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COMMUNICATION

Isolation of Base Stabilized Fluoroborylene and its Radical Cation

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Herein, we report the synthesis and characterization of the metal free low valent fluoroborylene [(Me-cAAC)₂BF] (**1**) stabilized by cyclic (alkyl)(amino) carbene (cAAC). The fluoroborylene **1** is obtained by reductive defluorination of Me-cAAC:BF₃ with 2.0 equivalents of KC₈ in the presence of 1.0 equivalent of Me-cAAC. Due to its highly electron rich nature, **1** underwent one-electron oxidation with 1.0 equivalent of lithium tetrakis(pentafluorophenyl)borate [LiB(C₆F₅)₄] to form the radical cation [(Me-cAAC)₂BF]^{•+}[B(C₆F₅)₄]⁻ (**2**). DFT studies suggested that the lone pair of electrons is localized on boron atom in **1**, which explains its unprecedented reactivity. Both compounds **1** and **2** were characterized by X-ray crystallography. The radical cation **2** was studied by EPR spectroscopy.

The boron analogues of carbene are known as borylenes which are isolobal to CO and N₂. With only one substituent, two vacant orbitals and the presence of a lone pair of electrons, borylenes are highly electron rich reactive transient species and thus more difficult to stabilize as compared to carbenes.¹ Consequently, free borylenes (R–B:) have never been obtained as stable compounds and can only be isolated by chemical trapping. In 1998, Braunschweig and co-workers were successful in isolating the first stable terminal borylene complex [(OC)₅WBN(SiMe₃)₂] stabilized with a metal carbonyl fragment.^[2a] Later, N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino) carbenes (cAACs) were used for the stabilization of different amino, cyano, aryl and alkyl borylene derivatives.²

Free diatomic borylenes such as :BH, :BX (X= F, Cl, Br, I) are highly unstable as compared to aryl/amino borylenes and have been detected by microwave spectroscopy.³ In 2007, Robinson and co-workers reported the isolation of NHC-stabilized neutral diborene (NHC)₂B₂H₂ by the reduction of (NHC)BBr₃ with KC₈.^{4a} In 2011, Bertrand and co-workers isolated the first hydroborylene (cAAC)₂BH (**B**) by the reduction of (cAAC)BBr₃ with an excess of KC₈ in the presence of cAAC.^{4b} But, the yield of the reaction is very low and the synthetic route of the formation of (cAAC)₂BH is still unclear.

The next higher analogues of parent hydroborylene (:BH) are the haloborylenes (:BX). Haloborylenes are low-valent boron compounds where the boron atom is in the formal +I oxidation state which is in sharp contrast with diarylboron halides (R₂BX) wherein the boron atom possesses +III oxidation state. Haloborylenes have the potential in unraveling hitherto unexplored aspects of borylene chemistry as they are the key intermediate compounds or species to synthesize unique and diverse borylene derivatives. Therefore, there is a need to synthesize and isolate such species. Synthesis of free fluoroborylene (:BF) was attempted by passing BF₃ over crystalline boron at 2000 °C/1 mm in the gas phase but it formed a green uncharacterized polymeric material even at -196 °C.^{3a} Very few metal BF complexes such as Fe(BF)(CO)₄,^{5a} Fe(PF₃)₄(BF),^{5b} Cp₂Ru₂(CO)₄(μ-BF)^{5c} and Fe(BF)(CO)₂(CNAr^{Tripp2})₂ [Ar^{Tripp2}, 2,6-(2,4,6-(*i*-Pr)₃C₆H₂)₂C₆H₃; *i*-Pr, *iso*-propyl]^{5d} were reported where first two were characterized spectroscopically and last two were structurally characterized by X-ray crystallography. Till date no synthesis or isolation of fluoroborylenes without metal sphere is reported and it still remains a challenging task. Very recently, Xie and co-workers reported bromoborylene (:BBr) using carborane-bridged bis(silylene) ligand^{6a,b} and Braunschweig and co-workers have isolated base stabilized chloroborylene (:BCl).^{6c}

