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Boron Radicals

Evidence for Extensive Single-Electron-Transfer Chemistry in Boryl Anions: Isolation and Reactivity of a Neutral Borole Radical**

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Abstract: *Despite the synthesis of a boryl anion by Yamashita et al. in 2006, compounds that show boron-centered nucleophilicity are still rare and sought-after synthetic goals. A number of such boryl anions have since been prepared, two of which were reported to react with methyl iodide in apparent nucleophilic substitution reactions. One of these, a borolyl anion based on the borole framework, has now been found to display single-electron-transfer (SET) reactivity in its reaction with triorganotetrel halides, which was confirmed by the isolation of the first neutral borole-based radical. The radical was characterized by elemental analysis, single-crystal X-ray crystallography, and EPR spectroscopy, and has implications for the understanding of boron-based nucleophilic behavior and the emergent role of boron radicals in synthesis. This radical reactivity was also exploited in the synthesis of compounds with rare B–Sn and B–Pb bonds, the latter of which was the first isolated and structurally characterized compound with a "noncluster" B–Pb bond.*

The isolation of a boryl anion by Yamashita et al. in 2006 was an astounding feat, and one that has changed the way we think about the properties of low-coordinate boron.[1] The discovery gave the field a well-defined species with a negative charge at boron, but most importantly, the anion showed unequivocal boron-centered nucleophilicity. Later, a handful of different anionic boryl species were reported with the hopes of extending the palette of nucleophilic boryl species. In 2008 we prepared the dimetalloboride anions $[\{(\eta^5\text{-}C_5H_4R)(OC)_2Mn\}_2B]^-$ (**A**; R = H, Me), which turned out to show an unusual mixture of apparent boron-centered nucleophilicity (with methyl iodide and Group 11 metal halides), electrophilicity (with zero-valent Group 10 metal species), as well as metal-centered nucleophilicity (with triorganyltetrel halides).[2] In 2010, Curran et al. reported the in situ preparation of the N-heterocyclic carbene (NHC)-stabilized boryl anion $Li[IDipp \rightarrow BH_2]$ (**B**, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which, although not isolated, showed formal nucleophilic behavior towards a range of organic electrophiles.[3]

Also in 2010 we described a π-boryl anion based on an NHC-stabilized borole framework—the borolyl anion $K[SIMes \rightarrow BC_4Ph_4]$ (**1**, SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, see Figure 1 and Scheme 1), which reacted with methyl iodide to give the corresponding boron-methylated NHC-stabilized borole.[4] The five-membered heterocyclic framework of boroles (Figure 1, top),[5] antiaromatic 4π-electron systems in their conventional state, has proven to be a versatile platform for the stabilization of charged and radical species. The first dianionic derivatives, borolyl dianions (Figure 1, middle),[6] were prepared in 1980, while the first borolyl radical anion was observed in 2010[7] and isolated in 2012 (Figure 1, bottom).[8]

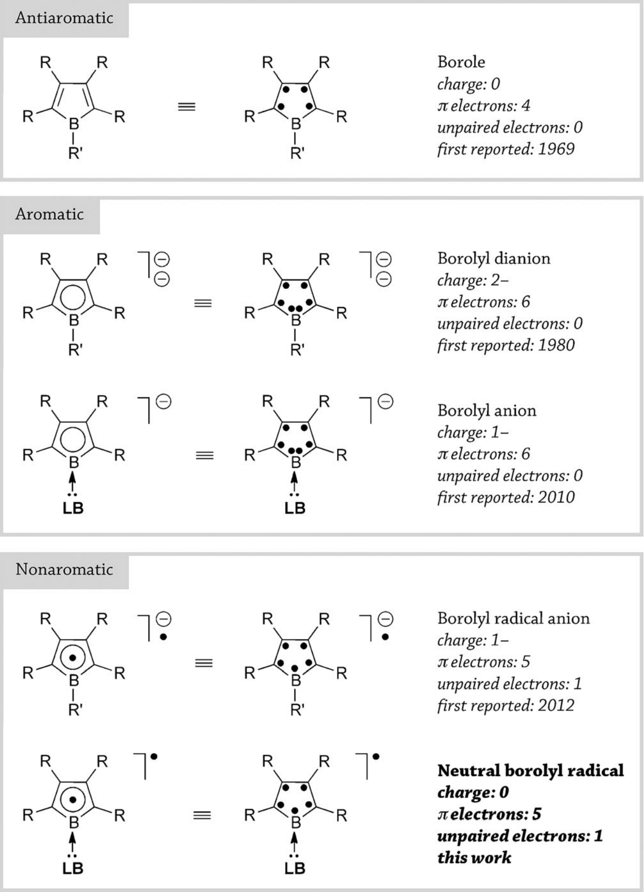

Figure 1. Antiaromatic, aromatic, and nonaromatic species based on the borole framework (**LB** = Lewis base).

