Angewandte Chemie International Edition

DOI: 10.1002/anie.201408462

Boron Peroxide from O_2

Dioxygen Reactivity with a Ferrocene–Lewis Acid Pairing: Reduction to a Boron Peroxide in the Presence of Tris(pentafluorophenyl)borane**

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Abstract: *Ferrocenes, which are typically air-stable outer-sphere single-electron transfer reagents, were found to react with dioxygen in the presence of $B(C_6F_5)_3$, a Lewis acid unreactive to O_2, to generate bis(borane) peroxide. Although several Group 13 peroxides have been reported, boron-supported peroxides are rare, with no structurally characterized examples of the BO_2B moiety. The synthesis of a bis(borane)-supported peroxide anion and its structural and electrochemical characterization are described.*

Dioxygen reduction to peroxide is an important chemical transformation for energy generation and storage applications in fuel cells and Li-O_2 batteries.[1] Transition-metal-supported peroxides are intermediates in the reduction of O_2.[2] Peroxides are also powerful oxidants that exhibit interesting and synthetically useful reactivity derived from the inherently weak O−O bond.[3] Next to carbon, organosilicon-based peroxides have been the most well-studied and developed of the main-group peroxides, and the combination of the weak O−O bond with the strong Si−O interaction has led to new and diverse reactivity.[4] Group 13 peroxides are comparatively less-developed. Several examples of In,[5] Ga,[6] and Al[7] have been isolated and structurally characterized. These compounds are typically prepared by treatment of Group 13 alkyl species with an organic hydroperoxide or inorganic superoxide, and by O_2 insertion to generate alkyl peroxide moieties. The isolation of these compounds is remarkable given the reducing power of the element–alkyl bonds and the oxidizing potential of the O−O bond are stored in the same molecule.[6c,d,7a] Organoboron-based peroxides are very rare. There have only been three reports on structurally characterized compounds containing a peroxyboranyl (RB−O_2) linkage.[8] This paucity of stable and structurally characterized molecules containing the peroxyboranyl moiety is likely due to its propensity to undergo oxidative C−B bond cleavage.[9] Herein we report the synthesis and structural characterization of the first bis(borane)-supported peroxide dianion, wherein the source of the O_2^{2-} moiety is dioxygen, generated in connection with decamethylferrocene (Cp^*_2Fe) and ferrocene (Cp_2Fe) as reductants.

Exposure of an equimolar mixture of Cp^*_2Fe and $B(C_6F_5)_3$ in deuterated dichloromethane to excess O_2 at room temperature led to a color change from yellow–orange to deep forest green upon addition [Eq. (1)], consistent with oxidation of Cp^*_2Fe to the decamethylferrocenium cation ($Cp^*_2Fe^+$). This assignment was further supported by ^1H NMR spectroscopic data that revealed the Cp* (pentamethylcyclopentadienyl) methyl peak had shifted upfield from 1.8 ppm to approximately −25 ppm. The ^{19}F NMR spectrum of the dark green solution revealed a set of new peaks at −130, −165, and −168 ppm, consistent with a tetrahedral boron center.[10] Toepler pump measurements indicate the consumption of 0.42 equiv of O_2, UV/Vis measurements show the generation of 0.85 equiv of $Cp^*_2Fe^+$, which is consistent with the two-electron reduction of O_2. If the reaction is sufficiently concentrated, dichromatic green/blue crystals precipitate from solution within minutes. An X-ray diffraction study of these crystals revealed the solid-state structure of the resulting product to contain an unprecedented bis(borane)-supported peroxide dianion $\mathbf{1}^{2-}$ with two decamethylferrocenium countercations (Figure 1). The O−O (1.485(2) Å) and B−O (1.472(2) Å) distances are similar to the previously reported examples of B−O−O moieties supported by four-coordinate boron and are consistent with the formation of a peroxide moiety. These distances are 1.527(3) and 1.456(2) Å, respectively, for a B−O−O−C moiety resulted from the reaction of 9-boraanthracene with O_2.[8b] For a B−O−O−C motif resulted from a phosphine–borane reaction with singlet O_2, the structural parameters are 1.454(6) and 1.473(4) Å, respectively.[8a] A B−O−O−Rh moiety resulted from the reaction of a Rh-peroxo with a boronic acid displays a trigonal boron,[8c] with the B−O distance shorter (1.400(2) Å) and the O−O distance longer (1.497(1) Å) than the above, likely because of the stronger interaction between O and three-coordinate boron. The B-O-O angle (106.9(1)°) is similar to the C-O-O angle (107.5(2)°) in bis(triphenylmethyl)peroxide.[11]

