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Synthesis and Characterization of B-Heterocyclic π-Radical and Its Reactivity as a Boryl Radical

Yoshitaka Aramaki,[†] Hideki Omiya,[†] Makoto Yamashita,*[,†,§] Koji Nakabayashi,[‡] Shin-ichi Ohkoshi,*[,‡] and Kyoko Nozaki*[,†]

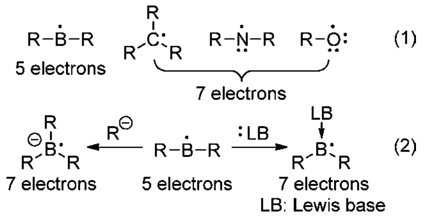
[†]Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[‡]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

S *Supporting Information*

ABSTRACT: The first isolation and full characterization of the stable, persistent diazaboracyclic neutral radical **3** is reported. Reduction of base-stabilized difluoroborane **2** provided radical **3** as a neutral molecule having a planar sp^2 boron atom attached to one fluorine and two nitrogen atoms. ESR spectroscopy and DFT calculations indicated that the unpaired electron is delocalized over the six-membered ring. Because of an electronic transition related to the singly occupied molecular orbital, **3** has a characteristic red color, as UV−vis spectroscopy showed an absorption maximum at 498 nm. Although DFT calculations suggested that radical **3** has relatively low spin density on the boron atom in comparison with the nitrogen and carbon atoms in the six-membered ring, **3** reacted as a base-stabilized boryl radical when treated with benzoquinone or benzoyl peroxide.

Since the isolation of triphenylmethyl radical by Gomberg,[1] a number of stable radicals have been isolated and characterized.[2] Among the second-row elements, most of the stable radicals are oxygen-, nitrogen-, or carbon-centered radicals having seven electrons around the central atom. In contrast, there has been no report on the direct observation of neutral boron-centered radicals in the literature.[3] The electron deficiency at the boron center of a neutral boron-centered radical having five electrons (eq 1) would contribute to its instability.



One can expect that a neutral boron-centered radical could be stabilized by the addition of an anionic ligand or a Lewis base on the boron center to reduce the electron deficiency of the boron atom (eq 2). In fact, triarylboron radical anions, $BAr_3^{\bullet-}$, have been well-studied with ESR spectroscopy[4] and X-ray crystallography.[5] In related studies, one-electron reduction of diborane(4) compounds was reported to form the corresponding radical anions $[R_2B{-}BR_2]^{\bullet-}$ possessing a one-electron π bond.[6] One-electron reduction of geometrically strained 1,8-diborylnaphthalene resulted in the formation of a similar type of radical anion in which the unpaired electron is σ-delocalized between the two boron atoms.[7] Recently, an anionic borole radical was also studied by X-ray crystallography, electron spin resonance (ESR) and UV−vis spectroscopy, cyclic voltammetry (CV), and trapping with dibenzoyl peroxide.[8] Examples of base-stabilized boron-centered radical species are limited to the N-heterocyclic carbene (NHC)- and pyridine derivative-stabilized boryl radicals $NHC{-}BR_2^{\bullet}$ (R = H, Mes) and $R'C_5H_4N{-}BH_2^{\bullet}$ [$R' = NMe_2$, $N(CH_2)_4$, $N(CH_2CH_2)_2O$] characterized by Lacôte and Curran,[9a] Gabbaï,[9b] and Lalevée[9c] and the singlet diradical $[t\text{-}BuB^{\bullet}{-}P(i\text{-}Pr)_2]_2$ reported by Bertrand,[10] which can be considered as a dimeric form of the base-stabilized boryl radical $t\text{-}BuB^{\bullet}{-}P(i\text{-}Pr)_2$. Thus, the reactivity of neutral base-stabilized boryl radicals is still waiting to be further explored.

