

Stable Borocyclic Radicals via Frustrated Lewis Pair Hydrogenations

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S Supporting Information

ABSTRACT: The synthesis and isolation of stable main group radicals remains an ongoing challenge. Here we report the application of frustrated Lewis pair chemistry to the synthesis of boron-containing radicals. H₂ activation with polyaromatic diones and B(C₆F₅)₃ leads to radical formation in good yields. These radicals are robust; they do not decompose on silica gel or react with O₂ and are stable at 35 °C under N₂ indefinitely. The mechanism of formation is explored experimentally, with support from DFT calculations. EPR and UV/vis spectroscopy as well as cyclic voltammetry data are provided, and the radicals are shown to react with cobaltocenes in one-electron chemical reductions to their corresponding borate anions.

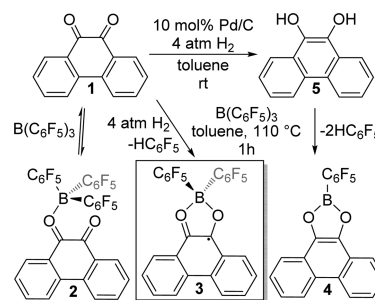
A number of chemical and biological processes are known to involve radicals. Since the seminal work of Gomberg more than 100 years ago, in which the triphenylmethyl radical was shown to be stable,¹ chemists have been challenged to develop new strategies for the preparation of isolable radicals. While paramagnetic transition metal species are frequently encountered, persistent or stable main group radicals are much less common.^{2–12} Boron radical anions of the type [[•]BAR₃][–], being isoelectronic with [•]CPh₃, were spectroscopically studied in 1970,¹³ and structurally characterized by Power in 1986;¹⁴ however, much less is known about neutral boron-containing radicals. Successful strategies to stabilize such odd-electron species include exploiting delocalization of the unpaired electron and using sterically demanding substituents to suppress undesired reactivity. Haddon used phenalenyl substituents to generate zwitterionic boron radicals for applications as conductors.^{15–17} The groups of Bertrand,¹⁸ Curran,^{19–21} and Braunschweig^{22,23} demonstrated in a number of recent literature reports how NHCs and CAACs can be used to prepare and/or isolate a number of neutral boron-containing radical species. In addition, bis-mesityl boron fragments were used to access acridinyl and pyrene-substituted radicals by Gabbai²⁴ and Marder,²⁵ respectively. In 2012, Yamashita, Ohkoshi, and Nozaki²⁶ generated a neutral boron radical by employing a β-diiminate ligand framework, and very recently Bourissou probed a persistent phosphine-stabilized Gomberg-type boryl radical.²⁷

The field of frustrated Lewis pairs (FLPs) has grown rapidly and is expanding in new directions.^{28–30} Nonetheless, reports of paramagnetic chemistry derived from FLP systems are sparse. In 2013, our group reported the generation of a frustrated radical pair via reaction of Mes₃P and Al(C₆F₅)₃ with N₂O.³¹ The Erker group captured NO by intramolecular FLPs to generate a family

of PNB-linked heterocyclic radicals.^{32–35} Here we report the facile preparation of remarkably stable, neutral borocyclic radicals from FLP hydrogenation reactions.

We recently reported the synthesis of borinic esters via a B(C₆F₅)₃-mediated hydrogenation of aliphatic ketones.³⁶ These products, containing a 3-coordinate Lewis acidic boron center, were difficult to handle and prone to decomposition. We envisioned that ketone substrates bearing adjacent donor functionality would generate more stable products. To that end, 9,10-phenanthrenequinone (**1**) was combined with 1 equiv of B(C₆F₅)₃ at room temperature (Scheme 1). The reaction

Scheme 1. Reactions of **1** with B(C₆F₅)₃ and/or H₂



mixture immediately turned a very dark red color. The phenanthrene resonances in the ¹H NMR spectrum broadened slightly, while a ¹¹B NMR signal appeared at 24.4 ppm. These data suggest formation of a weak Lewis acid–base adduct, (C₆F₅)₃B(O₂C₁₄H₈) (**2**). The molecular structure was confirmed crystallographically (see Supporting Information (SI)), revealing coordination of one of the ketones to boron, with a B–O bond distance of 1.604(3) Å.

