


Figure 2. (a) Molecular structure of **2** drawn with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^{\circ}$): B1-C1: 1.4471(16), B1-C2: 1.4464(16), C1-N1: 1.3936(14), C2-N2: 1.3911(13); C1-B1-C2: 176.03(12). (b) Frontier occupied orbitals of **2** (UPBE0-D3(BJ)/def2-TZVP). (c) Experimental (bottom) and simulated (top) solution EPR spectra of **2** (toluene, 308 K). $g_{iso} = 2.0029$, $a(^{11}\text{B}) = 0.45 \text{ G}$, $a(^{14}\text{N}) = 4.34 \text{ G}$.

Compound **2** is paramagnetic with an $S = \frac{1}{2}$ spin state ($\mu_{\text{eff}} = 1.7 \mu_{\text{B}}$ by Evans' method).⁷⁴ An EPR spectrum in toluene revealed hyperfine coupling constants of 0.45 and 4.34 G to ^{11}B and two ^{14}N nuclei, respectively (Figure 2c). Spin density calculations indicate that the boron atom bears the greatest fraction of the unpaired electron density (30%), with most of the remainder localized on both flanking carbene-carbon and nitrogen atoms (20% and 10% each, respectively). Compound **2** is the first isolated example of a neutral two-coordinate boron radical.⁷⁵⁻⁷⁶ In the crystalline state, **2** displays exceptional thermal stability and melts with decomposition at 171°C. A solid sample heated to 150°C under argon atmosphere shows no changes in its solution EPR or NMR spectra. Compound **2** is also stable in solution at ambient temperature under inert atmosphere – no decomposition was detected after 5 days dissolved in C_6D_6 . When in solution, **2** is sensitive to oxygen, decomposing unselectively in its presence. Somewhat surprisingly, **2** is inert to treatment with moderate pressures (4 bar) of N_2 , H_2 , or CO at ambient temperature.

Energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV) is a computational method that offers insight as to whether chemical bonds are better described as dative donor-acceptor ($\text{D} \rightarrow \text{A}$) or fully electron-sharing covalent ($\text{R}-\text{R}$).⁷⁷⁻⁷⁸ This is achieved by examining the orbital interaction energies (ΔE_{orb}) of molecular fragments bearing different electronic arrangements, where the fragment combination with the ΔE_{orb} term closest to zero offers the most accurate representation of the constituent fragments that contribute to a molecule's electronic structure. EDA-NOCV calculations (UPBE0-D3(BJ)/TZ2P) for **2** indicate the smallest ΔE_{orb} term (-394.12 kcal/mol) is found in a donor-acceptor model featuring singlet ${}^{\text{Me}}\text{CAAC}$ carbenes datively bound to a B^0 atom in a doublet configuration ($2s^0 2p_{\pi 1}^2 2p_{\pi 1}^1$) (Figures 3a-3c). This is reminiscent of the $(\text{CAAC})_2\text{Be}$ complexes described by Braunschweig and co-workers, where similar calculations indicated the most favorable fragments as singlet ${}^{\text{Me}}\text{CAAC}$ bound to a Be atom ($2s^0 2p_{\pi}^2$),¹⁵ but differs from the electron-sharing bonds found preferable by Frenking and co-workers in $(\text{CAAC})_2\text{C}$.⁷⁹ Notably, an electron-sharing model for **2** featuring quartet B ($2s^1 2p_{\sigma}^1 2p_{\pi}^1$) bound to two triplet ${}^{\text{Me}}\text{CAAC}$ ligands is only somewhat less favorable than the donor-acceptor model ($\Delta E_{\text{orb}} = -433.95 \text{ kcal/mol}$). While this suggests that **2** can be best described as an L_2B^0 complex according to this analysis, a 7-electron heteroallene radical should also be considered as a contributing resonance form (Figure 3c). All EDA-NOCV decompositions of **2** featuring charged CAAC and B fragments were found to be significantly larger in energy (Table S6).

