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## Bronsted acid-catalyzed skeletal rearrangements in polycyclic conjugated boracycles: a thermal route to a ladder diborole

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The dibenzodiboracyclobutylidene 1 was recently shown to undergo photochemical rearrangement to the more thermodynamically stable dibenzodiborapentalene 2. In order to discover a more efficient thermal route for this isomerization, the redox chemistry of both 1 and 2 were explored. Radical anions can be formed and characterized by EPR spectroscopy by one electron reduction using potassium graphite. The  $[Cp*_2Co]^+$  salt of the radical anion of 2 was characterized by X-ray crystallography. The dipotassium salts  $1K_2$  and  $2K_2$  can be prepared by using two equivalents of potassium naphthalenide; both were fully characterized. It was found that smooth rearrangement of  $1K_2$  to  $2K_2$  is mediated by weak Bronsted acids such as *tert*-butanol or 2,6-dimethylphenol; a mechanism based on similar rearrangements in the isoelectronic neutral all-carbon framework is proposed.

#### Introduction

In the last two decades, conjugated polycyclic hydrocarbons have garnered considerable interest in the area of organic electronics.<sup>1</sup> Amongst these organic semiconductors, pentacene's high hole mobility has made it a standard in the field.<sup>1-3</sup> However, its poor solubility in common organic solvents and its reduced light and oxygen stability has limited its applicability.<sup>4</sup> Incorporation of main group elements into these conjugated polycyclic acene hydrocarbons can modify their photophysical properties and provide enhanced stability.<sup>5</sup>, <sup>6</sup> In particular, molecules containing boron are promising candidates for use as organic light emitting diodes,<sup>7-9</sup> sensors<sup>10</sup> and field effect transistors<sup>11, 12</sup> because the empty p orbital can participate in the delocalization of electrons.<sup>13-15</sup> Furthermore,



the exchange of carbon for the more electropositive boron atom can also alter the electronic characteristics of a compound significantly. For instance, 9-boraanthracene and higher boraacenes show a considerably smaller HOMO-LUMO gap compared to the all-carbon analogues.<sup>16, 17</sup>Among boron containing heterocycles, boroles have attracted significant attention in the past few years, 18-24 and their incorporation into heteroacene frameworks is an emerging area of research. For example, Yamaguchi and co-workers have prepared a series of heteroacene-fused ladder boroles (I, Figure 1) and provided insight into the effect of the borole ring on the photophysical properties of the molecule when introduced into an extended  $\pi$ system.<sup>25, 26</sup> Recently, we reported the synthesis of a ladder diborole (2) as a new member of the heteroacene family.<sup>27</sup> Compound 2 was prepared by a light-driven photoisomerization of 1, which is the kinetic product in the KC<sub>8</sub> reduction of a 2boryl substituted diaryl acetylene precursor.27 While small quantities of pure 2 can be obtained in this way, attempts to garner workable amounts of 2 on a preparative scale using this procedure were hampered by difficulties in driving the reaction to completion while avoiding photochemical decomposition of the product 2 because of the prolonged irradiation required.

Therefore, we focused our attention on the discovery of a thermal pathway for the isomerization of 1 to 2. It has been reported that the carbon analogue of compound 1 (1,1'-di(benzocyclobutylidene), II, Scheme 1) undergoes a facile rearrangement in acetic anhydride containing sulfuric acid to 5,10-dihydroindeno[2,1-a]indene, III<sup>28</sup> via a sequence of 1,2-carbenium ion shifts (Scheme 1). Accordingly, we attempted to

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Scheme 1. Proton catalysed isomerization of 1,1'-bi(benzocyclobutylidene) (II).

catalyse the analogous isomerization of compound **1** using weaker acids (both Brønsted and Lewis), to no avail. In fact, when water was added to **1**, preferential ring opening of the boracycle took place, forming (E)-1,2-*bis*(hydroxy(tri*iso*propyl)boryl)-diphenylethene (**IV**, Figure 1).<sup>27</sup> Given the propensity of B-C bonds to undergo protic cleavage, this outcome is perhaps not too surprising.

Since compound 1 is electron deficient relative to the all-carbon analogue II, we postulated that its dianion,  $1K_2$ , might undergo acid catalysed isomerization as observed for the all-carbon system; subsequent oxidation of compound  $2K_2$  could be an alternative way to prepare compound 2. In this article we discuss the redox chemistry of neutral boron heterocycles 1 and 2, and the successful isomerization of the dipotassium salt of the dianion of 1 (1K<sub>2</sub>) to dibenzodiboratapentalene (2K<sub>2</sub>) as catalysed by weak Bronsted acids.

