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- Title: Reduction of Dioxygen by Radical/B(p-C6F4X)3 Pairs to Give Isolable Bis(borane)superoxide Compounds
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# Reduction of Dioxygen by Radical/B(*p*-C<sub>6</sub>F<sub>4</sub>X)<sub>3</sub> Pairs to Give Isolable Bis(borane)superoxide Compounds

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#### Dedication ((optional))

**Abstract:** Triplet dioxygen was reduced by TEMPO or trityl radicals in the presence of two molar equivalents of the strong  $B(p-C_6F_4X)_3$  (X: F or H) boron Lewis acids under mild conditions to give the bis(borane)superoxide systems **2**. The sensitive radical anion species were isolated and characterized including X-ray crystal structure analysis and EPR spectroscopy.

The reduced forms of dioxygen, superoxide  $[O_2]^-$  and peroxide  $[O_2]^{2-}$  are of great importance for chemical transformations as well as reactive species in biological system.<sup>[1]</sup> There is a rich chemistry of the alkali metal superoxides and of metal complexes with peroxo or superoxo ligands.<sup>[2-4]</sup>

Boranes were reported to undergo a variety of reactions with dioxygen species.<sup>[5]</sup> The reaction of triethylborane with triplet dioxygen is a typical example, which provides a method of generating ethyl radicals.<sup>[6]</sup> Bourissou et al reported about the addition/insertion reaction of singlet dioxygen to a phosphane/ borane pair,<sup>[7]</sup> and there were several ways to peroxy boron compounds reported.<sup>[8]</sup> Agapie et al recently described the reduction of dioxygen by two molar equivalents of ferrocenes in the presence of the strong boron Lewis acid  $B(C_6F_5)_3$  to yield the bis-ferrocenium bis(borane)peroxides  $1a, b.^{[9,10]}$  The cyclic voltamogram of 1a showed the redox potential of the [B]<sub>2</sub>O<sub>2</sub><sup>2-</sup>

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 $/[B]_2O_2$  pair being at a value close to the TEMPO/TEMPO<sup>+</sup> pair. This let us speculate that it might be possible to reduce triplet oxygen<sup>[11]</sup> by suitable persistent radicals to the superoxide state (or beyond) in the presence of the strong  $B(C_6F_5)_3$  Lewis acid. This actually turned out to be the case.



Scheme 1. Reduction of dioxygen in the presence of strong boron Lewis acids to bis(borane)peroxide/-superoxide compounds.

We exposed a mixture of TEMPO with two molar equivalents of  $B(C_6F_5)_3^{[12]}$  in deuterated dichloromethane to  $O_2$  (1.5 bar) at room temperature. This led to an immediate color change from orange to dark brown. The <sup>1</sup>H NMR spectra (see the Supporting Information for details) indicated the formation of a paramagnetic reaction product. From the concentrated solution, dark brown crystals of compound 2a precipitated during 48 h at -35°C; they were isolated in 88% yield. The X-ray structure analysis revealed the formation of the bis(borane)superoxide radical anion with one oxoammonium countercation, [C<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>N=O]<sup>+</sup>{O<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub>)<sup>--</sup> and two dichloromethane solvent molecules. The O1-O2 bond in compound 2a (2 CD<sub>2</sub>Cl<sub>2</sub>) is significantly shorter than the oxygenoxygen linkage in the B-O-O-B bis(borane)peroxide compound 1a (Δd = 0.18 Å).<sup>[9]</sup> The B1-O1/ B2-O2 distances are markedly longer than those of **1a** (average  $\Delta d = 0.11$  Å), and the B-O-Oangles are slightly larger by ca. 7°.<sup>[9]</sup> (the 2a ·2 CH<sub>2</sub>Cl<sub>2</sub> structure is depicted in the Supporting Information).

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We performed the reaction of TEMPO with O<sub>2</sub> and two molar equivalents of  $B(C_6F_5)_3$  in CDCl<sub>3</sub> at room temperature and obtained solvent free single crystals of 2a. The O1-O2 distance in 2a is close to that of the trimethylphenylammonium superoxide (of 1.332(2) Å) described by Jansen et al. which contains the unperturbed O2<sup>--</sup> superoxide radical anion <sup>[13-15]</sup> [see Fig. 1 and Table 1; for further details see the Supporting Information].



Figure 1. Molecular structure of compound 2a (thermal ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity).

