Boron-Centered Radicals

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The Reduction Chemistry of Ferrocenylborole**

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In the chemistry of functionalized metallocenes, borylated ferrocenes have drawn great attention owing to their potential applications as electron sponges,[1] anion chemosensors,[2] and redox-active macromolecules.[3] Electrochemical stimulation of the Fe^{II}/Fe^{III} couple can lead to significant changes in the molecular structure,[4] and to the anion binding properties of the system.[5] One distinct structural feature of borylated ferrocenes is the bending of the boryl group towards the iron atom. Both experimental and theoretical studies of these molecules reveal a direct through-space interaction between the filled iron 3d orbital and the empty 2p orbital at boron.[4a,6] This "dip" angle can be reduced by incorporation of π-donating substituents to the boron atom, coordination with Lewis bases, by increasing the number of boryl functionalities on the Cp rings, or oxidation of the ferrocene to ferrocenium.[4a,6] The structural changes induced by electronic reduction of the boryl group, however, have not received much attention.[7]

Investigations on the reduction chemistry of organoboranes have led to the isolation of various interesting boron-centered radical species. The reduction potential of the boron center can be tuned by substitution with fluorinated aryl groups,[8] introduction of a second boryl moiety,[9] attachment of cationic functionalities,[10] or by incorporating the boron atom into an antiaromatic ring system.[11] In line with our interests in antiaromatic boracycles and metallocene chemistry, we now report the reduction chemistry of 1-ferrocenylborole and the isolation of the resulting reduced species.

In our previous work, the most striking structural feature of 1-ferrocenyl-2,3,4,5-tetraphenylborole (**1**) is the large dip angle of 29.4°.[12] This observation is attributed to the strong Fe–B interaction resulting from the antiaromatic nature of the borole moiety.[13] The presence of electro-active ferrocene (Fc) and borole units in **1** prompted us to investigate its electrochemistry. The redox behavior of **1** in CH_2Cl_2 and in THF was studied by cyclic voltammetry (referenced against the Fc/Fc^+ couple). Compound **1** displays one broad irreversible oxidation peak around $E_{pa} = 0.5$ V in CH_2Cl_2. (see Figure S1 of the Supporting Information). The oxidation behavior of **1** is distinctly different from that observed for 9-ferrocenyl borafluorene, which shows a reversible Fe^{II}/Fe^{III} redox couple at 0.01 V (vs. Fc/Fc^+).[4b] The oxidation process of **1** is thus anodically shifted as a result of the stronger Fe–B interaction in **1**. The oxidation event is also more positively shifted than that of the ferrocenylboron dication ($E^0_{1/2} =$ 0.24 V), in which the effect on Fe^{II}/Fe^{III} couple is solely inductive.[14] According to the study of 9-ferrocenyl borafluorene, one-electron oxidation results in the formation of a ferrocenium cation and a dip angle decrease from 25.5° to 6.3°.[4b] However, the synthetic procedure for ferrocenium borafluorene is not applicable for the ferrocenium borole. This difference is because the transformation of a neutral borole to a cationic borole greatly enhances the electron deficiency and Lewis acidity of the boron center, and leads to undesired coordination and/or decomposition of the resulting cationic molecule.[15]

Most revealingly, two well-separated reduction waves for **1** were identified in THF solution. As shown in Figure 1, **1** displays a quasi-reversible reduction event centered at $E^0_{1/2} =$ −1.96 V indicating the formation of stable borole radical anion, $[\mathbf{1}]^{\bullet-}$. Note that in contrast to the well-studied borole dianions,[16] the paramagnetic 5π-electron radical anion of