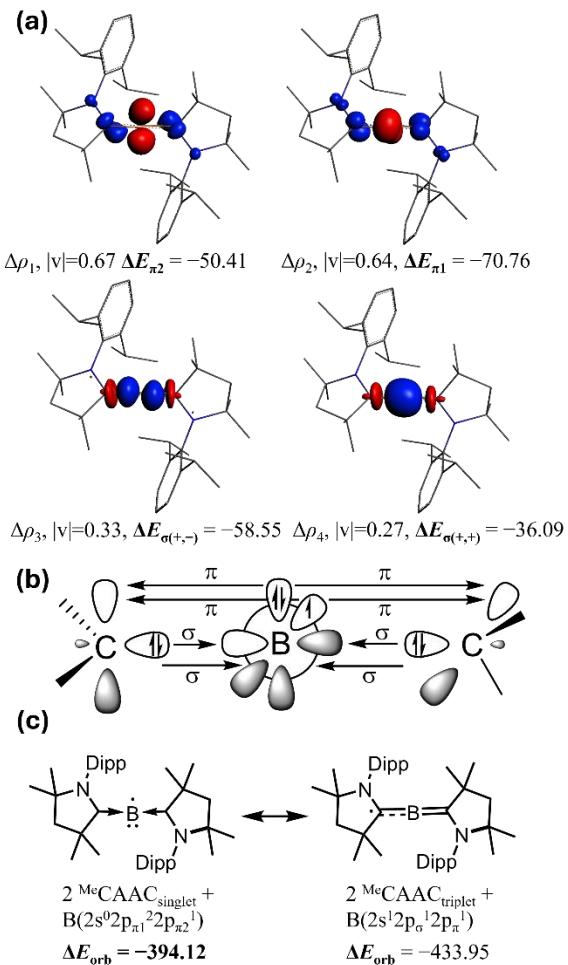


Figure 3. (a) Plot of deformation densities (α orbitals $\Delta\rho_1$ – $\Delta\rho_4$) of the orbital interactions in **2** together with the corresponding NOCV eigenvalues ($|\nu|$) and interaction energies (ΔE values are in kcal/mol) (UPBE0-D3(BJ)/TZ2P). The charge flows from red to blue. (b) Schematic representation of the orbitals involved in σ -donation and π -back-donation. (c) Resonance forms of the two lowest ΔE_{orb} contributors to **2**.

We next turned our attention to the electrochemical flexibility of **2**. Cyclic voltammetry of **2** (0.1M $[\text{NBu}_4]\text{[BF}_4]$) in THF revealed a reversible reduction event at -2.31 V vs Fc/Fc^+ (Figure 4), suggesting the stability of the two-coordinate boride anion $[({}^{\text{Me}}\text{CAAC})_2\text{B}]^-$. Accordingly, reduction of **2** with Li metal in THF cleanly yielded $({}^{\text{Me}}\text{CAAC})_2\text{BLi}$ **3**, which could be isolated as a red-pink solid in 95% yield (Scheme 2). Single crystals suitable for X-ray diffraction were grown from pentane, and its molecular structure was determined (Figure 5a). In the solid state, the Li cation is η^5 coordinated to the N–C–B–C–N linkage, and is further supported by close contacts with two isopropyl CH_{methine} positions. The Li–B distance is exceptionally short ($2.065(3) \text{ \AA}$), significantly shorter than those reported in boryllithium complexes (2.218 – 2.291 \AA),⁸⁰ suggesting the high degree of electron richness of the boron center in **3**. A broad ^{11}B NMR signal at 55 ppm was observed for **3** in C_6D_6 solution.

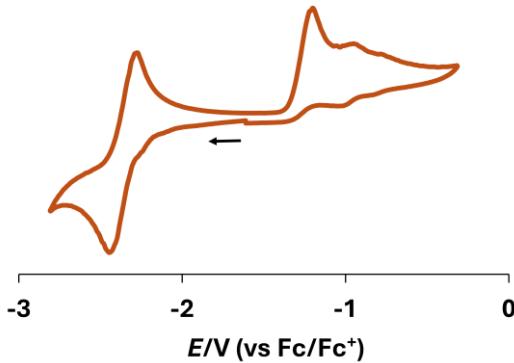
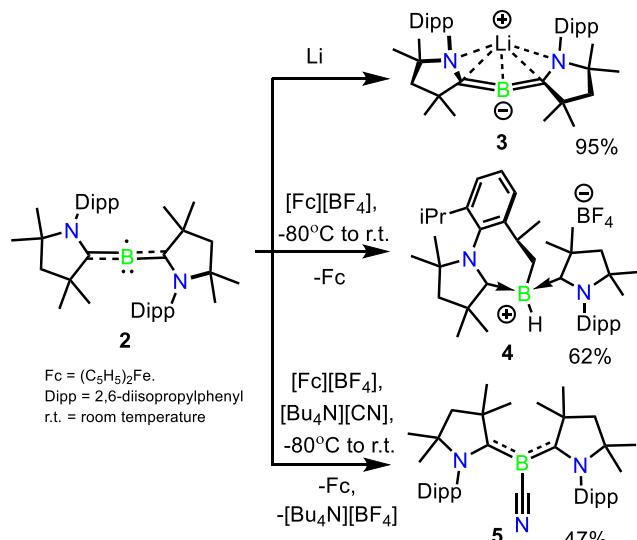


