

A Borenium Cation Stabilized by an N-Heterocyclic Carbene Ligand

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Summary: Reaction of Mes_2BF with trimethylsilyl triflate (Me_3SiOTf) and $[\text{Ag}(\text{IME})_2][\text{Ag}_2\text{I}_3]$ ($\text{IME} = 1,3\text{-dimethylimidazol-2-ylidene}$) in refluxing chlorobenzene affords the carbene-stabilized borenium salt $[(\text{IME})\text{BMe}_2]\text{OTf}$ ($[\text{I}][\text{OTf}]$). As indicated by cyclic voltammetry, $[\text{I}]^+$ is reversibly reduced to produce a radical that has been characterized by EPR spectroscopy.

N-heterocyclic carbenes (NHC) have become ubiquitous ligands in main-group chemistry.¹ Because of their strong σ -donor properties, such ligands have served to stabilize a number of otherwise highly reactive species, including unusual cations² and low-coordinate species,^{3,4} among others. Interestingly, however, such NHC ligands have never been introduced in diarylborenium cations ($[(\text{L})\text{BAR}_2]^+$, with $\text{L} = \text{neutral ligand}$ and $\text{Ar} = \text{aryl group}$).^{5–8} Taking into account the unusual ligative properties of NHC ligands, we postulated that the resulting $[(\text{NHC})\text{BAR}_2]^+$ cations may possess a robust core and be amenable to reversible redox chemistry. Stimulated by this possibility, we have now decided to synthesize such a $[(\text{NHC})\text{BAR}_2]^+$ cation.

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The reaction of Mes_2BF with trimethylsilyl triflate (Me_3SiOTf) and $[\text{Ag}(\text{IME})_2][\text{Ag}_2\text{I}_3]$ ($\text{IME} = 1,3\text{-dimethylimidazol-2-ylidene}$) in refluxing chlorobenzene affords, after 12 h, $[(\text{IME})\text{BMe}_2]\text{OTf}$ ($[\text{I}][\text{OTf}]$) (Scheme 1). The formation of $[\text{I}][\text{OTf}]$ was confirmed by ^1H NMR, which showed the presence of one IME ligand bound to the boron center. The detection of two resonances for the *o*-methyl groups of the mesityl substituent is indicative of a C_2 geometry whose handedness does not change on the NMR time scale at room temperature. The presence of a tricoordinate boron atom was confirmed by the detection of a ^{11}B NMR signal at 66 ppm. This chemical shift is comparable to the value of 64 ppm reported for $[(\text{DMP})\text{BMe}_2]^+$ ($\text{DMP} = p\text{-(dimethylamino)pyridine}$), which also features a tricoordinate boron atom.¹⁰ To our knowledge, NHCs have been incorporated in neutral borane^{4,11} and boraanthracene¹² adducts but not in boreniums.⁶ Hence, $[\text{I}][\text{OTf}]$ represents the first example of a borenium stabilized by a NHC ligand. The structure of $[\text{I}][\text{OTf}]$ has also been studied using single-crystal X-ray diffraction (Figure 1).¹³ The boron center is trigonal planar, as indicated by the sum of the bond angles, which is equal to 359.9° . The $\text{B}(1)\text{--C}(1)$ bond connecting the IME ligand to the boron center ($1.579(7)$ Å) is comparable to the $\text{B}(1)\text{--C}(6)$ ($1.562(7)$ Å) and $\text{B}(1)\text{--C}(15)$ bonds ($1.560(7)$ Å), suggesting a strong coordination of the carbene ligand. The dihedral angle of 37.3° formed between the boron trigonal plane and the plane containing the IME ligand is smaller than the average dihedral angle of 53.7° formed by the mesityl groups and the boron trigonal plane. This difference can be assigned to the lower steric hindrance of the IME ligand, whose *N*-methyl groups adopt a more divergent orientation.

The cyclic voltammogram of $[\text{I}]^+$ in CH_2Cl_2 displays a single reversible reduction wave at $E_{1/2}^{\text{Red}} = -1.81$ V vs Fc/Fc^+ (Figure 2). The reduction potential of $[\text{I}]^+$ is distinctively more positive than that of neutral boranes,^{14,15} such as

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(13) Crystal data for $[\text{I}][\text{OTf}]$: crystal dimensions $0.20 \times 0.20 \times 0.15$ mm, $\text{C}_{25}\text{H}_{31}\text{BCl}_3\text{F}_3\text{N}_2\text{O}_3\text{S}$, $M_r = 613.74$, orthorhombic, space group $Pbca$, $a = 14.1972(14)$ Å, $b = 10.9105(11)$ Å, $c = 36.276(4)$ Å, $V = 5619.1(10)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.451$ g cm⁻³, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $T = 110(2)$ K, 28958 measured reflections, 4415 unique reflections, $R_{\text{int}} = 0.0609$, $R1 = 0.0725$, $wR2 = 0.1581$ (all data).