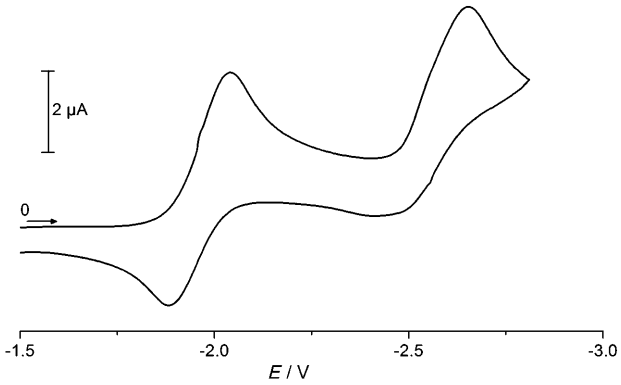

Figure 1. Cyclic voltammetry of **1** at room temperature in THF. Scan rate 100 $mV s^{-1}$, Pt/$[nBu_4N][PF_6]$/Ag, potential is reported versus Fc/Fc^+ as internal standard. Both redox waves show completely the same behavior in a second CV cycle; only one cycle is shown. An oxidation peak of very low intensity was observed in the return sweep at around −1.3 V, which may be attributed to decomposition products.

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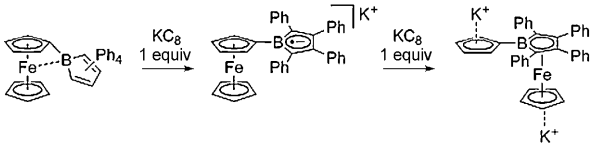
borole has never been reported before, except for a borafluorene that features an annulated molecular backbone.[11,17] This first reduction potential of **1** is significantly less negative than that observed for triarylboranes, which generally feature a reversible reduction processes around $E^0_{1/2} = -2.7$ V.[8] This observation is consistent with the enhanced electron deficiency of the boron atom in **1** as a result of the 4π-electron antiaromaticity. This reduction potential is also more positive than that reported for 9-(2,4,6-tri-*tert*-butylphenyl)borafluorene ($E^0_{1/2} = -2.2$ V vs. Fc/Fc^+), thus demonstrating the difference in antiaromaticity between non-annulated and annulated boroles.[11] As shown in Figure 1, the second reduction process centered at −2.56 V shows noticeably different electron transfer kinetics. It appears that the reduction process $[\mathbf{1}]^{\bullet-} + e^- \rightarrow [\mathbf{1}]^{2-}$ (Scheme 1) is accompanied by considerable structural changes.[18]



Scheme 1. One- and two-electron reduction of **1**.

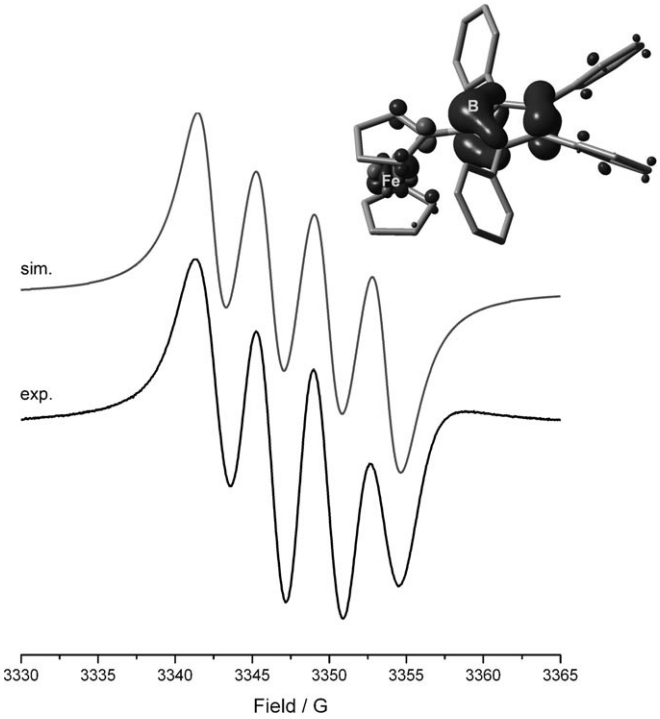


Figure 2. Experimental (exp.) EPR spectrum of $[\mathbf{1}]^{\bullet-}$ obtained in THF at 200 K, and the simulated (sim.) EPR spectrum of $[\mathbf{1}]^{\bullet-}$. Inset: The calculated spin distribution (isovalue = 0.004) over the optimized structure of $[\mathbf{1}]^{\bullet-}$.