Figure 4. Cyclic voltammogram of **2** at ambient temperature in THF/0.1 M $[n\text{Bu}_4\text{N}][\text{BF}_4]$ measured at 100 mV/s. Formal potentials: $E_{1/2} = -2.31$ V (reversible reduction), $E_{\text{ox}} = -1.24$ V (irreversible oxidation).



Scheme 2. Reduction and oxidation reactions of $(^{\text{Me}}\text{CAAC})_2\text{B}$ (2).

The B-C distances of 1.4271(18) and 1.4235(18) Å in **3** are shorter than in **2** and suggestive of B=C double bonds. This is further supported by calculated identical Mayer bond orders of 1.70. The two ^{Me}CAAC ligands are oriented nearly orthogonally to one another (89.04(18)°), and the C-B-C angle in **3** is strikingly bent (158.04(12)°). Similar to **2**, the frontier bonding orbitals (PBE0-D3(BJ)/def2-TZVP) are π -type and delocalized through the N-C-B-C-N linkage (Figure 5b). EDA-NOCV analysis of $[(^{\text{Me}}\text{CAAC})_2\text{B}]^-$ suggests the most favorable disconnection is $[(^{\text{Me}}\text{CAAC})_2\text{B}]^-$ bound to a neutral B atom in a doublet configuration ($2s^2 2p_{\pi 1}^2 2p_{\pi 2}^2$) ($\Delta E_{\text{orb}} = -462.09$ kcal/mol) (Table S7).

Borylenes are typically accessed through reduction of B^{III} species with strong reducing agents, or more rarely via deprotonation of a borohydride.^{55, 81} Given the computational indication of **2** as a formal compound of B⁰, we became curious as to whether we could access a borylene through its controlled oxidation. Cyclic voltammetry of **2** in THF indicated an irreversible oxidation event at -1.24 V vs Fc/Fc⁺ (Figure 5), revealing its exceptionally wide electro-

chemical stability range (1.07 V). A C-H activated species **4** was isolated in a 62% yield from the reaction of **2** with $[(\text{C}_5\text{H}_5)_2\text{Fe}][\text{BF}_4]$ (Scheme 2, Figure S31), reminiscent of the decomposition product observed from the $(^{\text{Me}}\text{CAAC})_2\text{B}$ -Duryl by Braunschweig and co-workers,⁸² and suggestive of the formation of the transient borylene $[(^{\text{Me}}\text{CAAC})_2\text{B}]^+$ in this reaction. Gratifyingly, when the same oxidation was performed in the presence of $[\text{NBu}_4][\text{CN}]$ as a trapping agent, the cyanoborylene $(^{\text{Me}}\text{CAAC})_2\text{BCN}$ **5** was instead isolated as a vibrant purple highly air-sensitive solid in 47% yield (Scheme 2). No reaction of **2** with $[\text{NBu}_4][\text{CN}]$ was observed in the absence of oxidant. Metric and spectroscopic parameters of **5** are similar to other doubly CAAC-stabilized borylenes (Figure S32).^{53, 83}