Subjecting the above reaction mixture to H₂ (4 atm) and heating to 110 °C led to complete consumption of the starting material after 1 h and formation of two new species, as evidenced by the ¹⁹F NMR spectrum (*vide infra*). Upon concentration, a dark green solid, **3**, was the major product, while a lesser amount of an unknown white solid, **4**, was also observed. Despite trituration and recrystallization attempts, we were unable to cleanly isolate **3** from **4**. Resorting to column chromatography, we were pleasantly surprised to find that **3** is stable on silica, affording isolation of green-black crystals in yields as high as 79%. Compound **3** is ¹H, ¹¹B, and ¹³C NMR silent, although it exhibits one broad resonance in the ¹⁹F NMR spectrum at –159.9 ppm.

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While **3** is a dark green solid, it is a very deep yellow color in solution, exhibiting an absorbance band at 471 nm in the UV/vis spectrum (see SI).

Interestingly, **3** is stable in solution under 1 atm of O₂ for several days, and in the solid state under N₂ indefinitely. X-ray crystallographic analysis of **3** confirmed the formulation as paramagnetic borocyclic species [(C₆F₅)₂B(O₂C₁₄H₈)][•] (Figure 1a,b). The EPR spectrum (Figure 1d) suggests delocalization of

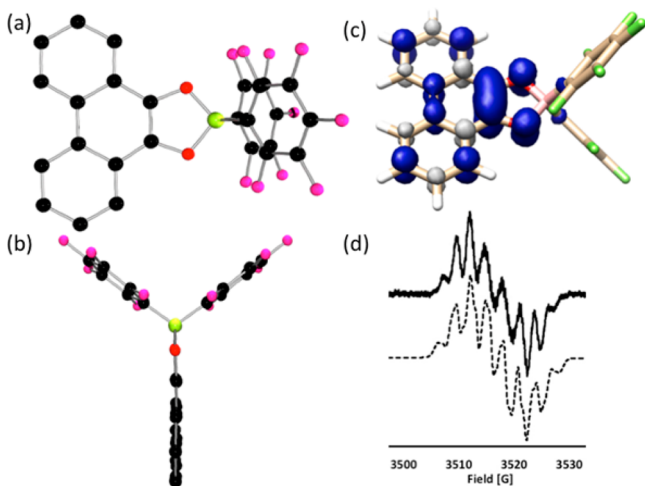


Figure 1. (a) Face-on and (b) side-on POV-ray depiction of **3**. H atoms are omitted for clarity. C, black; O, red; F, pink; B, yellow-green. (c) Spin density at a contour surface value of ± 0.03 au. (d) X-band EPR spectrum in toluene of **3** (observed spectrum, solid line; simulated spectrum, dashed line; $g = 2.0039$).

the unpaired electron over the phenanthrene backbone and coupling with the ¹¹B atom and ¹H atoms, with $a_B = 2.58$ G and $a_H = 3.39, 0.00, 2.43,$ and 1.01 G (simulated values agree with computed values, see SI). This was consistent with DFT computations of the spin density of **3** (Figure 1c). Related radicals, generated by UV irradiation of diones in the presence of BPh₃, were previously observed via EPR spectroscopy by Alberti and Pedulli.³⁷ For the present system, the formation of **3** proceeds under ambient light or in the absence of light, and any formation of **3** was undetected by NMR when **1** was treated with B(C₆F₅)₃ in the absence of H₂ under the optimized reaction conditions.