Electrochemical investigation of $\mathbf{1}^{2-}[Cp^*_2Fe]^+_2$ by cyclic voltammetry (Figure 2) revealed the reversible redox couple of $Cp^*_2Fe/Cp^*_2Fe^+$ referenced to −0.59 V (vs. Cp_2Fe/Cp_2Fe^+)[12] and a quasi-reversible redox event centered at +0.17 V (vs Cp_2Fe/Cp_2Fe^+) assigned to the $\mathbf{1}^{2-}$ fragment. This event was assigned to a single-electron oxidation to form a superoxide species that is unstable in solution. The double concentration of $Cp^*_2Fe^+$ vs $\mathbf{1}^{2-}$ results in the observed relative peak size. Attempts to access the presumed superoxide by means of chemical oxidation have resulted in

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[**] We thank Lawrence M. Henling and Dr. Michael Takase for crystallographic assistance. We are grateful to Caltech and NSF GRFP (J.T.H.) for funding.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408462.

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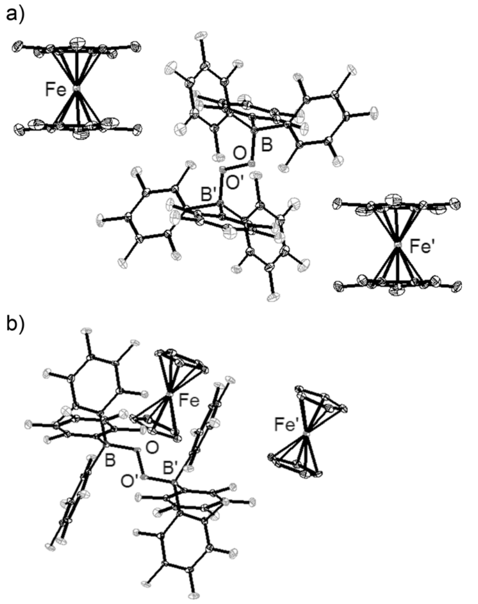


Figure 1. Solid-state structures of a) $1^{2-}[Cp^*_2Fe]^+_2{\cdot}2\,CH_2Cl_2$ and b) 1^{2-}-$[Cp_2Fe^+]_2$.[30] Ellipsoids are set at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity. F light gray, C black. Select bond distances [Å] and angles [°]: a) B–O 1.472(2), O–O′ = 1.485(2); B-O-O′ 106.9(1); b) B–O 1.472(5), O–O′ 1.487(5); B-O-O′ 108.0(3).

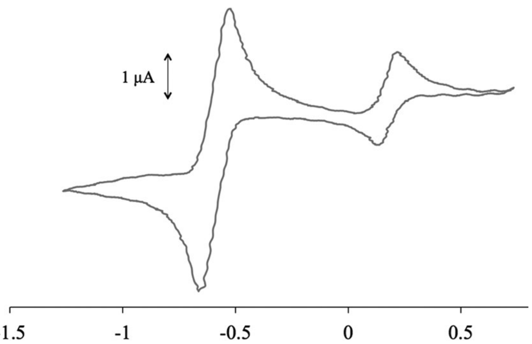
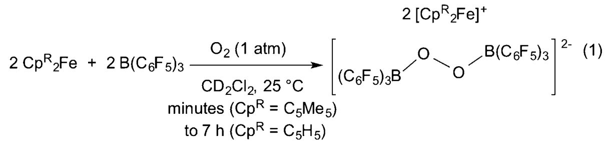