To shed more light on the electronic characteristics of $[\mathbf{1}]^{\bullet-}$ and the structural change upon reducing it to the dianion $[\mathbf{1}]^{2-}$, we preformed additional preparative and EPR spectroscopic investigations. Even though the isolation and structural characterization of $[\mathbf{1}]^{\bullet-}$ were not successful, some spectroscopic data of $[\mathbf{1}]^{\bullet-}$ have been recorded. Mixing one-equivalent of KC_8 and **1** in THF results in an immediate and drastic color change from light orange ($\lambda_{max} = 484$ nm) to dark purple ($\lambda_{max} = 541$ nm; see Figure S3 of the Supporting Information). The EPR signal of $[\mathbf{1}]^{\bullet-}$ was detected in THF at 200 K by in situ generation of the radical anion in a potassium-mirror-coated EPR tube. The EPR spectrum of $[\mathbf{1}]^{\bullet-}$ shows a four-line signal ($g_{iso} = 2.0037$) in accordance with an unpaired electron coupled to a ^{11}B nucleus ($I = {}^3/_2$; Figure 2). Indeed, simulation of the EPR signal shows that the unpaired electron is coupled to one ^{11}B nucleus giving a hyperfine-coupling constant of $A(^{11}B) = 3.73$ G, which is comparable to that observed for 9-arylborafluorene radical anions (between 3.1 and 4.5 G).[11] We note that this value is smaller than that observed for triarylborane radical anions, such as $[Ph_3B]^{\bullet-}$ (7.84 G) or $[Mes_3B]^{\bullet-}$ (10.32 G),[19] because of a stronger electronic delocalization within the C_4B ring. The relatively low value of $A(^{11}B)$ in $[\mathbf{1}]^{\bullet-}$ indicates that the unpaired electron density is associated with boron 2p orbital and that the geometry is planar rather than pyramidal.[20] This situation would be in accord with the disappearance of the Fe–B through-space interaction in **1** upon reduction. This hypothesis was further supported by density functional theory (DFT) calculations of $[\mathbf{1}]^{\bullet-}$ at the B3LYP (6-31g* for C, B, and H; Stuttgart ECP for Fe) and BP86/def2-TZVP level (see the Supporting Information). As indicated in the optimized geometry of $[\mathbf{1}]^{\bullet-}$, the dip angle of the borole moiety is essentially zero with the Fe–B distance significantly elongated from 2.664 Å (X-ray) in **1** to 3.334 Å (DFT) in $[\mathbf{1}]^{\bullet-}$. As expected, the boron atom in $[\mathbf{1}]^{\bullet-}$ is essentially trigonal planar. The calculated spin density of $[\mathbf{1}]^{\bullet-}$ reveals the unpaired electron to be predominantly localized within the C_4B ring (Figure 2). The Mulliken spin densities on the boron atom and the butadiene backbone were calculated to be 0.39 and 0.45, respectively, which is consistent with the EPR spectroscopic data. Furthermore, we noticed that the structure of $[\mathbf{1}]^{\bullet-}$ featuring this pendant C_4B ring, that is, $[CpFe(\eta^5\text{-}C_5H_4\text{-}BC_4Ph_4)]^{\bullet-}$, is energetically favored by 41.6 kJ mol^{-1} compared to the isomeric form $[CpFe(\eta^5\text{-}Ph_4C_4B\text{-}C_5H_4)]^{\bullet-}$ containing an η^5-coordinated C_4B ring (see Supporting Information). A close analysis of the spin density distribution in this hypothetical molecule revealed the unpaired electron to be primary located on the C atoms of the disconnected C_5H_4 entity with no contributions of the boron atom. These results are in full consistency with the electrochemical and EPR spectroscopic observations.