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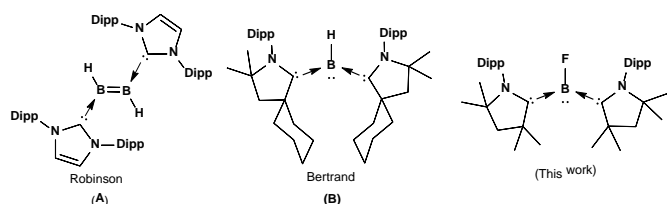
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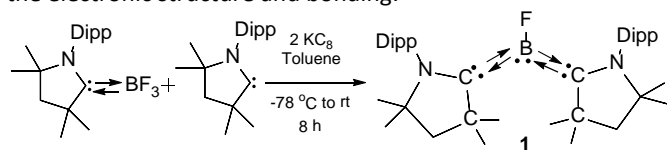
†Electronic Supplementary Information (ESI) available: [Experimental details, characterization data, cif files of **1** and **2** [CCDC: 1900360 (**1**), 1900361 (**2**)], the details of crystal structure refinements and crystal images, UV-Vis spectra, CV, EPR measurements, and theoretical investigations]. See DOI: 10.1039/x0xx00000x





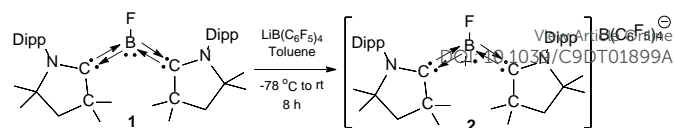
Scheme 1. Lewis base-stabilized borylenes.

Cyclic (alkyl)(amino) carbenes (cAACs) which are stronger σ -donor (nucleophilic) and better π -acceptor (electrophilic) compared to the classical N-heterocyclic carbenes (NHCs) have gained much interest owing to their versatile applications.⁷ Cyclic (alkyl)(amino) carbenes (cAACs) have been judiciously used for the stabilization of transition metals as well as p-block elements in low oxidation states.⁷ We have shown that cAACs can be utilized as excellent ligands for the stabilization of different low oxidation states of aluminum, germanium, silicon and phosphorus and their different radicals.⁸ Herein, we report the synthesis and isolation of cyclic alkylamino carbenes (cAACs) stabilized fluoroborylene (:BF) and its radical cation. The isolated compounds have been fully characterized by X-ray crystallography, multinuclear-spectroscopy, cyclic voltammetry and electron paramagnetic resonance (EPR) studies. Also, quantum-chemical studies have been performed to understand the electronic structure and bonding.



Scheme 2. Synthesis of **1**, (Dipp: 2, 6-diisopropylphenyl).

The synthetic route of (Me-cAAC)₂BF (**1**) is shown in Scheme 2. Me-cAAC:BF₃ was isolated as the white solid by a 1:1 reaction of Me-CAAC and BF₃·OEt₂ in hexane at room temperature. A 1:1:2 molar ratio of Me-cAAC:BF₃, cAAC: and KC₈ was reacted in toluene at -78 °C, the resultant suspension was slowly warmed up to room temperature to get a red violet solution. The reaction mixture was filtered and the resulting solution was reduced to 3 ml under vacuum. Red violet block-shaped crystals of (Me-cAAC)₂BF (**1**) were obtained in 78% yield at 0 °C after 24 h. (Me-cAAC)₂BF (**1**) was fully characterized by NMR (¹H, ¹³C, ¹¹B, ¹⁹F) and mass spectrometry (ESI, LIFDI). The composition of **1** was confirmed by single crystal X-ray diffraction and elemental analysis. Haloborylenes can be efficient precursors for the synthesis of B(I) cation by the treatment with halide scavengers. In our attempt to synthesize the boryl cation [(Me-cAAC)₂B]⁺ (Scheme 3) by the reaction of **1** with one equivalent of LiB(C₆F₅)₄, we observed an unprecedented 1 e⁻ oxidation of **1** to yield the radical cation [(Me-cAAC)₂BF]⁺[B(C₆F₅)₄]⁻ (**2**). The radical nature of **2** was deduced from broad resonances in the ¹H NMR spectrum. Compound **2** was isolated as brown color crystals at 0 °C after three days. The molecular structure of the radical cation (**2**) was unambiguously determined by single crystal X-ray analysis.



Scheme 3. Synthesis of **2**.

Compounds **1** and **2** are highly stable in the solid state as well as in solutions at room temperature under inert atmosphere for months. Also, **1** is stable in open air for a couple of weeks in solid form and in dry solution for about 10 to 15 hours and slowly changes its intense violet color to colorless. Compound **2** immediately loses its brown color upon exposure to air. The UV/vis spectra of **1** and **2** were recorded in dry n-hexane and THF, respectively. Compound **1** shows absorption maxima at 516 nm (Figure S12) and compound **2** at 450, 518 and 738 nm, respectively (Figure S13).