Figure 2. Cyclic voltammogram of $1^{2-}[Cp^*_2Fe]^+$ in 0.1 M $[nBu_4N]^+[PF_6]^-$ in CH_2Cl_2 recorded with a glassy carbon electrode. Scan rate 50 mV s^{-1}. Potentials referenced to Cp_2Fe/Cp_2Fe^+.



$$2\,Cp^R_2Fe + 2\,B(C_6F_5)_3 \xrightarrow[\text{CD}_2\text{Cl}_2,\ 25\,^\circ\text{C; minutes (Cp}^R = \text{C}_5\text{Me}_5\text{) to 7 h (Cp}^R = \text{C}_5\text{H}_5)]{\text{O}_2\ (1\ \text{atm})} 2\,[Cp^R_2Fe]^+\ [(C_6F_5)_3B{-}O{-}O{-}B(C_6F_5)_3]^{2-} \quad (1)$$

$$Cp^R_2Fe \xrightarrow[\text{CD}_2\text{Cl}_2,\ 25\,^\circ\text{C, 24 h}]{\text{O}_2\ (1\ \text{atm})} \text{no reaction} \quad (2)$$

$$B(C_6F_5)_3 \xrightarrow[\text{CD}_2\text{Cl}_2,\ 25\,^\circ\text{C, 24 h}]{\text{O}_2\ (1\ \text{atm})} \text{no reaction} \quad (3)$$

$$Cp^R_2Fe + B(C_6F_5)_3 \xrightarrow[\text{CD}_2\text{Cl}_2,\ 25\,^\circ\text{C, 24 h}]{\text{N}_2\ (1\ \text{atm})} \text{no reaction (Cp}^R = \text{C}_5\text{H}_5\text{)};\ < 15\%\ \text{conversion (Cp}^R = \text{C}_5\text{Me}_5\text{)} \quad (4)$$

$Cp^R = C_5H_5, C_5Me_5$

complex mixtures of diamagnetic species by ^{19}F NMR spectroscopy. The oxidation of peroxide $\mathbf{1}^{2-}$ occurs at a more positive potential than that of cryptand-encapsulated peroxide,[13] indicating a stronger interaction of the anionic peroxo moiety with the Lewis acidic boranes over the cryptand hydrogen bonding.

The weaker reductant ferrocene was also found to react with dioxygen in the presence of $B(C_6F_5)_3$, yielding a species similar to $\mathbf{1}^{2-}[Cp^*_2Fe]^+_2$ by ^{19}F NMR spectroscopy; however, the reaction is considerably slower, requiring several hours to complete.[14] The formation of the peroxide dianion $\mathbf{1}^{2-}$ was confirmed crystallographically (Figure 1), with structural parameters very similar for the two versions differing in the nature of the cation. Additional experiments were performed with ferrocenes and boranes to better understand the formation of $\mathbf{1}^{2-}$. As control reactions, solutions of Cp_2Fe, Cp^*_2Fe, and $B(C_6F_5)_3$ were exposed separately to an atmosphere of O_2 and monitored by ^{1}H NMR spectroscopy [Eqs. (2) and (3)]. No conversion was observed over 24 h. A mixture of Cp^*_2Fe and $B(C_6F_5)_3$ at room temperature, under N_2, led to slow formation of $Cp^*_2Fe^+$, with less than 15% conversion after 24 h, and unidentified species by ^{19}F NMR spectroscopy. There is no observable oxidation of Cp_2Fe in the presence of $B(C_6F_5)_3$ over similar timescales. These control experiments show that the reduction of O_2 [Eq. (1)] requires both the reductant and the Lewis acid. The observed slow conversion of the stronger reductant Cp^*_2Fe vs. Cp_2Fe in the absence of O_2 is reminiscent of the reduction of $B(C_6F_5)_3$ by Cp^*_2Co to generate the $[B(C_6F_5)_3]^-$ radical anion[15] that decomposes to a complex mixture of species in dichloromethane;[16] however, attempts to detect the $[B(C_6F_5)_3]^-$ radical anion by EPR spectroscopy have been unsuccessful to date. Although Cp^*_2Fe has a reduction potential significantly more positive than $B(C_6F_5)_3$ (see below), redox chemistry has been reported between $B(C_6F_5)_3$ and metal complexes that are weak reductants.[17]