We were able to synthesise and isolate the doubly reduced species $[\mathbf{1}]^{2-}$. Chemical reduction of **1** with excess KC_8 in THF leads to the formation of the dianionic compound in 61% yield. The ^{11}B NMR resonance signal of $[\mathbf{1}]^{2-}$ detected at $\delta = 11.7$ ppm is shifted to higher field than that observed for $[Ph_4C_4BPh]^{2-}$ ($\delta = 26$ ppm).[16a] The ^{11}B signal of $[\mathbf{1}]^{2-}$ is comparable to that measured for η^5-coordinated borole metal complexes, such as $[CpFe(C_4H_4BPh)]$ ($\delta = 13.8$ ppm).[21]

An X-ray structure analysis on bright red single crystals of $[\mathbf{1}]^{2-}$ (Figure 3)[25] unambiguously revealed an unusual reduction-induced [CpFe] migration from the C_5H_4 ring to the borole ring. Compound $[\mathbf{1}][K(THF)]_2$ crystallizes in the

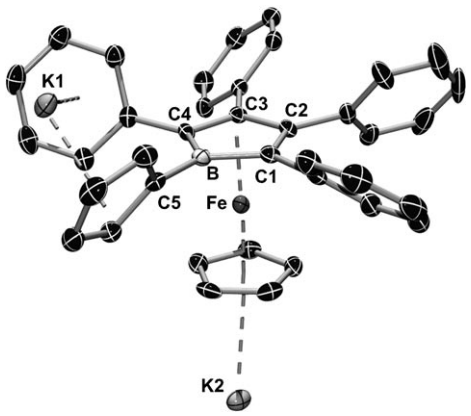


Figure 3. Molecular structure of [**1**][K(THF)$_2$]$_2$ with thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°]: B–C1 1.537(4), B–C4 1.553(4), C1–C2 1.455(3), C2–C3 1.440(3), C3–C4 1.448(3), B–C5 1.581(4), Fe–B 2.200(3), Fe–C1 2.111(2), Fe–C2 2.030(2), Fe–C3 2.031(2), Fe–C4 2.067(2); C1-B-C4 102.1(2), C1-B-C5 130.5(2), C4-B-C5 127.4(2).

monoclinic space group $P2_1/c$ as a potassium-bridged dimer. Within the dimeric unit, the two molecules are bridged by the cation–π interaction between potassium and the Cp ring. In each molecule, the borole is coordinated to Fe in a η^5 fashion. The distance between the centroid of the borole ring and the iron atom of 1.663 Å, is slightly longer than that between Cp and Fe (1.645 Å).

It is worth emphasizing that the above described linking of borole units by cation–π interactions results in the formation of a two-dimensional chain structure in the solid state in which ferrocenylboroles are linked together by π–metal–π–metal interactions.[22] Although the redox-induced hapticity changes in transition-metal complexes featuring polyaromatic ring systems or tub-to-chair isomerizations in cyclooctatetraene (COT) complexes have been well studied,[18a,23] the intramolecular migration of a metal fragment between ring systems is rare.[24] It appears that the electron-richer $[C_4Ph_4BR]^{2-}$ entity is a better π donor than Cp^-, consequently forming a stronger bond with the iron center. Thus, two-electron reduction of **1** gives rise to the formation of the putative $[CpFe(\eta^5\text{-}C_5H_4\text{-}BC_4Ph_4)]^{2-}$ species, which then undergoes an intramolecular [CpFe] migration to form $[CpFe(\eta^5\text{-}Ph_4C_4B\text{-}C_5H_4)]^{2-}$ ($[\mathbf{1}]^{2-}$). Remarkably, the intermolecular exchange process was not observed in the reaction between equimolar amounts of ferrocene and $[C_4Ph_4BPh]K_2$ in THF, which suggests that the ligation of the borole moiety prior to reduction is essential.

In summary, 1-ferrocenyl borole undergoes two one-electron reduction steps to form the corresponding borole radical anion and the η^5-borole-Fe-Cp dianion. The EPR spectrum of the borole radical anion in conjunction with the spin density calculations indicates a 5 π-electron delocalization within the C_4B ring. While the one-electron reduction of **1** affords a persistent radical anion, two-electron reduction of **1** results in the intramolecular migration of the [CpFe] fragment. Further studies on related molecules are currently under way.

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[25] CCDC 780514 ([**1**](K(thf)$_2$]$_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of chargefrom The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

