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Holger Braunschweig,* Ivo Krummenacher, Lisa Mailänder, Leanne Pentecost and Alfredo Vargas

Oxidation of a tetraorganoborate salt leads to selective formation of the corresponding zwitterionic radical rather than carbon–carbon bond formation of the boron substituents.
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Formation of a stable radical by oxidation of a tetraorganoborate†

Holger Braunschweig,†a Ivo Krummenacher,†a Lisa Mailänder,a Leanne Pentecostb and Alfredo Vargasb

Herein, we describe the selective formation of a stable neutral spiroborate radical by one-electron oxidation of the corresponding tetraorganoborate salt Li[B(C$_3$H$_7$)$_4$], formally containing a tetrahedral borate centre and a s-cis-butadiene radical cation as the spin-bearing site. Spectroscopic and computational methods have been used to determine the spin distribution and the chromism observed in the solid state.

The oxidation of tetraaryl, -alkenyl or -alkyl borates with the general formula [BR$_4$]$^-$ usually leads to the formation of C–C coupled products by skeletal rearrangements.$^{1,2}$ Oxidation thus represents a versatile method for the synthesis of disubstituted alkenes or biaryl compounds.$^3$ As depicted in Scheme 1, such reactions are also a feature of spiroborates, which in the case of a spirocyclic borafuorene derivative (1) afford a bis(biaryl) compound.$^{4,5}$ In general, these reactions can be initiated by a variety of oxidising agents or reaction conditions, such as photo- or electrochemically.$^6$ In a few instances, [BR$_4$]$^+$ radicals have been suggested as intermediates in the oxidative ligand coupling process, but never directly observed.$^7$ Herein, we show with a spiroborate (2) that the oxidation can be directed to the exclusive formation of such a boraryl radical species.

Spiroborate 2 was synthesised as previously reported by our group by salt elimination of two equivalents of 1,2-dilithio-1,2,3,4-tetraphenylbutadiene with BF$_3$Et$_2$O.$^8$ Whereas the redox chemistry of boroles, five-membered boron-containing, antiaromatic and highly Lewis acidic heterocycles,$^9$ has been explored extensively,$^{10}$ the redox behaviour of the related spiroborate salt 2 had not been investigated so far. As judged by cyclic voltammetry in tetrahydrofuran solution, compound 2 undergoes an irreversible oxidation at $-0.35$ V vs. the [FeCp$_2$/[FeCp$_2$]$^+$ couple (see ESI†) in the potential window. We wondered if the oxidation step could be realised on a preparative scale and the formed product be isolated. To this end, a stoichiometric amount of the one-electron oxidation agent ferrocenium hexafluorophosphate was added to a solution of 2 in benzene at rt (Scheme 2). Addition of the Fe(III) salt led to an immediate colour change from yellow to dark green and the precipitation of a colourless solid. Upon completion, the $^{11}$B NMR resonance of the starting material (2, $\delta_B = -1.4$ ppm) disappeared without the occurrence of a new signal. Similarly, the $^1$H NMR spectrum of the crude reaction mixture showed only the formation of ferrocene but no additional signals for the oxidation product. After the separation of Li[PF$_6$] and ferrocene, compound 3 was isolated as green amorphous, or alternatively, red crystalline, solids (80% crystalline yield).

The absence of NMR signals suggested the radical character of 3, which was supported by EPR spectroscopy (vide infra). X-ray diffraction of red single crystals of 3 confirmed the
The continuous-wave ESR spectrum of 3 in benzene solution shows that the unpaired spin density is delocalised into the benzene solvent. The electron paramagnetic resonance signal (EPR) of 3 is broad and weak, indicating a high degree of delocalisation. The EPR signal of 3 is broad and weak due to the delocalisation of the unpaired spin density. The EPR signal of 3 is broad and weak due to the delocalisation of the unpaired spin density.

**Fig. 2** X-band first (grey dotted line) and second (solid black line) derivative EPR spectrum of 3 at room temperature in benzene solution. A simulation of the second derivative spectrum is shown in red. Instrumental parameters: $\nu = 9.379$ GHz, modulation frequency = 100 kHz, modulation amplitude = 0.1 G, microwave power = 0.25 mW, conversion time = 40 ms, 4 scans.

