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Borane Reduction

Redox Chemistry of a Hydroxyphenyl-Substituted Borane**

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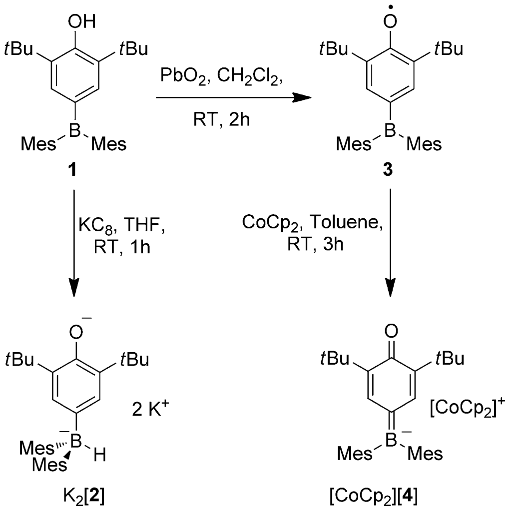
Abstract: *Chemical reduction of a hydroxyphenyl-substituted borane triggers a sequential electron- and intramolecular hydrogen-atom-transfer process to afford a hydridoborate phenoxide dianion. On the other hand, hydrogen-atom abstraction of the borane leads to the isolation of a neutral borylated phenoxyl radical, which can be transformed to the corresponding benzoquinone borataalkene derivative by reduction with cobaltocene.*

The affinity of the boron atom for electron density has made tricoordinate boron derivatives one of the most studied main-group compounds. Electron-deficient boranes have found numerous applications, for example as colorimetric chemosensors for anions,[1] in Lewis acid catalyzed organic transformations,[2] and as frustrated Lewis pairs in H_2 activation.[3] In addition, the low-lying empty p orbital at the boron center facilitates π-electron delocalization within the system, making triarylboranes excellent chromophores and electron-transporting materials.[4] While electrochemical measurement has been adopted as a standard procedure to evaluate the electron deficiency of boranes, there are relatively few examples where the reduced species has been isolated and structurally characterized.[5] Thus, studies on the reactivity and decomposition of reduced borane species are relatively limited.[5g,6]

Phytochemicals have attracted considerable attention owing to their ability to prevent disease, which is partly attributed to the antioxidative properties of the polyphenolic components.[7] Since the stability of a phenoxyl radical provides a measure of the antioxidative activity of the corresponding phenol, efforts have focused on the synthesis and isolation of stable phenoxyl radicals. To date, phenoxyl radicals with various *para* substituents have been prepared, including σ-donating alkyl groups,[8] π-donating heteroatom-containing groups,[9] and aromatic rings.[10] However, the combination of phenol and the redox-active boryl group has never been reported. Herein, we report the electrochemistry of a hydroxyphenyl-substituted borane, which undergoes two-electron reduction to afford the corresponding hydridoborate phenoxide dianion by sequential electron- and hydrogen-atom-transfer reactions. Characterization and chemical reduction of the borylated phenoxyl radical are also discussed.

The hydroxyphenyl-substituted borane (**1**) was prepared from the corresponding 4-bromophenol derivative in two steps (Supporting Information). The product was isolated as a colorless crystalline solid by the slow evaporation of solvent from a solution of **1** in hexane. The molecular structure of **1** was determined by single-crystal X-ray diffraction (Figure S3 in the Supporting Information). Interestingly, the cyclic voltammogram (CV) of **1** in THF contains an irreversible reduction wave with E_{peak} at −3.10 V (vs. Fc/Fc$^+$, Fc = [(η-C_5H_5)$_2$Fe]; Figure S6). This boron-centered redox event occurs at a particularly low potential compared with that measured for trimesitylborane (−2.73 V vs. Fc/Fc$^+$).[11] The irreversibility of this reduction contrasts with that observed for mesityl-substituted triarylboranes, which exhibit a fully reversible one-electron reduction to the corresponding radical anion.[12]

To better understand the redox behavior of **1**, chemical reduction of **1** was undertaken using KC_8 (Scheme 1). Surprisingly, the reaction mixture of **1** and KC_8 was EPR silent. The ^{11}B NMR spectrum of the 1:1 mixture of **1** and KC_8 contained two signals. While the broad signal detected at δ = 71 ppm is assigned to **1**, the new ^{11}B NMR resonance signal appearing as a doublet at δ = −11.8 ppm suggests the formation of a B−H bond. In combination, the ^{11}B NMR chemical shift and the $^1J_{\text{B-H}}$ coupling constant of 76 Hz suggest the formation of a hydridoborate derivative.[13] The complete transformation of **1** to the hydridoborate species ([**2**]$^{2-}$) requires two equivalents of KC_8 (Figure S1). After treatment



Scheme 1. Electron reduction and hydrogen atom abstraction reactions of **1**; Cp = η-C_5H_5.