#### **Results and discussion**

To assess the propensity of compounds 1 and 2 to undergo reductions, cyclic voltammetry experiments were performed in THF using Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte; the potentials were referenced against the ferrocene/ferrocenium ion couple. Compounds 1 and 2 are both reduced by one and two electrons in sequential one-electron processes (see ESI). Compound 1 exhibits irreversible reduction waves; the first reduction potential was observed at -2.47 V and the second at -2.89 V. Conversely, ladder diborole 2 shows a reversible reduction wave at -1.51 V followed by a second, irreversible, reduction wave at -2.42 V.<sup>29</sup> Both reduction potentials of **2** are considerably less negative than the ones observed for heteroacene-fused boroles I ( $E_{1/2}$  = -1.89 V to -2.25 V for the first reduction potential and  $E_{pc} = -2.78$  V to -3.04 V for the second reduction potential).<sup>25</sup> These results suggest that it is possible to reduce both compounds by one and/or two electrons, but powerful reducing agents, such as alkali metals, are required—especially when reducing compound 1.

Accordingly, addition of one equivalent of potassium graphite to a THF solution of **1** resulted in an immediate colour change of the solution from bright yellow to dark violet. Compound **1K** was crystallized as extremely air and moisture sensitive dark purple crystals by slow diffusion of hexanes into a THF solution of the product. Likewise, addition of one equivalent of potassium graphite to a THF solution of **2** affords air and moisture sensitive deep blue crystals of **2K** after crystallization using the same solvent mixture. Despite a myriad of attempts to obtain X-ray quality crystals of **1K** and **2K**, it has not been possible so far, due mainly to the poor thermal stability of the compounds over the timeframe necessary to form quality







**Figure 2.** Top: Overlap of the experimental (black) and simulated (red) EPR spectrum of **1K'** (left) and **2K'** (right) in a THF solution at 298 K. Simulations performed in PEST Winsim<sup>30</sup> to >99% correlation. Bottom: SOMO (UB3PW91/6-31+G(d)) of **1K'** (left) and **2K'** (right).

crystals. Nonetheless, radical anion formation was confirmed by electron paramagnetic resonance (EPR) spectroscopy, which in both cases, showed broad featureless resonances at  $g_{iso} =$ 2.00279 for **1K** and  $g_{iso} = 2.00248$  for **2K**. These  $g_{iso}$  values are in the range expected for organic  $\pi$  radicals<sup>31, 32</sup> and no hyperfine coupling could be resolved in either case, even at low temperatures. However, in the case of **1K**, clear hyperfine coupling was observed in the EPR spectrum when the radical was generated *in situ* by addition of **1** to a THF solution of the dianion species **1K**<sub>2</sub> (see below). An analogous comproportionation experiment using **2** and **2K**<sub>2</sub> failed to reveal a resolvable hyperfine splitting pattern in this case.

Due to the complicated nature of the EPR spectrum of 1K and the lack of information from the spectrum of 2K the structures of both compounds were modelled by DFT using the UB3PW91 functional with the 6-31+G(d) basis set.<sup>33</sup> The hyperfine coupling constants (hfcc) were calculated using the basis set EPR-II,<sup>34</sup> and were used as the initial values for the simulation of the EPR spectrum using the program PEST Winsim.<sup>30</sup> The computed hyperfine coupling constants are in reasonable agreement with those obtained from simulation of the experimental spectrum (Table 1), except for  $a(^{11}B)$ .<sup>35, 36</sup> The hyperfine coupling constants  $a(^{11}B)$  in **1K** and **2K** of 1.08 G and 0.55 G, respectively, are lower than those observed in other organic boron containing  $\pi$ -radicals (usually between 3.5 and 6 G),<sup>31, 37-39</sup> perhaps an indication of the larger degree of delocalization of the unpaired electron throughout the  $\pi$  system (Figure 2). Interestingly, although the tri-iso-propylphenyl (Tipp) groups on boron are essentially perpendicular to the ligand framework, hyperfine coupling to the iso-propylmethyne protons, H<sup>V</sup>, which are located above and below the boron center, is present. Yamaguchi has demonstrated the interaction of these protons with a planar  $\pi$  system and has used this feature to assess the antiaromaticity in thiophene-fused ladder boroles.40