To determine the identity of the byproduct **4**, the crude reaction mixture was dissolved in minimal CH₂Cl₂ and filtered, allowing the collection of a small amount of the white solid on a frit. While this material is sparingly soluble in CH₂Cl₂ and CHCl₃, elemental analysis and HRMS data suggested its identity as (C₆F₅)B(O₂C₁₄H₈) (**4**), the C₆F₅-substituted boronic ester (Scheme 1). This view was supported by the independent synthesis of **4** from the combination of 9,10-phenanthrenediol (**5**)³⁸ and B(C₆F₅)₃ at 110 °C in toluene for 1 h. ¹H, ¹⁹F, and ¹¹B NMR spectra of **4** in toluene are consistent with a diamagnetic, 3-coordinate boron species. Crystallographic characterization of **4** confirmed the molecular structure (Figure 2) and revealed its planarity and π -stacking in the solid state. The B–O distances were found to be 1.390(6) and 1.394(5) Å about the 3-coordinate B center, with O–B–O and O–B–C angles of 111.9(4)°, 124.0(4)°, and 124.0(4)°.

The analogous reaction of 4,5-pyrenediol (**6**)³⁹ with B(C₆F₅)₃ and H₂ pleasingly generates the corresponding dark blue, boron-containing radical **7** (Scheme 2) with a lesser

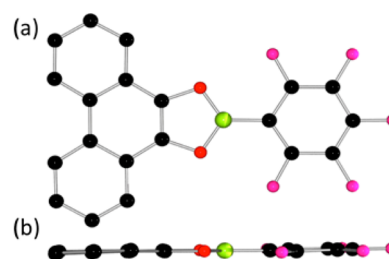
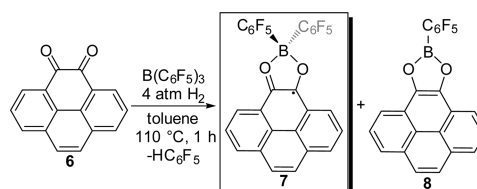


Figure 2. POV-ray depiction of **4**, with (a) and (b) showing perpendicular views. H atoms are omitted for clarity. C, black; O, red; F, pink; B, yellow-green.

Scheme 2. Reaction of **6** with B(C₆F₅)₃ and H₂



amount of a white precipitate, postulated to be the corresponding boronic ester **8**. The radical species **7** was purified via column chromatography and characterized by EPR spectroscopy. Simulation is consistent with hyperfine coupling to one ¹¹B atom ($a_B = 2.80$ G) and the eight ¹H atoms with $a_H = 3.38, 0.86, 2.89,$ and 2.21 G (Figure 3d), suggesting that the unpaired

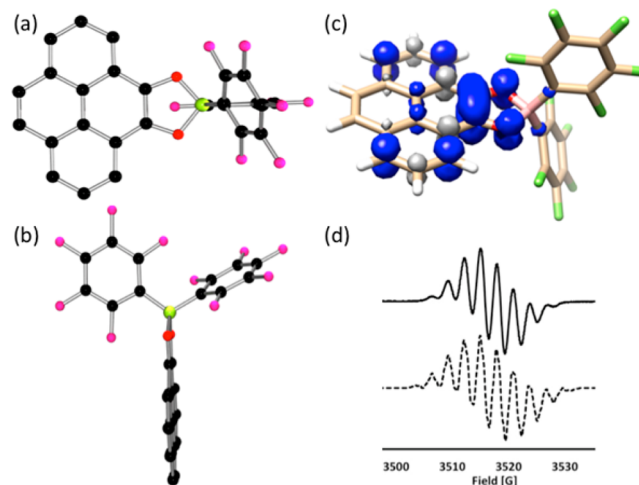


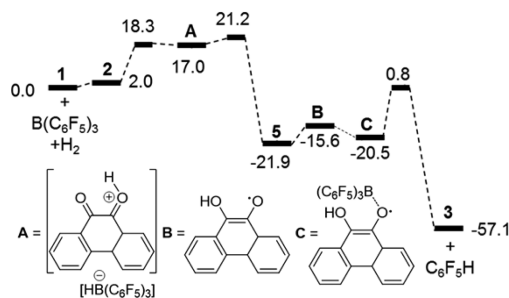
Figure 3. (a) Face-on and (b) side-on POV-ray depiction of **7**. H atoms are omitted for clarity. C, black; O, red; F, pink; B, yellow-green. (c) Spin density at a contour surface value of ± 0.03 au. (d) X-band EPR spectrum of **7** in toluene (observed spectrum, solid line; simulated spectrum, dashed line; $g = 2.0040$).

