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Carbon–Boron Radicals

A 9-Borylated Acridinyl Radical**

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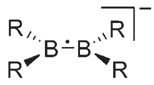
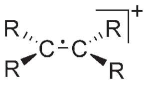
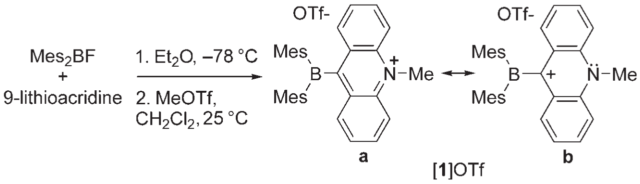
The formation of odd-electron bonds[1] in first-row main-group derivatives is a relatively rare phenomenon.[2,3] The rarity of such linkages can be correlated to the intrinsic instability of open-shell electronic configurations, which usually results in radical elimination or coupling processes. This situation applies to radical anions of diboranes (type **A**), for which the existence of a one-electron π bond has been proposed.[4–6] While spectroscopic evidence for such radicals was obtained early on,[4–6] their stabilization and isolation in the condensed state have only been achieved once.[7,8] Radical cations of alkenes (type **B**) are also too unstable to isolate[9–11] unless appropriate substituents are employed.[12,13] One of the added complications which jeopardizes the stability of radicals of types **A** and **B** is their charged character and associated reducing or oxidizing nature. Hoping to eliminate these destabilizing effects, we decided to focus on the synthesis and study of neutral radicals of type **C**.


A


B


C

It occurred to us that a radical of type **C** could be obtained by reduction of a borane bearing an α-methylium center. Keeping in mind that 9,9′-biacridinium ions undergo clean stepwise reductions,[14,15] we decided to focus on the synthesis of a 9-boryl-acridinium derivative. Treatment of 9-lithioacridine with Mes_2BF (Mes = 2,4,6-$Me_3C_6H_2$) affords the corresponding acridinyl borane, which could be easily alkylated in CH_2Cl_2 with MeOTf (Scheme 1). The resulting acridinium borane $[\mathbf{1}]^+$ has been isolated as a triflate salt which can be stored in air for extended periods of time. This novel derivative has been fully characterized. While the ^{1}H NMR spectrum shows all the expected resonances, the ^{11}B NMR signal detected at $\delta = 77$ ppm confirms the presence of a base-free trigonal-planar boron center. The ^{13}C NMR resonance of the C-9 carbon atom of the acridinium unit was detected at $\delta = 175$ ppm, which is close to that detected in other acridinium derivatives. We note in passing that the acridinium borane $[\mathbf{1}]^+$ (form **a**) can be alternatively described as an α-boryl methylium compound (form **b**; Scheme 1). The chemical shift of the C-9 carbon nucleus is similar to that reported for the methylium center of $[(4\text{-}Me_2NC_6H_4)_3C]^+$ ($\delta = 179$ ppm),[16] which points to the relevance of form **b**.



Scheme 1. Synthesis of [**1**]OTf.

As indicated by cyclic voltammetry, $[\mathbf{1}]^+$ undergoes two reversible reductions at −0.86 and −1.56 V versus ferrocene/ferrocenium (Fc/Fc$^+$; Figure 1), thus suggesting the formation of $\mathbf{1}^{\bullet}$ and $[\mathbf{1}]^-$ as stable reduction species. This behavior contrasts with that of other triarylboranes, which typically undergo a single reversible reduction and a subsequent irreversible one.[17] Moreover, the potential of the first reduction wave is distinctly more positive than that of triarylboranes, such as Mes_3B, which is typically observed at −2.6 V versus Fc/Fc$^+$.[17] It is also more positive than that of *N*-methylacridinium, which is reduced at −1.11 V versus Fc/Fc$^+$ (−0.58 V vs. SCE).[18] Encouraged by these results which suggest the formation of a stable radical, we attempted the isolation of $\mathbf{1}^{\bullet}$.

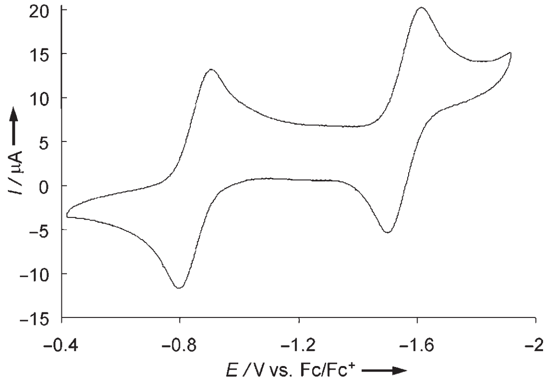


Figure 1. Cyclic voltammogram of [**1**]OTf in CH_2Cl_2 with a glassy carbon working electrode; scan rate 100 mV s^{-1}, 0.1 M NBu_4PF_6.