 Table 1 Calculated and simulated |hfcc| of 1K and 2K (in gauss)

		1K		2K		
Element	# Nuclei	Calc. <sup>a</sup>	Sim. <sup>b</sup>	Calc.	Sim.	
${}^{11}B^{c}$	2	3.75	1.08	1.87	0.55	
${}^{1}\text{H}^{z}$	2	2.54	3.72	0.89	0.98	
$^{1}H^{y}$	2	0.89	0.89	0.30	0.26	
$^{1}H^{x}$	2	1.41	1.80	1.10	1.21	
$^{1}H^{y}$	2	2.12	1.81	0.01	0.01	
$^{1}H^{v}$	4	0.70	0.70	0.49	0.41	

<sup>*a*</sup> Geometries were optimized using UB3PW91/6-31+G(d) and the hfcc were calculated using UB3PW91/EPR-II.<sup>*b*</sup> Simulated using PEST Winsim<sup>30</sup> to >99% correlation. <sup>*c* 10</sup>B was not included in the simulation.

In an effort to structurally characterize the radical anions in 1K or 2K, exchange of the potassium counterion for the bis-(triphenylphosphine)iminium (PPN<sup>+</sup>) cation via metathesis was attempted. In both cases, decomposition was the outcome of these experiments. However, since the first reduction potential of compound 2 is considerably lower than that of 1, it was possible to carry out one electron reduction of 2 using the milder reducing reagent bis-(pentamethylcyclopentadienyl)cobalt(II) (Cp<sup>\*</sup><sub>2</sub>Co) in THF or CH<sub>2</sub>Cl<sub>2</sub>.<sup>41</sup> Addition of one equivalent of Cp<sup>\*</sup><sub>2</sub>Co to a dichloromethane solution of 2 immediately produced the characteristic deep blue colour observed in 2K. In the freezer at -30° C the solvent was slowly removed by vapour diffusion into toluene and deep blue X-ray quality crystals were deposited after several days. The molecular structure of 2Co is shown in Figure 3. When compared to its neutral counterpart,<sup>27</sup> compound 2Co showed a lengthening of the C1-C1' bond (1.410(3) Å for **2Co** vs 1.367(5) Å for **2**) and a shortening of the B1-C1 bond (1.524(4) Å for 2Co vs 1.571(4) Å for 2). These bond length changes are also consistent with the nature of the SOMO as revealed by the DFT computations (Figure 2). The SOMO contains a node in the C1-C1' bond and is  $\pi$ bonding along the B1-C1 vector. The largest deviation from the mean plane defined by the core  $B_2C_6$  atoms (fused borole rings) amounts to 0.032(3) Å, showing that the  $\pi$  system in 2Co remains planar after reduction. This is in contrast to the planarized triarylborane radical anion reported by Yamaguchi<sup>37</sup> and the dibenzo(a,e)pentalene radial anion reported by Saito,<sup>42</sup> which both adopt a shallow bowl-shaped conformation after reduction with potassium, and reflects the high degree of delocalization of the unpaired electron throughout the B<sub>2</sub>C<sub>14</sub> framework of the ladder diborole.



Figure 3. Thermal ellipsoid (30%) diagram of the molecular structure of 2Co. Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1-B1 1.524(4), C1-C1' 1.410(3), C2-B1 1.586(4), C2-C3 1.420(3), C3-C1' 1.470(4); C2-B1-C1 102.3(2); C2-B1-C8-C13 -68.1(4), C4-C3-C1'-C1 179.4(3). Hydrogen atoms and THF molecules have been removed for clarity.

Having demonstrated facile one electron reduction of both compounds 1 and 2, we turned to preparing the dianionic species that would be isoelectronic to the all carbon frameworks II and III shown in Scheme 1. A freshly prepared

Journal Name

THF solution of potassium naphthalenide (2 eq) was slowly added into a solution of the respective starting materials 1 and 2 in THF at -78 °C. After stirring the solutions for an additional 2 hours at room temperature, the solvent was evaporated and the naphthalene removed by sublimation under high vacuum. Compound  $1K_2$  was isolated as a dark brown solid after crystallization in THF and hexanes in 60% yield, and compound  $2K_2$  as red crystals from the same solvent mixture in 55% yield (Scheme 3).