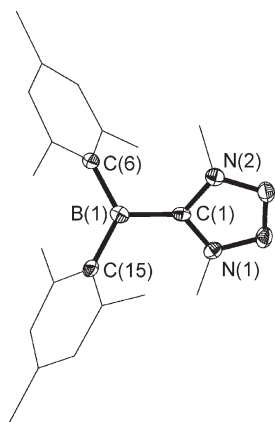
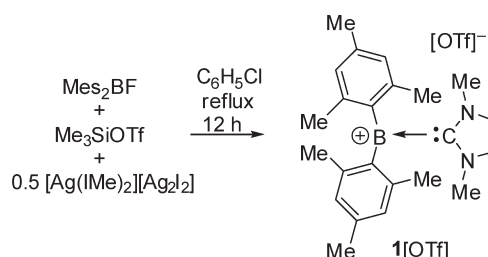


Figure 1. Partial ORTEP drawing of $[1]^+$ in $[1][OTf]$ (50% probability). Hydrogen atoms are omitted for clarity. Pertinent metrical parameters can be found in the text.

Scheme 1



Mes_3B , which is reduced at -2.73 V (vs Fc/Fc^+).¹⁵ This reduction potential difference may be assigned to the cationic character of $[1]^+$, which increases its electrophilicity. In fact, the reduction potential of $[1]^+$ is in the same range as that measured for $[(DMAP)BMes_2]^+$ ($E_{peak} = -2.03$ V), which, unlike $[1]^+$, undergoes an irreversible reduction.⁸ Encouraged by the reversibility of the reduction of $[1]^+$, we have investigated the chemical generation of the corresponding radical. To this end, $[1][OTf]$ was treated with powdered magnesium metal in THF to produce a deep purple solution containing the putative radical 1^\bullet . This radical appears to be persistent but has thus far eluded isolation in the condensed state. Since its crystal structure could not be determined, 1^\bullet was characterized by EPR spectroscopy (Figure 2). In order to simulate this spectrum, we first carried out a DFT optimization of 1^\bullet at the B3LYP/6-311g(d) level and computed the hyperfine coupling parameters using the resulting geometry at the UB3LYP/6-311g(d) level (Figure 2). Using these parameters as an initial guess, the EPR spectrum was then simulated by hand. The similarity of these parameters serves to validate the computed spin density which shows substantial localization of the unpaired electron in a B–C π -bonding orbital. The electronic structure of this radical is reminiscent of

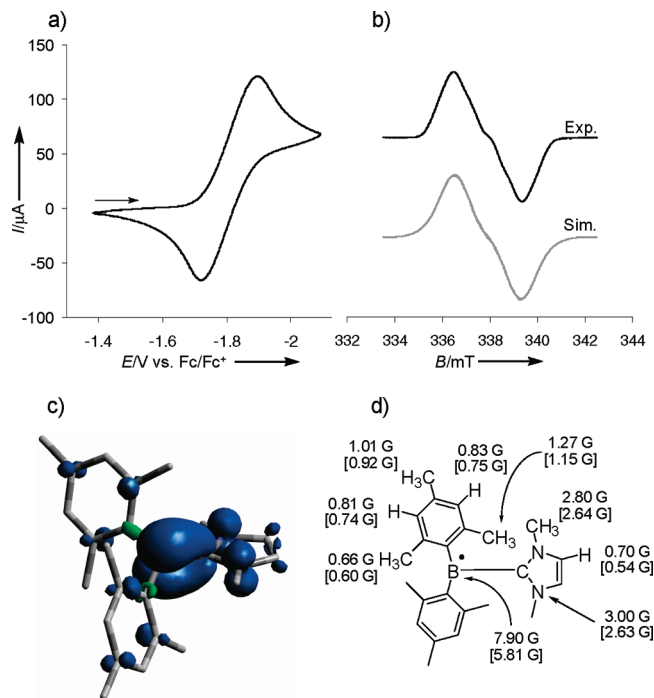
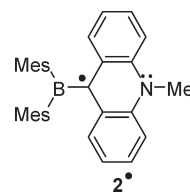


Figure 2. (a) Cyclic voltammogram of $[1][OTf]$ measured at a scan rate of 0.1 V/s. (b) EPR spectra at 293 K ($g = 2.003$, microwave frequency, 9.4730 GHz) for 1^\bullet in THF and the corresponding simulation. (c) Optimized structure of 1^\bullet with an overlay of the computed spin density (isovalue 0.003 , H atoms omitted for clarity). (d) Observed and computed (in brackets) hyperfine coupling constants for 1^\bullet .

that observed in the 9-borylated acridinyl radical 2^\bullet .^{7,16} Unlike in 2^\bullet , however, the resulting one-electron B–C π bond of 1^\bullet is notably polarized toward the boron atom, in agreement with the limited π -accepting properties of the IMe carbene ligand. As a final note, it is worth pointing out that 1^\bullet is related to $[NHC-BH_2]^\bullet$ radicals, whose formation has been proposed but not spectroscopically confirmed.¹⁷



In conclusion, we have isolated and characterized an NHC-stabilized borenium cation and have found that this cation is reversibly reduced to produce a radical which can be detected by EPR spectroscopy. We are currently attempting to isolate a crystalline analogue of such a radical.

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Supporting Information Available: Text, figures, tables, and a CIF file giving synthetic, spectroscopic, crystallographic, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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