Formation of $\mathbf{1}^{2-}$ is not inhibited by the presence of the bulky base 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) for either ferrocene or decamethylferrocene, which is inconsistent with a mechanism initiated by protonation of Fe[18] with adventitious strong acid.[19] Performing the reaction of Cp_2Fe, $B(C_6F_5)_3$, and O_2 in the presence of sub-stoichiometric strong acid $H(OEt_2)_2B[C_6H_3(CF_3)_2]_4$ resulted in conversion to a mixture of species by ^{19}F NMR spectroscopy, including the bis(borane)hydroxide anion $[\{(F_5C_6)_3B\}_2OH]^-$ as a major component.[20] With 50 mol% $H(OEt_2)_2B[C_6H_3(CF_3)_2]_4$, $[\{(F_5C_6)_3B\}_2OH]^-[Cp_2Fe]^+$ was isolated in 35% yield, and its structure was confirmed crystallographically (see the Supporting Information). In an attempt to access $\mathbf{1}^{2-}$ by an alternative route, reaction of four equivalents of $B(C_6F_5)_3$ with one equivalent of $DABCO{\cdot}2\,H_2O_2$ and one equivalent of DABCO (DABCO = [2.2.2]diazabicyclooctane) resulted in a mixture of species by ^{19}F NMR spectroscopy. Treating the isolated peroxide $\mathbf{1}^{2-}[Cp^*_2Fe]^+_2$ with acid also resulted in a mixture of unidentified species by ^{19}F NMR spectroscopy. These results suggest that in the presence of Brønsted acid, ferrocenes, and $B(C_6F_5)_3$, different O_2 reduction pathways are operative. Moreover, the B–O–O–B moiety of $\mathbf{1}^{2-}$ is not stable in the presence of protons (or the combination with

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conjugate bases). Therefore, the reductive synthesis from O_2 is instrumental for the isolation of $\mathbf{1}^{2-}$.

The difference in rates for Cp_2Fe vs. Cp^*_2Fe indicates that the stronger reductant better facilitates the reaction, even though neither reacts with O_2 directly. Several other boron-based Lewis acids were tested in combination with Cp^*_2Fe or Cp_2Fe for reactivity with O_2. $BF_3{\cdot}OEt_2$, $B(C_6H_5)_3$, and $B(C_6F_5)_2(C_6H_5)$ show generation of the respective ferrocenium cations, namely Cp_2Fe^+ for $BF_3{\cdot}OEt_2$ and $Cp^*_2Fe^+$ for $B(C_6H_5)_3$ and $B(C_6F_5)_2(C_6H_5)$), indicating that electron transfer does occur. However, the only characterized boron products were borates resulting from ligand scrambling and oxygenation (BF_4^-, $B(OC_6H_5)(C_6H_5)_3^-$, and $B(C_6F_5)_2(C_6H_5)_2^-$, respectively), without a peroxide moiety.[21] These studies indicate that the electron deficient C_6F_5 moiety, less prone to migration, is instrumental for the isolation of the B_2O_2 species.