To check the unprecedented formation of **2**, we performed the cyclic voltammogram experiments of **1** in both, CH₃CN and THF at room temperature with 0.1 M and 0.2 M *n*Bu₄NPF₆ respectively as an electrolyte (Figures S14-16). In both solvents a well-defined one electron reversible redox couple was observed at -0.99 V (-0.92 V in THF vs Fc/Fc⁺) suggesting the radical stability at the operative condition. The reversible cyclic voltammogram and single electron activation suggest that compound **1** is catalytically active. Also, this gives an indication that **1** can be utilized as an excellent single electron transfer catalyst for many catalytic reactions. Further, in THF an irreversible two electrons oxidation peak (E_{pc}) showed up at -0.01 V but in CH₃CN it was not clearly resolved, perhaps due to the instability of the oxidized species in CH₃CN.

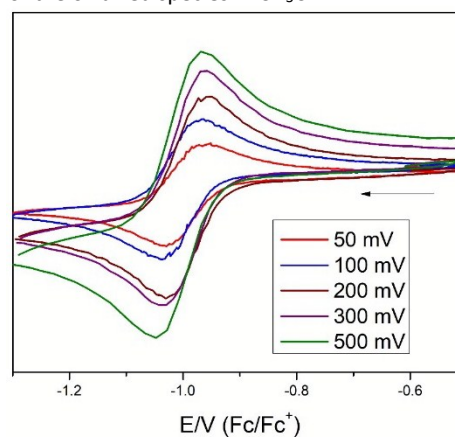


Figure 1. Scan rate dependent reversible cyclic voltammograms of **1** in acetonitrile (CH₃CN) (0.1 M *n*Bu₄NPF₆, 298 K) (scan rates: 50, 100, 200, 300, 500 mV s⁻¹).

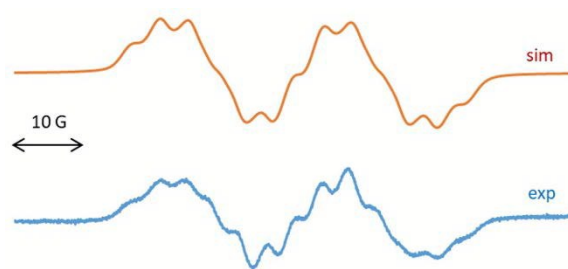


Figure 2. EPR spectrum of **2** (computer simulation, top) and (experimental, down) in THF at room temperature.



To understand the radical nature of **2**, EPR spectroscopy was performed. The EPR spectrum of the radical cation **2** at $g = 2.0063$ is dominated by a doublet of 23.2 G (Figure 2), attributed to the coupling of the unpaired electron with one ^{19}F nucleus. This large hyperfine splitting is comparable to the 16.5 G reported for the radical anion of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene, an isoelectronic species to durosemiquinone^{9a} or to the 16.8 G ^{19}F coupling of SiF_3 bonded to cAAC.^{9b} Each of the two doublet EPR lines for **2** is partially resolved by spin coupling with ^{14}N ($I = 1$, $a = 4.1$ G) and ^{11}B ($I = 3/2$, 80%, $a = 2.1$ G) and ^{10}B ($I = 3$, 20%, $a = 0.7$ G). The low values of $^{11,12}\text{B}$ isotope coupling have been noted earlier.^{9a} A ^{14}N splitting of a few Gauss would agree with the typical values observed for cAAC stabilized paramagnetic species.^{9a,c} Single crystal X-ray analyses of **1** (Figure 3) reveal that the bond distances of B1-C1 (1.513 Å) and B1-C3 (1.527 Å) are almost equal and are average of the B-C single (1.59 Å) and double (1.44 Å) bonds. The B-C (~1.52 Å) and C-N (~1.38 Å) bond lengths of **1** are identical to the bond lengths of (cAAC)₂BH (**B**).^{4b} The longer B-C bonds and shorter C-N bonds in **2** (Figure 3) compared to **1** suggest that the single electron in the oxidation from **1** to **2** is removed from a delocalized C-B-C moiety. Comparing with the (cAAC)₂BH radical cation,^{4b} relatively 0.04 Å shorter B-C bonds and 0.02 Å longer C-N bonds were observed for **2** which indicating the closer B-cAAC interaction. The B1-F1 (1.399 Å) bond length in **1** is comparable to the covalent radii for boron and fluorine (1.46 Å),¹⁰ and the longest among all the reported low-valent BF complexes,^{5c,d} albeit a shorter B1-F1 bond was observed in **2** because of one electron oxidation (Table T4, supporting information).