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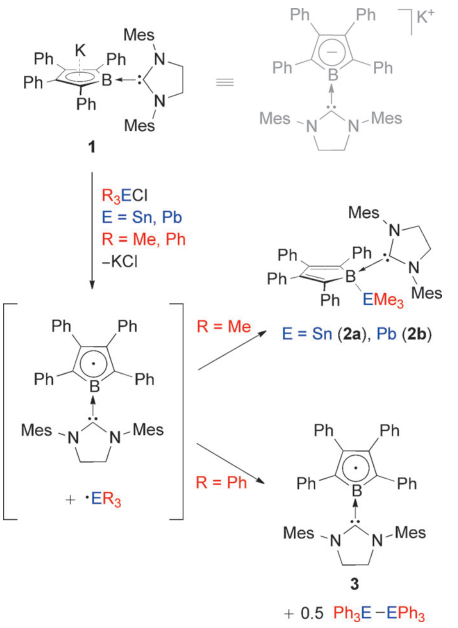

Scheme 1. Reaction of heavier trimethyl- and triphenyltetrel halides with borolyl anion **1**. Mes = mesityl (2,4,6-trimethylphenyl).

Although the facile reactivity of a dimetalloboride anion **A** with methyl iodide was indicative of a formal nucleophilic substitution reaction, we observed no analogous reactivity with longer-chain primary alkyl iodides.[2d] This finding led us to suspect the possible operation of a radical mechanism in the reaction and a neutral radical intermediate species, based on the growing body of literature on the isolation and/or generation of neutral boryl radicals[9–12] and the reported radical reactivity of methyl iodide.[13] However, we were unable to generate or observe any long-lived radical species derived from **A** in order to confirm this. Similarly, our NHC-stabilized borolyl anion **1** appeared to possess significant boron-centered nucleophilicity, although this was evidenced only from its reaction with methyl iodide and a weak Brønsted acid.[4] We thus set out to explore the nucleophilicity (or lack thereof) of **1**, leading us to attempt its reaction with triorganyl halides of tin and lead.

Herein, we report the reaction of borolyl anion **1** with heavier triorganyltetrel halides, yielding (depending on the nature of the organyl group) both products of formal nucleophilic substitution and the first ever isolated neutral borolyl radical. This radical is confirmed to be an intermediate in the process, leading us to conclude that the apparent nucleophilicity of the borolyl anion **1** is in fact a consequence of radical reactivity. Furthermore, the ultimate products of the radical reaction possess rare B–Sn and B–Pb bonds (including the first isolated molecule with a "noncluster" B–Pb bond), both of which have been characterized by acquisition of a range of one- and two-dimensional ^{119}Sn and ^{207}Pb NMR spectra.