The analogous reaction of a 1:2 mixture of the TEMPO radical and  $B(p-C_6F_4H)_3^{[16]}$  with  $O_2$  gas (1.5 bar) in  $CD_2Cl_2$  at r.t. gave dark brown crystals of 2b in ca. 90% yield. The X-ray crystal structure analysis confirmed the formation of the analogous B-O-O-B bis(borane)superoxide radical anion/oxoammonium salt  $[C_5H_6Me_4N=O]^+$  { $O_2[B(p-C_6F_4H)_3]_2$ }<sup>-</sup> with similar structural parameters as compound 2a (for further details see Table 1 and the Supporting Information).



Scheme 2. Reaction of Gomberg dimer with dioxygen in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

Trityl radical, available by in situ equilibration from the Gomberg dimer,<sup>[17]</sup> is known to react with O<sub>2</sub> giving bis(triphenylmethyl)peroxide (3).<sup>[18]</sup> We mixed the Gomberg dimer with four equivalents of  $B(C_6F_5)_3$  in  $CD_2CI_2$  at room temperature, and confirmed by NMR spectroscopy that no reaction had occurred. We then exposed this mixture to  $O_2$  (1.5 bar, r.t.) (Scheme 2). Within ca. 30 min the color of the reaction mixture had changed from orange to dark yellow. Diffusion of pentane to the reaction solution gave compound 2c as dark yellow crystals, which we isolated in ca. 40% yield. Compound 2c was characterized by elemental analysis, spectroscopy and X-ray diffraction. In

addition to the typical NMR features of the trityl cation [e.g. <sup>13</sup>C:  $\delta$  = 209.9 (233 K)] we observed a broad <sup>19</sup>F NMR singlet at ca.  $\delta$ = -158.5 similar as it was observed in compound 2a [see the Supporting Information for experimental details and the depicted NMR spectra]. The X-ray crystal structure analysis of compound 2c confirmed the formation of the  $[Ph_3C]^+$  {O<sub>2</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub>}bis(borane)superoxide radical anion/trityl cation salt (see Figure 2 and Table 1).



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<b>igure 2.</b> Molecular structure of compound <b>2c</b> (thermal ellipsoids are shown the 15% probability level; hydrogen atoms are omitted for clarity).								
Table 1.Selecompounds 2.[a]	cted structural pa	arameters of	the bis(borane	e)superoxide				
compound	2a · (2 CH <sub>2</sub> Cl <sub>2</sub> )	2a	2b	2c				
cation	TEMPO+	TEMPO <sup>+</sup>	TEMPO <sup>+</sup>	Ph₃C+				
01-02	1.305(4)	1.325(2)	1.280(4)	1.310(6)				
B1-O1	1.582(6)	1.608(3)	1.581(6)	1.590(9)				
B2 O2	1 591(6)	1 604(3)	1 579(6)	1 576(0)				

cation	TEMPO <sup>+</sup>	TEMPO+	TEMPO <sup>+</sup>	$Ph_3C^+$
01-02	1.305(4)	1.325(2)	1.280(4)	1.310(6)
B1-O1	1.582(6)	1.608(3)	1.581(6)	1.590(9)
B2-O2	1.581(6)	1.604(3)	1.578(6)	1.576(9)
B1-O1-O2	114.6(3)	116.8(2)	116.0(3)	114.0(5)
B2-O2-O1	115.1(3)	112.4(2)	115.7(3)	114.2(5)
B1-O1-O2-B2	177.3(3)	-178.1(2)	169.8(4)	179.2(5)

<sup>[a]</sup> Bond lengths in (Å), angles in (°).

The effective magnetic moments were determined for the compounds **2a** ( $\mu_{eff} = 1.60(1) \mu_B$ ), **2b** ( $\mu_{eff} = 1.51(1) \mu_B$ ), and **2c**  $(\mu_{eff} = 1.54(1) \mu_B)$  (for details see the Supporting Information). The values are slightly lower than the expected value for a free single electron ( $\mu_{eff}$  = 1.73  $\mu_B$ ), which might be due to impurities present in these very sensitive materials.[13d,e]

We characterized compounds 2a and 2c by EPR spectroscopy. The X-band EPR spectrum of the oxoammonium cation/bis-(borane)superoxide radical anion salt (see Figure 3) shows a seven-line signal centered at g = 2.01101. The multiplicity confirms the influence of two symmetry-equivalent boron nuclei with dominating contribution of the <sup>11</sup>B-<sup>11</sup>B isotopologues. Simulation of the spectra gave a <sup>11</sup>B hyperfine coupling constant

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of 3.23 G (9.1 MHz) for compound **2a**. Compound **2c** showed analogous EPR behavior [g = 2.01101, septet, A(<sup>11</sup>B) = 3.26 G (9.2 MHz), for further details see the Supporting Information)].