Treatment of [**1**]OTf with Mg in acetonitrile/hexane (Scheme 2) produces a deep-blue hexane solution which can be separated from the acetonitrile layer. Upon cooling to −40 °C, the hexane solution affords single crystals of the neutral radical $\mathbf{1}^{\bullet}$. The crystal structure of $\mathbf{1}^{\bullet}$ has been

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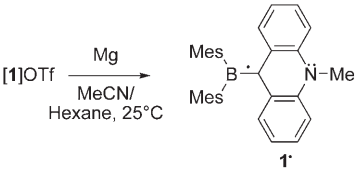

Scheme 2. Synthesis of $\mathbf{1}^{\bullet}$.

experimentally determined (Figure 2).[19] The boron atom B1 and the carbon atom C9 adopt a trigonal-planar geometry. The B1–C9 bond (1.559(5) Å) is shorter than the B–C bond observed in bulky triarylboranes such as 9,10-bis(dimesitylboryl)anthracene (1.59 Å).[20] It is however longer than that typically observed in borataalkenes[21] such as 8,10,11a-trimethyl-7-mesityl-11a*H*-7-boratabenzo[de]anthracene, which features a B–C double bond of length 1.48 Å.[22] Other salient structural features include: 1) a twist angle α of 44.8° for the B1–C9 bond and 2) a slight puckering of the central C_5N ring of the acridine moiety leading to the displacement of the C9 and N1 atoms by 0.12 and 0.16 Å, respectively, above the C10-C11-C12-C13 plane. A geometry optimization of this radical using DFT methods (B3LYP, 6-31g) affords a structure that closely matches that determined experimentally (B1–C9$_{\text{calcd}}$ 1.566 Å; $\alpha_{\text{calcd}} = 43.8°$).

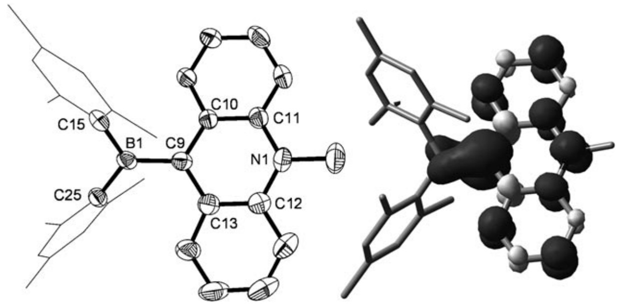

Figure 2. Left: Crystal structure of $\mathbf{1}^{\bullet}$: Selected bond lengths [Å] and angles [°]: B1-C9 1.559(5), B1-C15 1.581(5), B1-C25 1.593(5), C9-C10 1.430(4), C9-C13 1.447(4); C9-B1-C15 119.3(3), C9-B1-C25 121.2(3), C15-B1-C25 119.4(3), C10-C9-C13 116.2(3), C10-C9-B1 121.4(3), C13-C9-B1 122.5(3). Right: DFT-optimized geometry of $\mathbf{1}^{\bullet}$ with an overlay of the computed spin density (isovalue = 0.0025).

Radical $\mathbf{1}^{\bullet}$ was analyzed by EPR spectroscopy in hexane at room temperature. The observed EPR spectrum could be satisfactorily simulated based on the hyperfine coupling constants shown in Figure 3. This fitting suggests delocalization of the spin on the acridyl moiety with a nonnegligible contribution from the boron atom ($a(^{11}\mathrm{B}) = 2.55$ G). In accordance with this view, the computed spin density of $\mathbf{1}^{\bullet}$ shows substantial localization of the unpaired electron in a B–C π-bonding orbital which is noticeably polarized toward the carbon atom (Figure 2).

In conclusion, we report the synthesis of a new boron-containing radical[23–28] in which the unpaired electron is partly localized in a polarized boron–carbon π bond. The B1–C9 bond length falls between that typically observed for B–C single bonds and B–C double bonds. It is also intermediate between that observed for $[\mathrm{Mes_2BBMesPh}]^{\bullet-}$ (1.65 Å)[8] and $[\mathrm{An_2CCAn_2}]^{\bullet+}$ (1.42 Å; An = 4-MeOC$_6$H$_4$)[13] radicals. For these reasons, we propose that $\mathbf{1}^{\bullet}$ be regarded as possessing a weak boron–carbon π bond. We are currently focusing on the isolation and structural characterization of crystalline salts of $[\mathbf{1}]^{+}$ and $[\mathbf{1}]^{-}$, whose structures will be compared to that of $\mathbf{1}^{\bullet}$.