**Fig. 1** Left: Molecular structure of 3 in the solid state. Hydrogen atoms and the ellipsoids of the phenyl residues are omitted for clarity. Table S1 in the ESI. Right: Side view showing the relative arrangement of the two rings.

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The structures of the neutral radicals reported by Haddon and coworkers, which have attracted considerable theoretical and 24 calculations, the striking colour change between the crystalline and the solution/amorphous state could be attributed to structural changes of the spiro compound. Further investigations regarding the intriguing electronic and optical properties of the compound, as well as its reactivity, are underway.

We thank the Deutsche Forschungsgemeinschaft (H. B.), the University of Sussex and the EPSRC (A. V.) for support of this work.

Notes and references


HOMO – 2 to LUMO (spin-down) at around 15 500 cm⁻¹ (645 nm), and HOMO to LUMO (spin-up) at around 21 000 cm⁻¹ (476 nm).

Another geometry-dependent feature of 3 is that of the spin-density distribution, which unsurprisingly is dictated by the structure. Calculations show that the spin population in the radical is essentially localised on one borole moiety in both the gas and solution phase; the dominant spin density is found on the two carbon atoms adjacent to the boron atom. Imposing $D_2$ symmetry distributes the spin density evenly on all four carbon atoms adjacent to the boron atom that extends into the phenyl substituents. Furthermore, in this symmetrical configuration the molecular orbitals (MOs) are delocalised across both borole moieties (see Fig. 3). Both the spin density and MO profiles are well in line with experimental results (vide supra).

The total electronic energy of the symmetrised structure is only slightly (0.6 kcal mol⁻¹) higher than that of the non-symmetrisated structure. This could be ascribed in part to interaction of the two perpendicular π planes connected by the boron centre, via so-called spiroconjugation.

The difference in reactivity of 2 compared to its benzannelated analogue 1, the latter undergoing coupling of the organic substituents upon oxidation, most likely arises from the stochiometric use of the outer-sphere oxidant ferrocene, which can accept precisely one electron from the borate.

Isolation of the stable spiro radical (3) suggests that a radical mechanism might be operative in the oxidative ligand coupling reaction of other organoborates, as previously proposed. The possible resonance forms of the zwitterionic species 3 all consist of a borate anion and a $s$-cis-$1,3$-butadiene radical cation bearing the unpaired spin density (see Scheme 1). The structure thus draws immediate comparison to simple butadiene radical cations which have attracted considerable theoretical and experimental attention, but have eluded characterisation by X-ray crystallography thus far. Moreover, radical 3 resembles the structures of the neutral radicals reported by Haddon and coworkers, in which two phenalenyl units are attached to a tetrahedral boron atom. In this family of compounds, however, the neutral spiro radical is based on $N,N$- or $N,O$-containing six-membered heterocyclic systems and thus not susceptible to a competing oxidative ligand coupling reaction. Closely related to 3 are also the neutral borocyclic radicals of the general formula $[(\text{C}_n\text{F}_3)_2\text{B}(\text{O}_2\text{C}_1\text{H}_4)_2]^*$ and $[(\text{C}_n\text{F}_3)_2\text{B}(\text{O}_2\text{C}_{13}\text{H}_2)_2]^*$ in which the boron atom has two oxygen substituents.

In summary, we have shown that by chemical one-electron oxidation of an organoborate, a neutral stable radical of the form $[\text{BR}_3]^*$ can be generated. The stability and persistency of the radical species enabled characterisation by X-ray crystallography, besides spectroscopic techniques (ESR and UV-vis). Assisted by DFT and TD-DFT calculations, the striking colour change between the crystalline and the solution/amorphous state could be attributed to structural changes of the spiro compound. Further investigations regarding the intriguing electronic and optical properties of the compound, as well as its reactivity, are underway.

Fig. 3 MO62X/6-311G* calculated (a) singly-occupied molecular orbital (SOMO), and (b) spin-density distribution for 3 with imposed $D_2$ symmetry.


17 A Cambridge Structural Database (CSD) search with the ConQuest program resulted in no match (accessed February 2, 2016).