The formation of compound $\mathbf{1}^{2-}$ is a rare example of using ferrocenes to reduce dioxygen to peroxide in the absence of additional transition-metal catalyst or strong Brønsted acid. Although the reaction of ferrocene with O_2 in the presence of excess Lewis acids of the form MX_3 ($X = Cl$ for $M = Al$, As, Bi, and Sb; $X = F$ for $M = B$) to yield the corresponding ferrocenium salts $[Cp_2Fe]^+[MX_4]^-$ was previously reported, the oxygen-containing by-products eluded characterization.[22] More recently, Zheng et al. reported the $B(C_6F_5)_3$ catalyzed disproportionation of superoxide into dioxygen and peroxide,[23] though the putative $B{-}O_2^{n-}$ species remained elusive. Activation of O_2 either inner-sphere[24] or outer-sphere[25] by ferrocenes has been proposed. Additionally, the generation of reduced borane, ${}^{\bullet}B(C_6F_5)_3^-$ by species less reducing than Cp^*_2Fe has been reported.[17,26] Although the one-electron reduction potentials are mismatched with Cp_2Fe or even Cp^*_2Fe (-1.18 V vs. Cp_2Fe/Cp_2Fe^+ in DMSO for O_2^-/O_2 couple[27] and -1.79 V vs. Cp_2Fe/Cp_2Fe^+ in CH_2Cl_2 for ${}^{\bullet}B(C_6F_5)_3^-/B(C_6F_5)_3$ couple[16,28]), the presence of the Lewis acidic $B(C_6F_5)_3$ may facilitate direct reduction of O_2 by ferrocenes, as demonstrated for rates of electron transfer that increase with coupling to proton or metal transfer.[29]

In summary, a facile synthesis and structural characterization of the bis(borane)-supported peroxide $\mathbf{1}^{2-}$ was reported. Taking advantage of readily available starting materials, reduction of dioxygen with ferrocenes in the presence of $B(C_6F_5)_3$ generates the B_2O_2 moiety. Notably, the precursors are separately unreactive with O_2 under ambient conditions, highlighting the reduction of O_2 facilitated by Lewis acid binding. Other boron-based Lewis acids underwent ligand disproportionation, indicating that the electron-deficient C_6F_5 moiety is important for the stability of the bis(borane)peroxide.

Experimental Section

For full experimental details and spectroscopic data, see the Supporting Information.

Synthesis of bis(decamethylferrocenium) bis(tris(pentafluorophenyl)boranyl)peroxide $\mathbf{1}^{2-}[Cp^*_2Fe]^+_2{\cdot}2\,CH_2Cl_2$: In an N_2 atmosphere glove box, $B(C_6F_5)_3$ (0.1336 g, 0.261 mmol) and Cp^*_2Fe (0.0861 g, 0.264 mmol) were dissolved in CH_2Cl_2 and added to a Schlenk tube charged with a stir bar. The tube was then removed from the glovebox and connected to a Schlenk line, where the solution was degassed by three freeze–pump–thaw cycles, and an atmosphere of O_2 was added to the headspace with rapid stirring. After 5 seconds the solution had turned from yellow-orange to deep forest green. After 2 min the stirring was stopped and the solution left standing at room temperature. After 10 min at room temperature, crystals began forming. After 30 min the solution was degassed by three freeze–pump–thaw cycles, and the Schlenk tube was taken back into the glovebox and the crystals collected on a medium-porosity glass frit, washing with minimal amounts of cold CH_2Cl_2. Volatile materials were removed under vacuum to yield 0.1297 g (53.9 %) of $\mathbf{1}^{2-}[Cp^*_2Fe]^+_2{\cdot}2\,CH_2Cl_2$. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta =$ 34.7 ppm (br). ^{19}F NMR (125 MHz, CD_2Cl_2, 25 °C): $\delta = -130.0$ (br), -164.7 (br), -168.0 ppm (br). λ_{max} (CH_2Cl_2, nm), ε ($L\,mol^{-1}\,cm^{-1}$): 780, 1091; 710, 653; 650, 444. Anal. calcd (%) for $\mathbf{1}^{2-}[Cp^*_2Fe]^+_2{\cdot}2\,CH_2Cl_2$ ($C_{78}H_{64}B_2Cl_4F_{30}Fe_2O_2$): C 49.87, H 3.43; found: C 50.04, H 3.49.

Received: August 22, 2014

Published online: September 22, 2014

Keywords: dioxygen reduction · ferrocene · peroxide · tris(pentafluorophenyl)borane

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