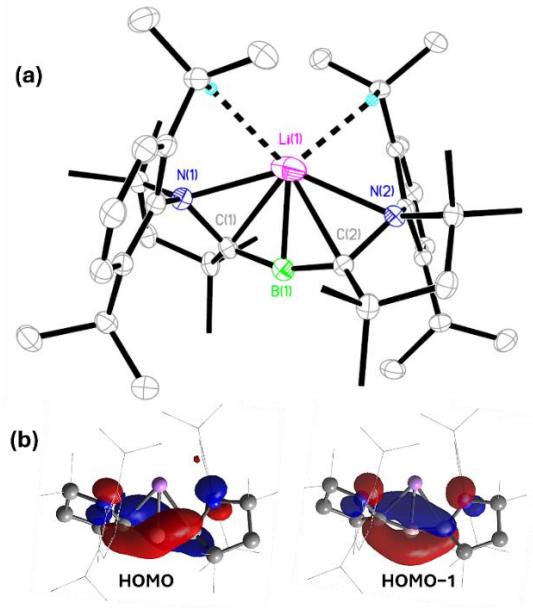
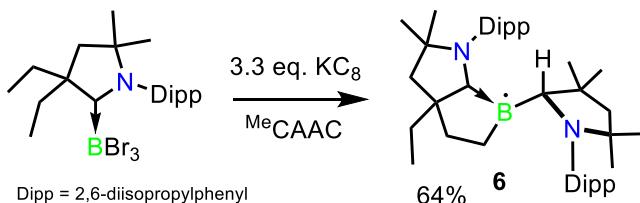


Figure 5. (a) Molecular structure of $(^{\text{Me}}\text{CAAC})_2\text{BLi}$ **3**. Selected hydrogen atoms and methyl groups on each CAAC are removed for clarity. All other atoms are drawn as 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): B1-C1: 1.4271(18), B1-C2: 1.4235(18), Li1-B1: 2.065(3), Li1-C1: 2.257(3), Li1-C2: 2.293(3), Li1-N1: 2.321(3), Li1-N2: 2.357(3); C1-B1-C2: 158.04(12). (b) Frontier bonding orbitals of **3** (PBE0-D3(BJ)/def2-TZVP).

The isolation of **5** suggests the persistence of the two-coordinate borylene cation $[(^{\text{Me}}\text{CAAC})_2\text{B}]^+$ at low temperatures. Unrestricted DFT calculations (UPBE0-D3(BJ)/def2-TZVP) indicate a closed-shell singlet ground state for this species with a very small $\Delta E_{\text{S-T}}$ of 5.6 kcal/mol, and a ground state electronic structure featuring a 3c-2e⁻ π -bond delocalized through the C-B-C linkage (Figure S40). This is further supported by high-level multireference calculations, which indicate a negligible biradical character for this system (Tables S8-S10).



Scheme 3. Reduction of an $^{Et}CAAC$ derivative.

Finally, we have also explored the utility of other CAAC-type ligands in the synthesis of B^0 complexes. It was found that reducing $(^{Et}CAAC)BBr_3$ with KC_8 in the presence of an additional equivalent of $^{Me}CAAC$ resulted in the formation of the C-H activated product **6**, which was isolated in a 64% yield as orange crystals (Scheme 3). No evidence for the formation of B^0 species was found in this case. Compound **6** was fully characterized by EPR spectroscopy (Figure S2) and a single crystal X-ray diffraction study (Figure S33), and its formulation further supported by HRMS. Metric parameters of **6** are similar to other CAAC-stabilized neutral borane radicals.⁷⁶ Compound **6** is conceptually derived from 1,2-addition of the proximal ethyl C-H bond across a B=C bond of the target B^0 species. This result suggests that selecting donor ligands where C-H activation is discouraged will be key to expanding the scope of this new class of low-valent boron molecules.

Conclusions

In summary, we have isolated and fully characterized the first example of a neutral Group 13 atom stabilized only by neutral ligands. Two-coordinate $(^{Me}CAAC)_2B$ displays remarkable thermal stability, an exceptional degree of geometric flexibility, readily undergoes reduction to form a stable $[(^{Me}CAAC)_2B]^-$ anion, and oxidation to form the putative borylene cation $[(^{Me}CAAC)_2B]^+$ which has been trapped with a nucleophile. Further exploration of the reactivity of these highly unsaturated species is ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information. Experimental details, experimental spectra, crystallographic details, computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystal structure .cif files of **2-5** have been deposited (CCDC#s 2377619 (2), 2377620 (3), 2407842 (3·THF), 2377630 (4), 2377618 (5), 2407843 (6).)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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TOC: The first ambient-temperature stable example of a monoatomic boron(0) complex has been isolated, fully characterized by spectroscopic methods, and its structure determined by single crystal X-ray diffraction. DFT calculations support its oxidation state assignment of boron(0), and reactivity studies have established that this stable radical species may lose or reversibly gain an electron to form isolated examples of boron(I) and boride complexes, respectively.