To obtain a radical structure satisfying the above requirements, we became interested in the reduction of β-diiminate boron difluoride **2**[11] to give a neutral boron-centered radical. While the reactions of base-stabilized aminodifluoroboranes with Lewis bases to give six-π-electron borenium cations were extensively studied,[12] reduction of a difluoride to isolate a base-stabilized boryl radical has never been explored.[13] Here we report the first isolation and full characterization of a stable, persistent diazaboracyclic neutral radical, **3**.[14] Although radical **3** has very low spin density on the boron atom in the ground state, it reacts as a base-stabilized boryl radical when treated with benzoquinone (BQ) or benzoyl peroxide (BPO).

The precursor, base-stabilized difluoroborane **2**, was synthesized by deprotonation of β-diimine **1** with KH followed by reaction with $BF_3{\cdot}OEt_2$ (Scheme 1). The C_{2v}-symmetric pattern of the signals in the ^{1}H NMR spectrum of **2** and the presence of only one singlet signal in the ^{19}F NMR spectrum indicated rapid interconversion between distorted structures or a C_{2v}-symmetric structure with a planar B-heterocycle. The ^{11}B NMR signal at relatively high field (δ_B 0.9) indicated the presence of an sp^3-hybridized boron center. Single-crystal X-ray analysis of **2** revealed a planar structure of the B-heterocycle with small dihedral angles in the six-membered ring (Figure 1).

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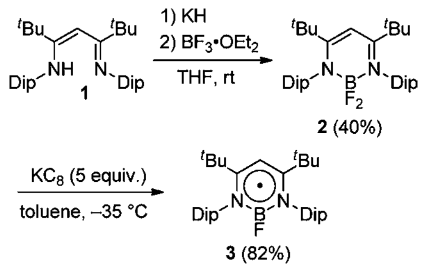
Scheme 1. Synthesis and Reduction of Base-Stabilized Difluoroborane 2



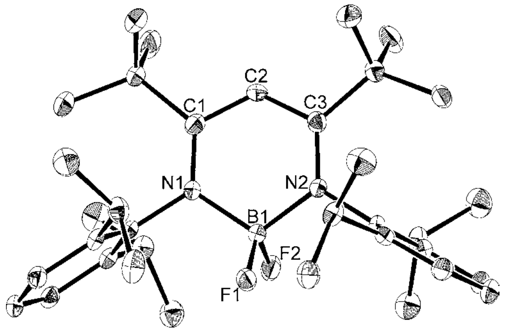


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are set at 50% probability. Selected bond distances (Å), bond angles (deg), and dihedral angles (deg): B1–N1, 1.564(3); B1–N2, 1.560(3); N1–C1, 1.332(2); C1–C2, 1.391(3); C2–C3, 1.396(3); C3–N2, 1.331(2); F2–B1–F1, 108.73(16); F2–B1–N2, 109.52(15); F1–B1–N2, 109.45(15); F2–B1–N1, 109.17(15); F1–B1–N1, 109.28(15); N2–B1–N1, 110.66(15); N2–B1–N1–C1, 16.6(2); B1–N1–C1–C2, –5.9(3); N1–C1–C2–C3, –7.9(3); C1–C2–C3–N2, 8.0(3); C2–C3–N2–B1, 5.6(3); N1–B1–N2–C3, –16.4(2).

The two B–N bond lengths [1.564(3) and 1.560(3) Å] are in the range between typical B–N single bond (1.50 Å)[15] and a B–N dative bond (1.66 Å),[16] as calculated for the complexes $H_2N{-}BH_2{\leftarrow}NH_3$ and $H_3B{\cdot}NH_3$. The B–N, N–C, and C–C bond lengths are also comparable to those observed in the previously reported β-diiminate-substituted borane (1.507–1.550 Å).[11b]