Upon addition of the electrophiles Me$_3$ECl (E = Sn, Pb) to the borolyl anion **1**, the color of the reaction solution changes from deep purple to yellow and the formal nucleophilic substitution products **2a** (E = Sn, Scheme 1) and **2b** (E = Pb) were obtained. In the case of the lead derivative the color change is much slower and the reaction requires over 12 h to reach completion. In this reaction (E = Pb), a red coloration was observed during the reaction period, which we confirmed to be due to a radical borolyl intermediate (vide infra). The ^{11}B NMR resonances of the products (**2a**: $\delta = -12.8$ ppm, **2b**: $\delta = -7.3$ ppm) are shifted to higher field compared with compound **1** ($\delta = +12.7$ ppm), due to the formation of tetracoordinate boron centers. A similar shift was observed upon treatment of **1** with MeI, resulting in an NHC-coordinated 1-methyl-2,3,4,5-tetraphenylborole ($\delta = -10.8$ ppm).[4a] Broad quartet signals in the ^{119}Sn NMR spectrum of **2a** ($\delta = -40.3$ ppm, q, $^{1}J(^{11}\mathrm{B},^{119}\mathrm{Sn}) \approx 400$ Hz) and in the ^{207}Pb NMR spectrum of **2b** ($\delta = 58.2$ ppm, q, $^{1}J(^{11}\mathrm{B},^{207}\mathrm{Pb}) \approx 450$ Hz) were detected and indicate a direct bond between the tin/lead nuclei and the boron atom ($I(^{11}\mathrm{B}) = 3/2$). The ^{11}B–^{119}Sn/^{207}Pb coupling constants are significantly smaller than those found for B-stannylboranes and B-plumbylboranes as a consequence of the reduced s character of the B–Sn/Pb bond.[14] In addition, a triple-resonance NMR experiment $^{207}\mathrm{Pb}\{^{1}\mathrm{H},^{11}\mathrm{B}\}$ was performed for compound **2b**. The broad quartet at 58.2 ppm (full width at half height (fwhh) ca. 1600 Hz, Figure S10) was observed to substantially narrow with application of ^{11}B decoupling (fwhh = 57 Hz, Figure S10). Furthermore, 2D HMQC NMR spectroscopy (^{1}H-^{119}Sn and ^{1}H-^{207}Pb) displayed typical cross-peaks between the tin or lead atoms and their attached CH$_3$ groups. In the ^{1}H-^{207}Pb HMQC NMR spectrum, cross-peaks from the lead signal to the backbone CH$_2$ protons of the SIMes mesityl units were also observed, corresponding to a $^{5}J_{\mathrm{HPb}}$ coupling constant of roughly 5 Hz. The ^{1}H NMR spectrum of **2a** displayed ^{119}Sn/^{117}Sn satellites for the CH$_2$ backbone moiety of the NHC ligand with a coupling constant of roughly 8 Hz. The four separate ^{1}H NMR resonances (intensity ratio: 6:3:3:6) for the methyl groups of the SIMes mesityl moieties of **2a** and **2b** indicate that the rotation of the NHC around the carbene C–B bond is hindered at room temperature due to the congested situation around the boron atom.

Crystals of **2a** and **2b** suitable for X-ray analysis were obtained from concentrated Et$_2$O solutions at room temperature and confirm the spectroscopic findings (Figure 2). The molecular structures of **2a** and **2b** exhibit distorted tetrahedral environments for the boron centers: the C5-B1-E1 angles are significantly wider (E = Sn: 122.3°; E = Pb: 119.2°) than a perfect tetrahedral angle of 109.5°. The bond lengths in the planar borolyl rings are in accordance with those of isolated butadiene systems (**2a**: C1–C2 1.371, C2–C3 1.472, C3–C4 1.370 Å; **2b**: C1–C2 1.370, C2–C3 1.466, C3–C4 1.372 Å) and correlate well with those of known NHC–borole adducts.[4,15] The few examples of structurally characterized compounds with B–Sn bonds display bond lengths from 2.236 up to 2.316 Å for B-stannylboranes[16] and up to 2.404 Å for B-stannylborane adducts.[17] The B–Sn distance in **2a** (2.332 Å) lies between these values. It should also be mentioned that **2b** represents the first compound with a classical ("noncluster") B–Pb bond (2.405 Å).

To gain more insight into the reaction mechanism we considered the reaction of borolyl anion **1** with the more