electron is delocalized over the aromatic backbone. This was again supported by computations of the spin density (Figure 3c) and the SOMO (see SI). Like that of **3**, the ¹⁹F NMR spectrum of **7** exhibits a broad singlet at -158.7 ppm. Compound **7** also exhibits a broad singlet in the ¹H NMR spectrum at 7.52 ppm, although **7** is ¹¹B and ¹³C NMR silent. **7** is a dark blue solid and an intense navy blue color in solution, exhibiting several low-energy absorbance bands, in particular at 766 nm (see SI) in the UV/vis spectrum. X-ray crystallographic analysis (Figure 3a,b) confirmed the formulation of **7** as the radical [(C₆F₅)₂B(O₂C₁₆H₈)][•]. The metric parameters were similar to those

seen for **3**. A small amount of **8** was isolated from the crude reaction mixture, and this was used to collect EA, HRMS, and NMR data in d_6 -DMSO at 25 °C as well as d_8 -toluene at 100 °C (see SI), although repeated efforts to crystallize **8** were unsuccessful. These data were consistent with the formulation of **8** as $(C_6F_5)_2B(O_2C_{16}H_8)$.

The formation of radicals **3** and **7** and boronic esters **4** and **8** stands in contrast to previous reports of treatment of carbonyl-containing substrates with borane/ H_2 that led to either catalytic hydrogenations^{40–42} or stoichiometric formation of borinic esters and deoxygenated products.^{36,43} To understand the present reactions, it is important to note the previous report by Pampaloni³⁸ describing the Pd-catalyzed reduction of **1** to **5** (Scheme 1). Further, those authors noted that a 1:1 mixture of **1** and **5** in toluene generates 2 equiv of the radical species $(HO_2C_{14}H_8)^\bullet$ (**B**). This led us to postulate two possible routes to the formation of **3** from **1**, H_2 , and $B(C_6F_5)_3$. Both pathways involve FLP H_2 activation and subsequent hydride delivery to generate **5** *in situ*. The combination of **5** with **1** generates 2 equiv of **B**, and the subsequent reaction of **B** with $B(C_6F_5)_3$ liberating HC_6F_5 would afford **3**. An alternative pathway could involve the reaction of **5** with $B(C_6F_5)_3$, resulting in loss of HC_6F_5 and generating a borinic ester as an intermediate, which could then lose H^\bullet to form **3**. However, we noted that treatment of **5** with $B(C_6F_5)_3$ under the reaction conditions (toluene, 110 °C) generates **4** in quantitative yield (Scheme 1) with no evidence for the formation of **3**. This finding suggests that the former pathway to **3** involving the radical **B** is more plausible (Scheme 3). This

Scheme 3. Computed Reaction Profile for the Formation of **3 from **1**, $B(C_6F_5)_3$, and H_2 at the PW6B95-D3/def2-TZVP (COSMO-RS, toluene)//TPSS-D3/def2-TZVP Level of the theory (All values are given in kcal/mol)**



view is further supported by the observation that **4** is consistently generated as a minor product in the formation of **3**. This indicates that **5** is available to react with $B(C_6F_5)_3$ en route to **4**, but it is more prone to react with **1** to give **B** and ultimately **3**. It is interesting to note that species similar to **B** and **3** have been proposed by Renaud as intermediates formed during the reduction of trialkylboranes with catechols.^{44,45}

The above reaction mechanism was further supported by DFT calculations. All structures were optimized at dispersion-corrected TPSS-D3 level of theory^{46–48} with a Gaussian AO basis set of def2-TZVP quality,^{49,50} followed by single-point energy calculations at the PW6B95-D3 level^{47,48,51} with the same basis set. The COSMO-RS (Conductor-like Screening Model for Real Solvents) solvation model^{52,53} was used to compute Gibbs free energies with toluene as the solvent (see SI). The resulting mechanism for the formation of **3** from **1** computed as a multiple-step process (Scheme 3). Compound **1** forms a typical FLP with 1 equiv of $B(C_6F_5)_3$ coordinated to a carbonyl group (**2**). This