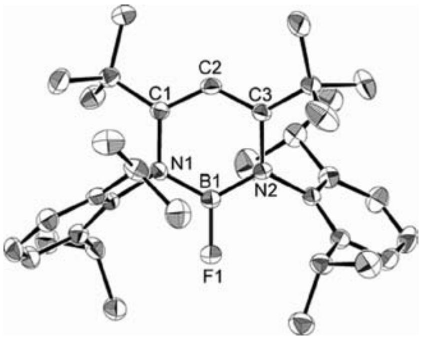


Figure 2. ORTEP drawing of base-stabilized boryl radical **3**. Thermal ellipsoids are set at 50% probability. Selected bond distances (Å), bond angles (deg), and dihedral angles (deg): B1–F1, 1.342(4); B1–N1, 1.416(4); B1–N2, 1.415(4); N1–C1, 1.440(3); C1–C2, 1.388(4); C2–C3, 1.373(4); C3–N2, 1.438(3); F1–B1–N2, 118.5(3); F1–B1–N1, 118.5(3); N2–B1–N1, 123.0(3); N2–B1–N1–C1, 8.2(4); B1–N1–C1–C2, –15.5(4); N1–C1–C2–C3, 7.3(4); C1–C2–C3–N2, 8.8(4); N1–B1–N2–C3, 8.0(4); C2–C3–N2–B1, –16.0(4).

Reduction of **2** with KC_8 at –35 °C gave an NMR-silent red crystalline solid, **3** (Scheme 1). X-ray crystallographic analysis revealed that **3** is a neutral molecule having a planar sp^2 boron atom attached to one fluorine and two nitrogen atoms (Figure 2). The relatively short B1–F1 bond length of 1.342(4) Å, which is shorter than the sum of the covalent radii (1.46 Å), is close to that in triplet states of fluoroboraethene $H_2C{=}BF$ (1.356 Å),[17] indicating an electrostatic interaction between the boron and fluorine atoms.[18] The two B–N bond lengths of 1.416(4) and 1.415(4) Å are similar to those calculated for borazine ($B_3N_3H_6$) (1.432 Å),[19] indicating the sharing of π electrons as observed for the other N–B–N systems.[20] The hybridization of the boron center was estimated to be sp^2 as the sum of the angles around the boron center was 360.0°; two nitrogen atoms were somewhat pyramidalized (357.2 and 357.9°). In the boron-containing six-membered ring, the two N–C bonds [N1–C1 = 1.440(3) Å and C3–N2 = 1.438(3) Å] are longer than those in **2** while the C–C bonds [C1–C2 = 1.388(4) Å and C2–C3 = 1.373(4) Å] are similar to those in **2**, suggesting that the bonding between the nitrogen and carbon atoms was changed by the reduction. On the basis of the NMR-silent character and these structural features, a structure with seven π electrons delocalized over the six-membered heterocycle was suggested for the open-shell compound **3**. In fact, **3** is ESR-active, and the EPR spectrum of its toluene solution at 180 K is shown in Figure 3. A simulated spectrum with hyperfine splittings corresponding to one hydrogen atom at the 4-position (17.4 MHz, $I = {}^1/_2$ for ^1H), two nitrogen atoms at the 2- and 6-positions (4.1 MHz, $I = 1$ for ^{14}N), one boron atom (7.2 MHz, $I = {}^3/_2$ for ^{11}B), and one fluorine atom (3.5 MHz, $I = {}^1/_2$ for ^{19}F) showed good agreement with the observed spectrum. Similarly, the ESR spectrum of **3** was observed at room temperature and could be reproduced using nearly identical hyperfine splitting parameters [Figure S5 in the Supporting Information (SI)].

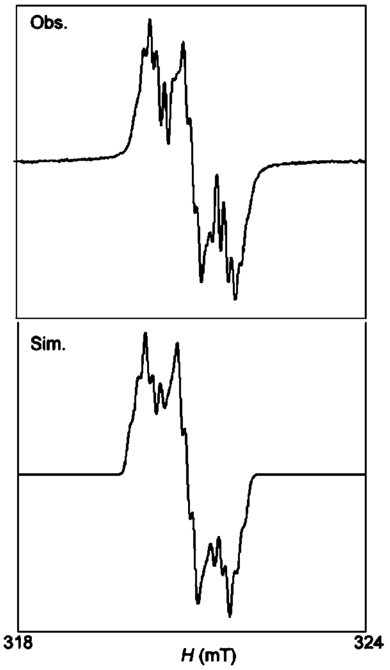


Figure 3. (top) Observed ESR spectrum of **3** in toluene solution at 180 K; (bottom) simulated ESR spectrum obtained using $g = 2.002$, $A_H = 17.4$ MHz, $A_B = 7.2$ MHz, $A_N = 4.1$ MHz, and $A_F = 3.5$ MHz.