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of **1** with excess KC_8, the compound K_2[**2**] was obtained in moderate yield as a colorless crystalline product after recrystallization. The B-H signal was identified unambiguously in the ^{1}H NMR spectrum of [**2**]$^{2-}$ at $\delta = 3.59$ ppm as a quartet. The long-range interaction of this proton with the mesityl *ipso*-carbon atom was detected using a HMBC NMR experiment. The absence of a signal attributed to the phenolic hydroxy group suggests the simultaneous deprotonation of the phenol to afford the phenoxide hydridoborate dianion in solution.

The molecular structure of [**2**]$^{2-}$ was confirmed by single-crystal X-ray diffraction (see Figure 1). Single crystals of K_2[**2**] were obtained by hexane diffusion into a solution of K_2[**2**] in THF at ambient temperature in a dry box. K_2[**2**] crystalized in the $P2_1/n$ space group as a potassium-bridged tetramer (Figure S4). Within the tetramer, two distinct potassium bridges could be identified, involving O–K–O and the O–K–arene interactions. The tetramers are linked to form an extended structure with additional cation–π interactions. The tetramer has C_i symmetry and contains two independent molecules which share similar structural parameters (Figure 1, one of the independent molecules is displayed). In both molecules, the C-B-C angles sum to 341.23° and 337.96°, respectively, confirming the presence of sp^3-hybridized boron centers. The C4–O bond lengths of 1.311 Å and 1.316 Å are slightly shorter than the corresponding bond in the structure of **1** (1.375(2) Å), a common structural feature observed for phenoxide derivatives.

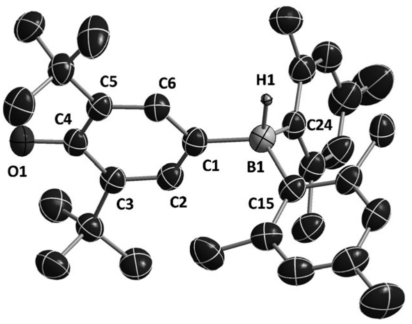
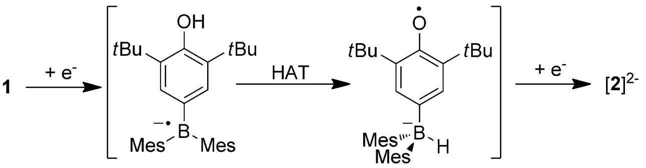


Figure 1. ORTEP representation of one of the independent molecules of [**2**]$^{2-}$. Countercations and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å], bond angles [°]: O1-C4 1.311(3), C1-C2 1.394(4), C2-C3 1.399(3), C3-C4 1.433(3), C4-C5 1.427(4), C5-C6 1.401(3), C6-C1 1.396(3), B1-C1 1.647(4), B1-C15 1.657(4), B1-C24 1.653(4); C1-B1-C15 119.1(2), C1-B1-C24 107.8(2), C15-B1-C24 114.4(2).

The boron-centered redox event of **1** was shown by CV to be an irreversible one-electron process. By monitoring the redox process using ^{11}B NMR spectroscopy, it is evident that the conversion of **1** into [**2**]$^{2-}$ requires two equivalents of reducing agent. On the basis of these observations, we propose that the transformation of **1** to [**2**]$^{2-}$ proceeds through stepwise electron and hydrogen-atom transfers. Directly after the one-electron reduction, an intramolecular hydrogen-atom transfer from the hydroxy group to the boron radical anion occurred to generate the more stable phenoxyl radical. This radical was then reduced with another electron to afford the hydridoborate phenoxide dianion [**2**]$^{2-}$ (Scheme 2). Since the reduction potential of the phenoxyl radical is considerably higher than that of **1**, it was not possible to detect the anionic phenoxyl radical intermediate even in the presence of less than one equivalent of KC_8.



Scheme 2. Proposed reaction mechanism for the transformation of **1** to [**2**]$^{2-}$ by reduction. HAT = hydrogen-atom transfer.