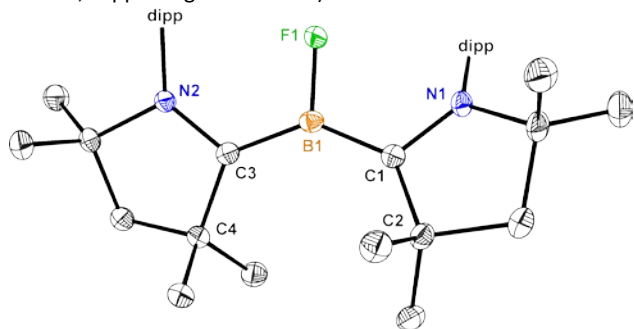


Figure 3. Crystal structure of **1** and **2** [in brackets], $[\text{B}(\text{C}_6\text{F}_5)_4]^+$ is omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å): B1-F1 1.3999(15) [1.369(6)], B1-C1 1.5137(19) [1.541(4)], N1-C1 1.3955(16) [1.376(4)], C1-C2 1.5462(17) [1.526(6)], B1-C3 1.5270(19) [1.541(4)], C3-N2 1.3787(16) [1.376(4)], C3-C4 1.5360(17) [1.526(6)].

Density functional theory is used to provide insight into the electronic structure of **1** and **2** ($[\text{B}(\text{C}_6\text{F}_5)_4]^+$ has been removed for simplicity). Calculations are carried out using dispersion corrected functional BP86-GD3(BJ) with def2-tzvp basis set.¹¹ All the optimized geometrical parameters of **1** and **2** are in good agreement with the crystal structure data which are summarized in Table T1.

Table 1. Comparison of selected structural parameters (bond length, Å) of **1** and **2** from X-Ray Structure analysis and DFT (BP86-GD3(BJ)/def2-tzvp).

Parameter	Structure 1		Structure 2	
	X-Ray	DFT	X-Ray	DFT
B1-F1	1.399	1.415	1.369	1.369

B1-C1	1.513	1.521	1.541	1.563
B1-C3	1.527	1.526	1.541	1.567
C1-C2	1.546	1.533	1.526	1.534
C3-C4	1.536	1.541	1.526	1.528
N1-C1	1.395	1.380	1.376	1.348
C3-N2	1.378	1.393	1.376	1.339

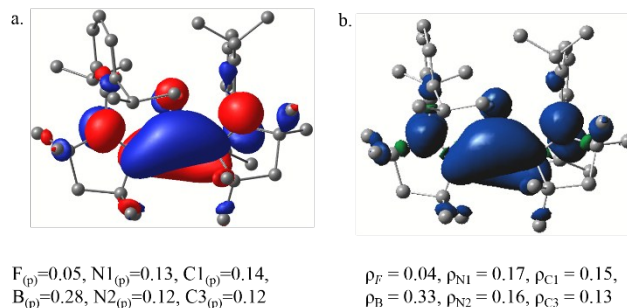


Figure 4. (a) SOMO of **2** with percent of p orbital contribution at BP86-GD3(BJ)/def2-tzvp level of theory. (b) Spin density plot of **2** with the Mulliken atomic spin densities at BP86-GD3(BJ)/def2-tzvp level of theory.