complex subsequently effects the intermolecular activation of H_2 with an energy barrier of 16.3 kcal/mol. The resulting hydride delivery from $[HB(C_6F_5)_3]^-$ affords phenanthrene-9,10-diol (**5**) in a step that is strongly exergonic ($\Delta G = -38.9$ kcal/mol), having an energy barrier of only 4.2 kcal/mol. As previously reported, the combination of **1** and **5** generates 2 equiv of the 9,10-phenanthrenequinhydrone radical **B**.³⁸ This was computed to be an endergonic process (6.3 kcal/mol, see SI). Subsequent coordination to $B(C_6F_5)_3$ affords the radical Lewis acid–base adduct, analogous to **2**; however, this leads to loss of C_6F_5H , yielding the final radical product **3**. This proton delivery is also strongly exergonic (-36.6 kcal/mol), but this reaction is computed to have a barrier of 21.3 kcal/mol, consistent with experimental reaction conditions.

The redox properties of the radicals **3** and **7** were examined via cyclic voltammetry. Both species exhibit pseudo-reversible waves centered at $E_{1/2} = 0.27$ V (vs Fc/Fc^+) (see SI). Given these observations, attempts to effect one-electron chemical reductions of **3** and **7** were undertaken. To this end, **3** and **7** were treated with 1 equiv of $CoCp_2$, leading to the formation of the corresponding cobaltocenium salts $[CoCp_2][C_{14}H_8O_2B(C_6F_5)_2]$ (**9**) and $[CoCp_2][C_{16}H_8O_2B(C_6F_5)_2]$ (**10**), respectively (Scheme 4). Similarly, reaction of **3** with $CoCp^*_2$ gave $[CoCp^*_2][C_{14}H_8O_2B(C_6F_5)_2]$ (**11**). The molecular structures of **10** and **11** were confirmed crystallographically (Figure 4).

Scheme 4. Reactions of **3 and **7** with $CoCp_2$ or $CoCp^*_2$**

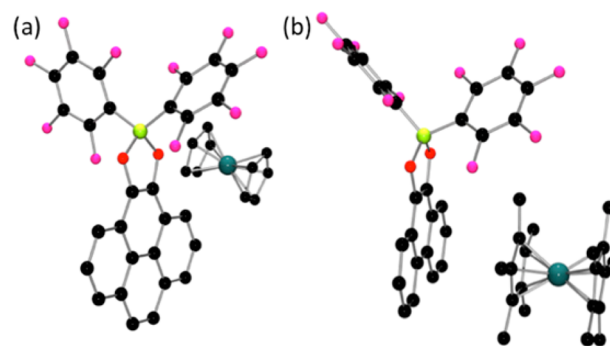
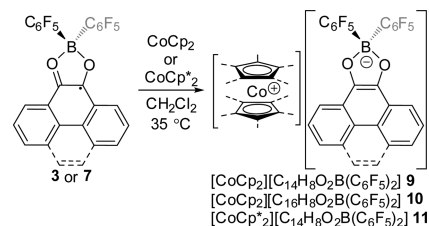


Figure 4. POV-ray depictions of (a) **10 and (b) **11**. H atoms are omitted for clarity. C, black; O, red; F, pink; B, yellow-green; Co, slate gray.**

In summary, FLP-mediated hydrogenation of ketones has been applied to prepare a new class of isolable, stable borocyclic radicals. DFT calculations reveal that the rate-determining step in the formation of these radicals is the protonation of an aryl substituent by the quinhydrone radicals. These radicals also undergo facile one-electron reductions with cobaltocenes to give the corresponding cobaltocenium borate salts. The reactivity of these unusual radicals and the utility of FLP reductions in the generation of new, stable radicals are the subjects of ongoing studies.

■ ASSOCIATED CONTENT**■ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12823. Full metrical parameters for solid-state structures are available free of charge from the Cambridge Crystallographic Data Centre under reference CIF files (CCDC Nos. 1441085–1441090).

Materials, instrumentation, procedures, characterization data, computational details, and Cartesian coordinates (PDF)

CIF files for compounds **2**, **3**, **4**, **7**, **10**, and **11** (ZIP)

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Notes

The authors declare no competing financial interest.

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