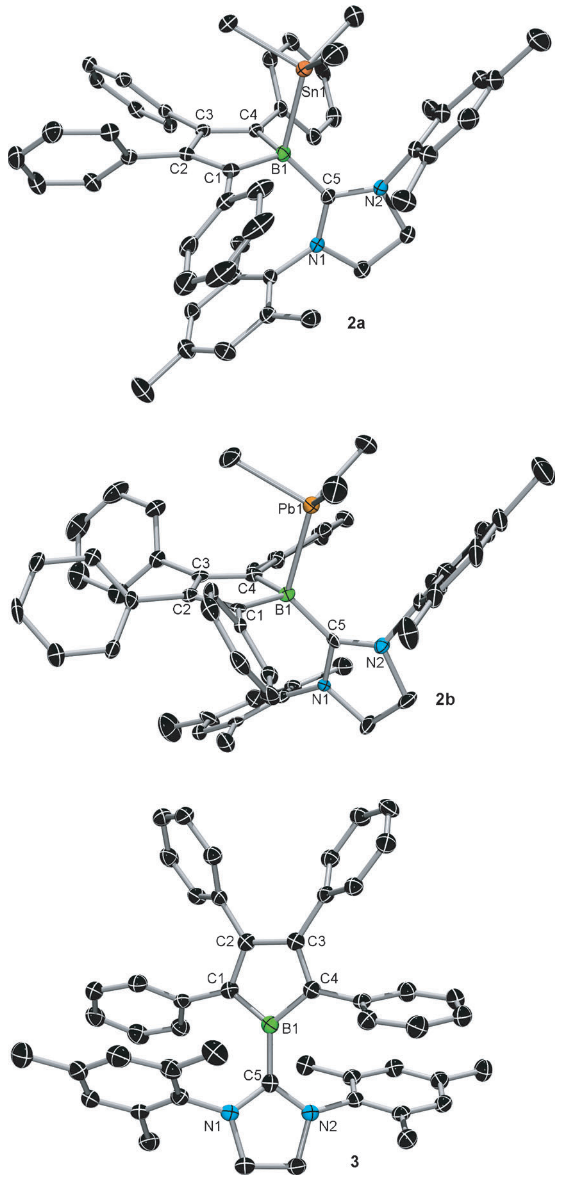

Figure 2. Molecular structures of **2a**, **2b**, and **3**, as derived from single-crystal X-ray crystallography. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, one molecule of CH_2Cl_2 for **2a**, and one molecule of Et_2O for **2b** are omitted for clarity. Selected bond lengths [Å] and angles [°]: for **2a**: B1–C1 1.592(5), B1–C4 1.623(5), B1–Sn1 2.332(4), B1–C5 1.612(5), C1–C2 1.371(5), C2–C3 1.472(5), C3–C4 1.370(5), C5-B1-Sn1 122.3(3). For **2b**: B1–C1 1.572(9), B1–C4 1.622(9), B1–Pb1 2.405(7), B1–C5 1.614(9), C1–C2 1.370(8), C2–C3 1.466(9), C3–C4 1.372(9), C5-B1-Pb1 119.2(4). For **3**: B1–C1 1.544(3), B1–C4 1.547(3), B1–C5 1.567(3), C1–C2 1.384(2), C2–C3 1.482(2), C3–C4 1.380(2), N2-C5-B1-C1 −39.7(3), N1-C5-B1-C1 −40.7(3).

bulky triorganyltetrel halides Ph_3ECl (E = Sn, Pb). In contrast to trimethyl derivatives Me_3ECl (E = Sn, Pb), no instant color change was observed after addition of the electrophiles to an Et_2O solution of **1**. After 12 h at room temperature the reaction mixture turned red and the formation of KCl was observed. Deep red crystals suitable for X-ray diffraction studies were obtained from an Et_2O/hexane solution. The molecular structure indicated that we had isolated the neutral borolyl radical **3**, which is formed by single-electron oxidation of the anion **1** and salt elimination (Scheme 1). The presumed triphenylstannyl/plumbyl radical intermediates do not recombine with the radical **3**, but rather undergo homocoupling to yield the respective hexaphenyldistannane/diplumbane. The generation of the hexaphenylditetrels was confirmed by ^{119}Sn, ^{207}Pb, and ^{1}H NMR spectroscopy (^{119}Sn: $\delta = -142.2$ ppm, ^{207}Pb: $\delta = -72.7$ ppm).[18] It can be assumed that the recombination of the sterically demanding triphenyl radical with the neutral radical **3** is disfavored due to steric hindrance.