To clarify the electronic character of **3**, unrestricted density functional theory (DFT) calculations were performed. The UB3LYP/6-31G*-optimized structure of **3** reproduced the experimentally obtained structure. The singly occupied molecular orbital (SOMO) and highest occupied molecular orbital (HOMO) for the optimized structure are illustrated in Figure 4. The SOMO has antibonding character for the π bond over the N1−C1 and N2−C3 bonds, which is consistent with the N−C bonds in **3** being longer than those in **2** longer because of the half occupation of the antibonding orbital. Also, the HOMO has π-bonding character of the B1−N1 and B1−N2 bonds, in accord with the shortened B−N bonds found in the crystallographic study. In the HOMO and SOMO of **3**, the C1−C2−C3 unit has allylic radical character, with the HOMO having bonding character over three carbons and the SOMO having a small MO coefficient for the central carbon.[21] Calculation of the spin density in **3** (Figure 5) showed that it is mainly localized on C1 and C3 (0.517), followed by C2 (−0.233), N1 and N2 (0.075), and a relatively small spin density on B1 (−0.008). This distribution of spin density is consistent with a small MO coefficient on the boron atom in SOMO; in other words, allylic radical character is dominant in **3**. In fact, the frontier orbitals and the spin density distribution in radical **3** are close to those of allyl radical,[22] with the HOMO of **3** corresponding to the HOMO of allyl radical and the SOMO of **3** to the SOMO of allyl radical. It is noteworthy that the calculated LUMO+1 and LUMO+4 have a noticeable orbital coefficient on the central boron atom (see below). From the X-ray crystallography, ESR, and DFT results, the following three resonance structures are suggested to contribute the properties of **3** (Figure 6): boron-centered radical **3a**, allylic radical **3b**, and the ylide structure of nitrogen radical **3c**. The major contribution comes from structure **3b**.

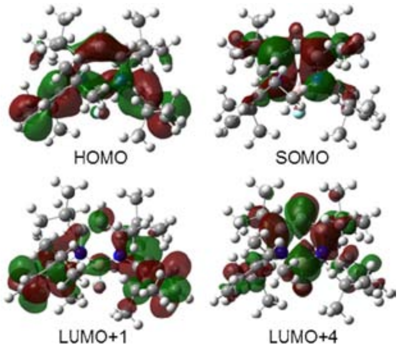


Figure 4. UB3LYP/6-31G*-calculated MOs of radical **3**: (upper left) HOMO; (upper right) SOMO; (bottom left) LUMO+1; (bottom right) LUMO+4.

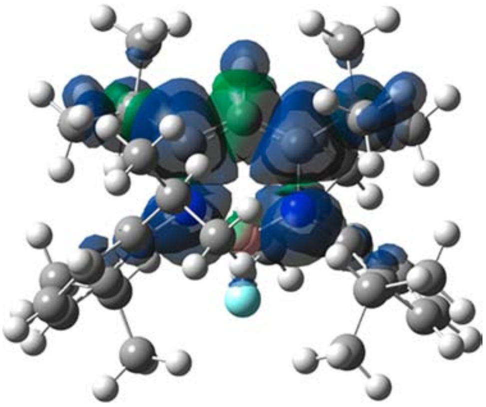


Figure 5. UB3LYP/6-31G*-calculated spin density of **3**.