In an attempt to generate the proposed anionic phenoxyl radical, an alternative synthetic route was employed. A solution of **1** in CH_2Cl_2 was treated with a large excess of PbO_2, resulting in the immediate formation of a dark purple solution (Scheme 1). After filtration and the removal of solvent, neutral radical **3** was isolated as a black powder in excellent yield. The EPR spectrum of **3** in hexane contains a complicated signal centered at $g_{iso} = 2.0036$ (Figure 2), a typical value for organic free radicals. A computer simulation of the spectrum reveals a hyperfine coupling constant of 3.424 G and 1.142 G to the ^{11}B ($I = 3/2$) and ^{10}B ($I = 3$) nuclei, respectively. The $a(^{11}B)$ value of **3** is slightly larger than that determined for the 9-boryl acridinyl radical,[14] but is considerably smaller than that of boron-centered radicals, such as triarylborane radical anions.[6a,15] Surprisingly, the simulation result also suggests that the hyperfine coupling of $a = 0.58$ G is attributable to the *para* methyl group of mesityl substituents, confirming the delocalization of spin density through the empty boron p orbital.

The isolation of the borylated phenoxyl radical **3** was further confirmed by single-crystal X-ray diffraction. Black single crystals were obtained from a solution of **3** in hexamethyl disiloxane (HMDSO) at −35 °C in a dry box. Compound **3** crystalizes in the monoclinic $P2_1/n$ space group as a HMDSO solvate with eight molecules in the unit cell. Two independent molecules were identified in the crystal, one of which is shown in Figure 2. In both molecules, the geometry around the boron center can be described as trigonal planar, with the sum of the C-B-C angles measuring 359.95° and 359.99°, respectively. The observed structural parameters of the phenol moiety are comparable to those of previously determined phenoxyl radical structures.[8–10] The C19–B bond lengths of 1.565 and 1.566 Å are comparable to that observed in the 9-boryl acridinyl radical,[14] suggesting the presence of partial π-bonding character in the B–C bond. This situation is in good agreement with the observed hyperfine splitting arising from the *para* methyl group of each mesityl substituent (six protons with $a(^1H) = 0.58$ G).

The cyclic voltammogram of **3** measured in CH_2Cl_2 reveals a fully reversible reduction process at −0.56 V (vs.

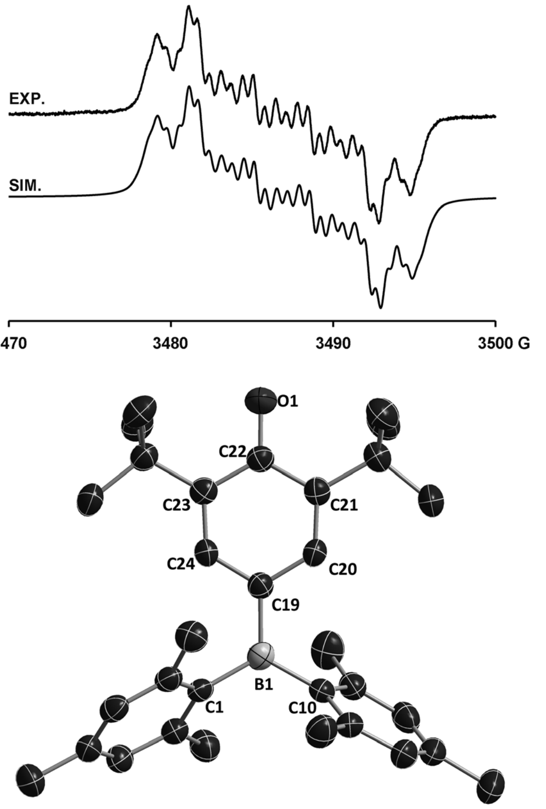


Figure 2. Top: Experimental and simulated EPR spectra of **3** in hexane at room temperature. Bottom: Molecular structure of **3** with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and bond angles [°] for **3**: O1-C22 1.300(4), C19-C20 1.406(5), C20-C21 1.378(5), C21-C22 1.450(5), C22-C23 1.444(5), C23-C24 1.378(5), C24-C19 1.408(5), B1-C19 1.565(5), B1-C1 1.578(6), B1-C10 1.589(5); C1-B1-C10 122.4(3), C1-B1-C19 119.5(3), C10-B1-C19 118.1(3).