Ground state of **1** is singlet and **2** is doublet. The triplet state of **1** lies 21.3 kcal/mol higher in energy. The HOMO of **1** indicates that **1** is best described as borylene stabilized by Lewis bases where the lone pair at the B-atom is stabilized by the π back-bonding to both the cAAC ligands (Figure S22). The formation of **2** is accomplished by removing one electron from the delocalized π -orbital of **1**, reflecting longer B-C1 and B-C3 bonds and shorter C1-N1 and C3-N2 bonds in **2** in comparison to **1**. We have found that $\Delta E = -11.9$ kcal/mol for the reaction which infer that the forward reaction is highly feasible (BP86-GD3(BJ) with def2-tzvp basis set). Natural population analysis shows that the unpaired electron in **2** is delocalized over the boron atom and the ligand skeleton (Figure 4a). The spin density plot (Figure 4b) further substantiates the delocalized nature of the radical system, yet another example to show the crucial role of cAAC ligand to stabilize the radical system.¹² In order to further understand the nature of bonding in **1** and **2**, we carried out a EDA-NOCV analysis by dividing the molecule into two fragments, BF and $[\text{cAAC}]_2$ for **1**, and BF^+ and $[\text{cAAC}]_2$ for **2**.¹³ Various different electronic states of two different fragments were considered to identify the smallest orbital interaction energy (E_{orb}) term and hence the best fragments.¹⁴ Table T5 (supporting information) summarizes the results for most favorable fragments. The deformation densities associated with the pairwise orbital interactions for the three strongest orbital interactions obtained from the EDA-NOCV analysis are shown in Figures 5a and 5b.



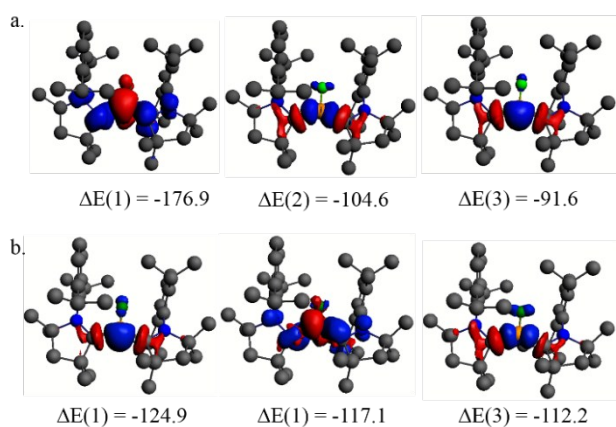


Figure 5. Plot of the deformation densities of the interactions for the pairwise orbital interactions of three strongest orbital interactions with associated interaction energies between (a) BF and [cAAC]₂ in **1** and (b) BF⁺ and [cAAC]₂ in **2**. The direction of the charge flow is red→blue.

The $\Delta E(1)$ in Figure 5a shows that the strongest orbital interaction is the π -back donation from BF to [cAAC]₂ and $\Delta E(2)$ and $\Delta E(3)$ correspond to the σ -donation from [cAAC]₂ to BF in **1**. Similarly, $\Delta E(1)$ and $\Delta E(3)$ in Figure 5b correspond to the σ -donation from [cAAC]₂ to BF⁺ and $\Delta E(2)$ gives the π -back donation from BF⁺ to [cAAC]₂. The strength of σ -donation is stronger in **2** and the π -back donation is weaker compared to **1**. Therefore, the formation of **2** takes place at the cost of π -delocalization and the benefit of stronger σ -bonding.

In summary, an efficient synthetic approach was developed to synthesize cAAC stabilized fluoroborylene and its radical cation. The one e⁻ oxidation of **1** with one equivalent of LiB(C₆F₅)₄ leads to the formation of a stable radical cation which is confirmed by EPR measurement. Compounds **1** and **2** were fully characterized by single crystal analyses. DFT computational studies infer that the electron(s) residing on the B-atom are delocalized over cAAC ligands and thereby providing stability for both the complexes **1** and **2**. Cyclic voltammetry experiments show that two electrons oxidation of (cAAC)₂BF is highly feasible to obtain diradical dication and the synthesis of boryl cation [(Me-cAAC)₂B]⁺ by removing the fluorine atom from **1** is possible under suitable reaction conditions. Both the works are in progress. Also, we are investigating the catalytic activity of **1** as a single electron transfer catalyst.

Crystal Structure determination: Crystal handling and selection was carried out under an inert atmosphere and at low temperatures provided by the x-temp2 device.¹⁵ Subsequent data collection has been carried out on Bruker Smart Apex II systems with the enclosed software suit. The resulting experimental data has been integrated with saint¹⁶ and an additional multi-scan absorption correction and a 3 λ correction¹⁷ was applied with sadabs.¹⁸ The structure solution was then calculated by shelxt¹⁹ and refined by shelxl²⁰ via the shelxle GUI.²¹

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Conflicts of interest

There are no conflicts to declare.

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