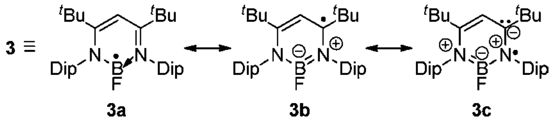
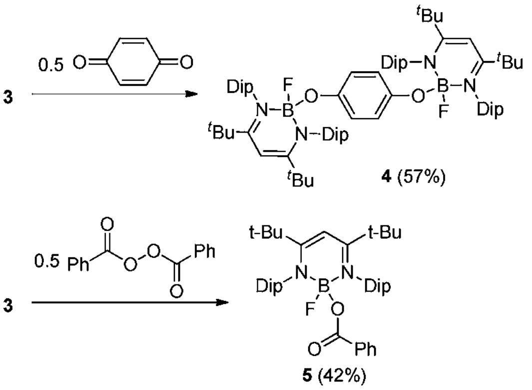


Figure 6. Possible resonance structures of **3**.

Since **3** has a bright-red color, in contrast to its precursor **2**, the UV−vis absorption spectrum of **3** was recorded. It contains two absorption maxima, one at 498 nm (broad, $\varepsilon = 750\ M^{-1}\ cm^{-1}$) and the other at 316 nm (sharp, $\varepsilon = 4450\ M^{-1}\ cm^{-1}$) (Figure S2). Time-dependent DFT calculations indicated two absorptions at 467 and 315 nm with oscillator strengths of 0.0193 and 0.0562, in good agreement with the experimentally obtained spectrum. The absorption in the visible region at 467 nm could be mainly assigned to an excitation from the SOMO to the LUMO+1 (78%) and the LUMO+4 (12%), where both the LUMO+1 and LUMO+4 possess a significant MO coefficient on the boron center.

Radical **3** was trapped the boron center by reactions with oxygen-containing reagents (Scheme 2). A reaction of **3** with BQ provided 1:2 adduct **4** having two newly formed B−O bonds, as revealed by X-ray crystallographic analysis. Radical **3** was also trapped with 0.5 equiv of BPO to give **5**. The structures of **4** and **5** were confirmed by single-crystal X-ray analysis (see the SI). The doublet signals at relatively high field in the ^{11}B NMR spectra of **4** and **5** (δ_B 1.4, $^1J_{FB}$ = 50 Hz for **4**; δ_B 1.7, $^1J_{FB}$ = 60 Hz for **5**) indicated an sp^3-hybridized boron atom bound to a fluorine atom. Such reactivity of **3** is similar to the previously reported B−O bond formation between anionic borole radical and BPO.[8a,23] Thus, the reactivity of **3** with oxygen-containing reagents may be explained as follows: Steric repulsion between the oxygen-containing reagent and the bulky ^{t}Bu and Dip substituents of **3** inhibits the direct reaction of **3** at the C1, C3, N1, and N2 positions having an unpaired electron in the resonance structures **3b** and **3c**.[24] On the other hand, more space is available around the B1 center. Therefore, although **3** mostly exists as the allylic radical **3b**, it is reactive toward BQ and BPO as the boryl radical **3a**.

Scheme 2. Reactions of 3 with (top) BQ and (bottom) BPO



In conclusion, we synthesized and isolated B-heterocyclic radical **3** with seven π electrons. Its ESR spectrum showed delocalization of the unpaired electron over the six-membered ring. While DFT calculations suggested that allylic radical character (resonance structure **3b**) is dominant in **3**, radical **3** behaves as a boryl radical (resonance structure **3a**) in its reactions with BQ and BPO to form B−O bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization of radical **3**, and crystallographic data (CIF) for **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

makoto@oec.chem.chuo-u.ac.jp; ohkoshi@chem.s.u-tokyo.ac.jp; nozaki@chembio.t.u-tokyo.ac.jp

Present Address

[§]Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.

Notes

The authors declare no competing financial interest.

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(23) For the reaction of **3** with BQ, single electron transfer (SET) from radical **3** to BQ to generate a borenium cation[9b] and quinone radical anion might be proposed. However, this seems less likely because **3** also reacts with BPO. In addition, no oxidation wave but only irreversible reduction waves were detected for radical **3** by CV (Figure S8).

(24) Although one may consider the possibile photoexcitation of radical **3b** to give a boron-centered radical, the reaction of **3** with BQ proceeded under light-shielded conditions.