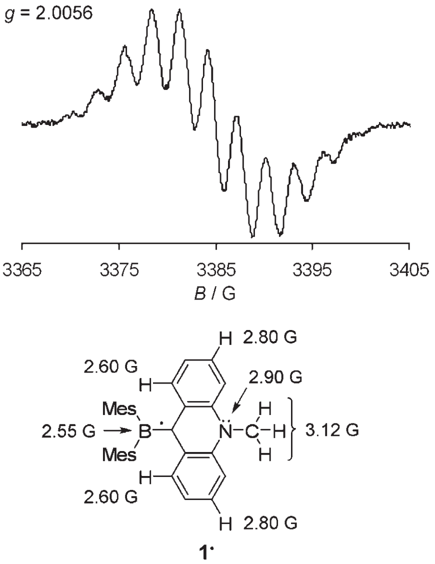

Figure 3. Top: EPR spectrum of $\mathbf{1}^{\bullet}$ in hexane at room temperature. Bottom: Experimental hyperfine coupling constants.

Experimental Section

[**1**]OTf: A hexane solution of *n*BuLi (1.6 M, 3 mL, 4.8 mmol) was added to a solution of 9-bromoacridine (1 g, 4 mmol) in diethyl ether (60 mL) at −78 °C. After 30 min, a solution of dimesitylboron fluoride (1.26 g, 4.7 mmol) in diethyl ether (15 mL) was added to the reaction mixture. The reaction mixture was allowed to warm to room temperature. After stirring for 12 h, the reaction was quenched with water. The product was extracted with diethyl ether. The organic phase was washed with brine, dried over MgSO$_4$, filtered, and dried under vacuum to afford a viscous oil. Extraction of this oil with hexane afforded crude 9-dimesitylborylacridine as a brown solid. Without further purification this solid was dissolved in dichloromethane and allowed to react with an excess of methyl triflate in the glove box. After stirring for 1 h, [**1**]OTf was precipitated as a bright yellow solid by addition of diethyl ether. Yield: 0.71 g, 30 % based on 9-bromoacridine; ^{1}H NMR (499.95 MHz, [D]chloroform, TMS): $\delta =$ 1.88 (s, 12 H, Mes-CH$_3$), 2.28 (s, 6 H, Mes-CH$_3$), 5.03 (s, 3 H, NMe), 6.82 (s, 4 H, Mes-CH), 7.65 (dd, ^3J(H,H) = 5 Hz, ^3J(H,H) = 8.5 Hz, 2 H), 8.24 (d, ^3J(H,H) = 8.5 Hz, 2 H), 8.29 (dd, ^3J(H,H) = 5 Hz, ^3J(H,H) = 9.5 Hz, 2 H), 8.73 ppm (d, ^3J(H,H) = 9.5 Hz, 2 H); ^{13}C NMR (125.7 MHz, [D]chloroform, TMS): $\delta = 21.4$ (Mes-*p*-CH$_3$), 24.1 (Mes-*o*-CH$_3$), 39.6 (NMe), 119.5, 127.5, 128.2, 129.9, 130.8, 138.9, 139.6, 141.0, 142.8, 143.9, 174.8 ppm; ^{11}B NMR (128.2 MHz, [D]chloroform, BF$_3$·OEt$_2$): $\delta = 76.5$ ppm. Elemental analysis (%) calcd for $C_{33}H_{33}BF_3NO_3S$: C 67.01, H 5.62; found: C 66.73, H 5.53.

$\mathbf{1}^{\bullet}$: [**1**]OTf (30 mg, 0.05 mmole) was allowed to react with excess Mg powder at room temperature in acetonitrile (2 mL). After stirring for 10 minutes, the dark green solution was extracted with hexane (3 × 10 mL). The resulting dark blue hexane solution was concentrated to about 5 mL and cooled to −40 °C to afford dark crystals of **1**˙. Yield: 8.5 mg, 35 %; the yield has not been optimized at this time.

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[1] The term "odd-electron bond" has been used in the description of compounds where two elements are linked by an odd number of electrons; for recent examples, see: T. Kato, H. Gornitzka, W. W. Schoeller, A. Baceiredo, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5633 – 5636; *Angew. Chem. Int. Ed.* **2005**, *44*, 5497 – 5500; H. Grutzmacher, F. Breher, *Angew. Chem.* **2002**, *114*, 4178 – 4184; *Angew. Chem. Int. Ed.* **2002**, *41*, 4006 – 4011.

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[19] Crystal data for **1**˙: crystal dimensions 0.13 × 0.11 × 0.02 mm, $C_{32}H_{33}BN$, $M_r = 442.40$, monoclinic, space group $P2_1/n$, $a = 15.979(3)$, $b = 9.0599(18)$, $c = 18.109(4)$ Å, $\beta = 104.34(3)°$, $V = 2540.0(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.157\ g\,cm^{-3}$, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $T = 110(2)$ K, 17755 measured reflections, 3573 unique, $R_{int} = 0.0793$, $R_1 = 0.0985$, $wR_2 = 0.1819$ (all data). The crystal was mounted onto a nylon loop with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 with the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. CCDC-623112 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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