The molecular structure of neutral radical **3** features a planar tricoordinate boron atom (Figure 2). The N2-C5-B1-C1 and N1-C5-B1-C1 torsion angles (ca. 40°) are similar to the angles found in the borolyl anion **1**. The characteristic structural motif of the formally aromatic anion **1** is the decreased single/double bond alternation in the borole ring due to its six delocalized π electrons. The neutral radical **3** holds only five π electrons and thus is formally nonaromatic. Accordingly, the bond alternation in the borolyl moiety is more distinct and corresponds well with that of the previously reported 5π-electron radical anion of 1-mesityl-2,3,4,5-tetraphenylborole.[8]

The radical nature of **3** was further established by EPR spectroscopy, which shows a four-line signal at 295 K in benzene centered at $g_{iso} = 2.003$ (Figure 3a). In agreement with the simulation and the interaction of the unpaired electron with two boron isotopes (^{11}B, $I = 3/2$, $A(^{11}\mathrm{B}) = 3.02$ G; ^{10}B, $I = 3$, $A(^{10}\mathrm{B}) = 1.02$ G), the hyperfine splitting indicates that the electron is mainly delocalized within the five-membered borole ring by comparison with previous borolyl radicals.[7,8a] The borolyl radical **3** joins the B-

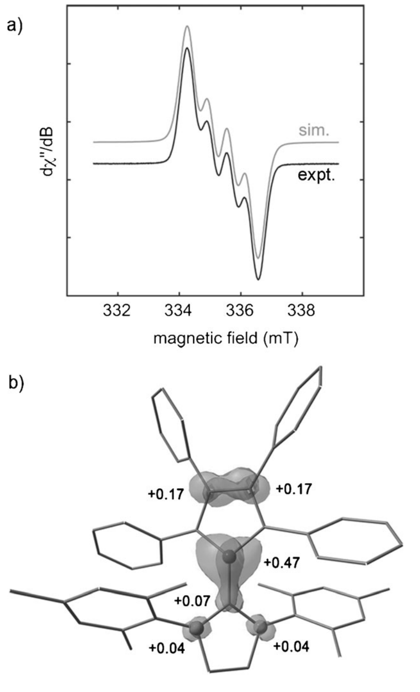

Figure 3. a) Experimental (expt., black line) and simulated (sim., gray line) EPR spectrum (X-band) of **3** in benzene at 295 K. b) Spin density plot of **3** (0.005 isocontour). Numbers correspond to spin populations based on a Mulliken population analysis.

heterocyclic π radical of Yamashita et al.[11] and the acridinylborane radicals of Gabbaï and Chiu[10a,b] as very rare examples of structurally characterized neutral boryl radicals.

The intermediacy of **3** in the reaction to form **2a** and **2b** was indicated by the repeated observation of a red color during the reaction of **1** with Me_3PbCl, as well as of deep red, crystalline **3**, which formed on the side of the reaction vial. The identity of the red crystalline material was confirmed by means of single-crystal X-ray diffraction by comparison of its cell parameters with those of an authentic sample of **3**. As the reaction progresses the red crystals disappear and the red color of the solution dissipates. This finding is persuasive evidence that these reactions are radical in nature rather than nucleophilic, leading us to also question the mechanism of the previously reported reactions of anions **A** and **1** with methyl iodide.[4a] The preference for an SET mechanism over an S_N2 pathway due to steric hindrance was discussed by Tolbert et al. in the reaction of a carbanion with methyl iodide, wherein the latter acts as a one-electron oxidant.[13]

The similarity of the reactivity of borolyl anion **1** with the acyclic NHC-stabilized boryl anion of Curran et al.[3] is unsurprising given that the negative charge in both cases is significantly localized to the boron atom, as calculated in our previous report.[4a] Similarly, the spin density of the radical **3** is mainly localized to the boron atom. A Mulliken population analysis indicated that the boron atom has a spin population of 0.47 (Figure 3b, see the Supporting Information for details).

Herein, a borolyl anion has been found to display single-electron-transfer (SET) reactivity in its reaction with triorganotetrel halides, which was confirmed by the isolation of the first neutral borolyl radical. The radical was characterized by elemental analysis, single-crystal X-ray crystallography, and EPR spectroscopy. The isolation of the neutral radical shows that care must be taken in assigning a mechanism to boryl anion reactivity, as either nucleophilic substitution or single-electron transfer may be occurring. The finding has implications for the understanding of both boron-based nucleophilic behavior and the emerging use of boron-based radicals in organic synthesis.[3,12] This reactivity was also exploited in the synthesis of compounds with rare B–Sn and B–Pb bonds, the latter of which is the first isolated and structurally authenticated compound with a "noncluster" B–Pb bond.

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