Figure 3. X-band EPR spectrum of a  $10^{-2}$  M CH<sub>2</sub>Cl<sub>2</sub> solution of the oxoammonium cation/bis(borane)superoxide radical anion salt **2a**; experimental (bottom) and simulated spectrum (top).

The bis(borane)superoxide compounds 2 are rather labile in solution at ambient temperature. Free superoxide O2<sup>--</sup> can undergo back electron transfer to oxoammonium cation to give **TEMPO** O<sub>2</sub>,<sup>[19]</sup> and and so can apparently the bis(borane)superoxides 2. Treatment of 2a with tetrahydrofuran (THF) or dimethylsulfoxide (DMSO) resulted in the rapid formation of the corresponding donor solvent-borane adducts with liberation of a gas, probably dioxygen. The formation of TEMPO was observed by EPR spectroscopy in both reactions. The reaction of the trityl compound 2c with DMSO gave a slightly different outcome. We observed the formation of the (dimethylsulfoxide)B(C $_6F_5$ )<sub>3</sub> Lewis adduct and trityl peroxide (Ph<sub>3</sub>C-O-O-CPh<sub>3</sub> 3)<sup>[18]</sup> as major components (see Scheme 3). We assume that in this case liberated dioxygen was trapped by trityl radical, in situ formed by back electron transfer.



Scheme 3. Reaction of bis(borane)superoxide 2a THF or DMSO.

Direct characterization of the sensitive superoxide radical salts by cyclic voltammetry proved difficult. Therefore, we added a slight excess of decamethylferrocene to the solution of **2c**, which served as a pre-reductant and an internal standard. The cyclic voltamogram (Figure 4) showed the strong signal of the Fc<sup>\*+</sup>/Fc<sup>\*</sup> redox couple at -0.59 V (vs. Fc/Fc<sup>+</sup>), followed by the weak trityl cation/trityl radical redox feature (-0.16 V) and the bis(borane)superoxide radical anion/bis(borane)-peroxide signal at +0.22 V.<sup>[9]</sup> We note from an independent experiment (for details see the Supporting Information) that the latter value is almost identical with the oxoammonium/ TEMPO redox potential, which is in accord with the apparently facile back-electron transfer under suitable conditions (see above).<sup>[20]</sup>



Figure 4. Cyclic voltamogram of the trityl/bis(borane)superoxide system 2c in dichloromethane (0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>]) in the presence of a slight excess of decamethylferrocene.

Treatment of the in situ generated compound 2c with an additional molar equivalent of trityl radical led to the formation of the trityl cation/bis(borane)-peroxide dianion salt 1c, featuring tetra-coordinate borate NMR signals (Scheme 4). (<sup>11</sup>B:  $\delta$  = -2.1,  $\Delta \delta^{19} F_{m,p} = 2.9 \text{ ppm } \{O_2[B(C_6F_5)_3]_2\}^{2-}, \text{ for the depicted NMR}$ spectra and experimental details see the Supporting Information) Workup gave compound 1c as a yellow amorphous solid in ca. 49% vield. Single crystals were obtained from dichloromethane/pentane by the diffusion method. The X-ray structure analysis (see the Supporting Information for details and the depicted molecular structure) revealed that compound 1c features a B-O-O-B bis(borane)-peroxide dianion with two trityl counter cations similar to that previously observed by Agapie et al in the respective ferrocenyl systems<sup>[9]</sup> [d(O-O): 1.488(2) Å (1c); 1.485(2) Å (1a)].

$$\begin{bmatrix} Ph_{3}C^{\bullet} & 2 Ph_{3}C^{\bullet} \\ (C_{6}F_{5})_{3}B^{-O} & B(C_{6}F_{5})_{3}\end{bmatrix}^{-} \xrightarrow{Ph_{3}C^{\bullet}} \\ \hline CD_{2}Cl_{2} \begin{bmatrix} (C_{6}F_{5})_{3}B^{-O} & B(C_{6}F_{5})_{3} \end{bmatrix}^{2-} \\ \mathbf{1c} \end{bmatrix}$$

Scheme 4. Reduction of compound 2c by trityl radical.

Our study has shown that triplet dioxygen is readily reduced to the superoxide stage by treatment with suitable radicals in a 1:1 stoichiometry, here TEMPO or the trityl radical, in the presence of two molar equivalents of strong boron Lewis acids  $B(p-C_6F_4X)_3$  (with X: F or H) to give the bis(borane)superoxide compounds **2**. The isolation and characterization of these rather sensitive compounds underlines the extraordinary ability of these strongly electrophilic bulky boranes to serve as reagents in small molecule activation and suitable stabilization of their reaction products.

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Keywords: dioxygen • superoxide • peroxide • radicals • boron

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