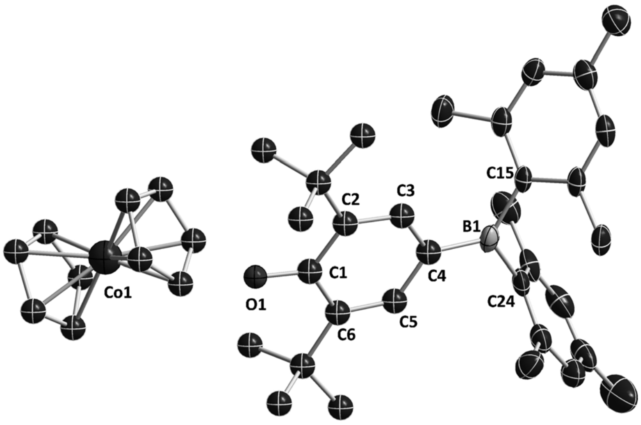


Figure 3. Molecular structure of [CoCp$_2$][**4**]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and bond angles [°] for [**4**]$^-$: C1-O1 1.275(5), C1-C2 1.452(6), C2-C3 1.375 (5), C3-C4 1.426(6), C4-C5 1.414(6), C5-C6 1.376(5), C1-C6 1.468(6) B1-C4 1.512(6), B1-C15 1.608(6), B1-C24 1.605(7); C3-C4-C5 115.9(4) C3-C4-B1 121.6(4), C5-C4-B1, 122.4(4), C4-B1-C15 120.2(4), C4-B1-C24 121.3(4), C15-B1-C24 118.5(3).

Fc/Fc$^+$; Figure S7). This reduction potential is about 2.6 V higher than that determined for **1**, emphasizing the greater stability of the phenoxyl radical in comparison with the borane radical anion. The CV data also explains the fact that it was not possible to isolate the anionic phenoxyl radical during the reaction of **1** with KC$_8$. It was also not possible to isolate the hydridoborate-tethered phenoxyl radical by hydride addition to **3**. The addition of LiAlH$_4$ to a solution of **3** in ether results in an immediate color change from deep purple to light yellow. The single-crystal X-ray structure of crystals obtained from the reaction mixture confirms the formation of the lithium phenoxide salt Li[**4**] (Figure S5). The borylated phenoxide [**4**]$^-$ could also be isolated in good yield from the reaction of **3** and one equivalent of cobaltocene, a reducing agent that is not strong enough to reduce boranes (Scheme 1). Upon treating a toluene solution of **3** with cobaltocene, the color of the solution turned instantly from dark purple to dark green. Diffusion of hexane into a solution of [CoCp$_2$][**4**] in THF resulted in the formation of single crystals suitable for X-ray diffraction analysis. [CoCp$_2$][**4**] crystalizes in the $P2_1/c$ space group and has considerably short C–O and C–B bond lengths of 1.275 Å and 1.512 Å, respectively (Figure 3). Considering the short C–O and C4–B1 bonds and the significant C–C bond length alternation within the phenol ring, [**4**]$^-$ could also be described as a benzoquinone borataalkene that features a formal B–C double bond.[16] Interestingly, changing the countercation from the non-coordinating cobaltocenium to the oxophilic lithium ion reduces the π-electron delocalization, and diminishes the contribution of the quinonoid resonance structure (Figure S5).

To verify the hydrogen-atom-transfer process, the reaction between phenol and the borane radical anion was examined. By monitoring the ^{11}B NMR spectrum of a mixture of the trimesitylborane radical anion (K[Mes$_3$B]) and 2,6-di-*tert*-butyl-4-methyl phenol, the formation of the [Mes$_3$BH]$^-$ was confirmed by the detection of a doublet at $\delta = -14.6$ ppm ($^1J_{\text{B-H}} = 77$ Hz; Figure S2). Although the intermolecular hydrogen-atom-transfer reaction can be identified unambiguously, the process is considerably slower than the intramolecular transfer process observed during the chemical reduction of **1**.

In summary, we have demonstrated that the two-electron reduction of a hydroxyphenyl-substituted borane led to the formation of the hydridoborate phenoxide dianion, achieved by a sequential electron-transfer, hydrogen-atom-transfer, electron-transfer process. When the hydrogen-atom abstraction was conducted prior to the one-electron reduction, a stable borylated phenoxyl radical could be isolated and structurally characterized. Further reduction of the neutral radical with one-electron afforded the corresponding benzoquinone borataalkene derivative. The generation of [**2**]$^{2-}$ from the two-electron reduction of **1** is proposed to proceed through a hydridoborate-tethered phenoxyl radical anion intermediate. It was not possible to generate the proposed radical anion by the controlled chemical reduction of **1** or by the addition of hydride to **3**. However, detection of the characteristic ^{11}B NMR signal for the hydridoborate anion in the reaction mixture containing phenol and the borane radical anion provides irrefutable evidence for the occurrence of

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a hydrogen-atom transfer from the phenolic hydroxy group to a boron radical anion. Currently, the antioxidative properties of **1** are under investigation. This study also suggested that the substitution of boryl functionality could potentially enhance the stability of organic free radicals. Thus, the incorporation of diarylboryl group to other organic free radicals will also be explored.

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