The <sup>1</sup>H NMR spectrum of compound  $1K_2$  isolated in this way is intriguing. All the signals are broad and it is not possible to distinguish any fine structure due to coupling with adjacent protons. Furthermore, the chemical shifts of the aromatic protons (except for the resonance belonging to the Tipp group) are shifted considerably upfield (between 5.5 and 4.2 ppm) from where they are expected to resonate. Since the second reduction potential of compound 1 is very negative, we surmised that 1K2 might be contaminated with small amounts of the radical anion 1K, resulting in the broadness observed in the <sup>1</sup>H NMR spectrum. EPR spectroscopy on isolated samples of  $1K_2$  confirmed the presence of 1K; furthermore, augmentation of the signal was observed upon addition of small aliquots of 1 to the EPR sample (see Figure S2 in the ESI). In contrast to the broadening observed in the <sup>1</sup>H NMR spectrum, in the  ${}^{13}C$  NMR spectrum of  $1K_2$  minimal broadening was apparent, and all the resonances are clearly identified. Even the resonances for the carbons attached to the boron center appear as small, broad peaks, their identity confirmed by <sup>1</sup>H-<sup>13</sup>C Heteronuclear Multiple-Bond Correlation (HMBC) spectroscopy. The <sup>11</sup>B NMR spectrum shows a broad resonance at 38.7 ppm and it is comparable to the one reported for 9boraanthracene (39.7 ppm).<sup>16</sup> This signal is considerably upfield shifted compared to the resonance of 1 (70.1 ppm), which is consistent with a more electron rich boron center.

X-ray analysis of single crystals of  $1K_2$  reveals the structure of the dianionic species (Figure 4). The largest deviation from the mean plane defined by the  $B_2C_6$  core atoms amounts to 0.010(3) Å, showing that compound  $1K_2$  remains planar after direduction. The boron center adopts a distorted trigonal planar

geometry, with a small C7-B1-C1 angle of 87.49(12)° due to the constrained four membered ring. There are two potassium atoms situated on opposite sides of the  $\pi$  system, coordinating to the bay regions on either side of the central C1-C1' bond. The distance between the potassium centers and the B1-C1-C1'-B1' plane is 2.623 Å. There are three molecules of THF coordinated to each potassium center (not shown in Figure 4); however, only one solvent molecule per metal remains coordinated when the crystals are dried under vacuum based on <sup>1</sup>H NMR spectroscopy and elemental analysis.



Figure 4. Thermal ellipsoid (30%) diagram of the molecular structure of 1K<sub>2</sub>. Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1-B1 1.504(3), C1-C1' 1.437(4), C7-B1 1.629(4), C7-C2 1.437(3), C2-C1 1.492(3); C7-B1-C1 87.49(12); C1-B1-C8-C13 -56.2(4). Hydrogen atoms and THF molecules have been removed for clarity.

While the bond angles within the molecular core do not change significantly upon reduction, the bond distances in the diboratacyclobutylidene  $\pi$  system change significantly. For example, in neutral starting compound 1, the B1-C1 bond distance is 1.581(5) Å,<sup>27</sup> which is indicative of a B-C single bond, but in compound  $1K_2$  the B1-C1 bond distance is considerably shorter (1.504(3) Å) suggesting double bond character. Similar B=C values have been reported for 9phenyl-9-borataanthracene (1.532(3) Å)<sup>43</sup> and 9-boraanthracene (1.507(4) Å).<sup>16</sup> Conversely, the C1-C1' distance in neutral 1  $(1.330(7) \text{ Å})^{27}$  is consistent with a C=C double bond, but in  $1K_2$ the distance is considerably longer (1.437(3) Å) which is indicative of a Csp<sup>2</sup>-Csp<sup>2</sup> single bond. These observations are again completely consistent with the characteristics of the LUMO of  $1^{27}$  and the SOMO of 1K as revealed by computations.

Unlike the <sup>1</sup>H NMR spectrum of  $1K_2$ , there is no broadening of the signals in the spectrum of  $2K_2$  and all of the coupling between neighbouring hydrogen atoms is observed. Furthermore, all the resonances appear in the expected region of the spectrum. The boron chemical shift appears at 32.1 ppm, very close to  $1K_2$  (38.7 ppm) and is again considerably upfield shifted compared to the starting material 2 (68.6 ppm).<sup>27</sup>

X-ray crystal structure analysis of compound 2K<sub>2</sub> reveals a sandwich complex (Figure 5), with the potassium atoms situated just above and below of the center of the pentalene framework in a centrosymmetric arrangement. The largest deviation from the mean  $B_2C_6$  plane is only 0.010(3) Å. The separation between the two potassium atoms measures 5.506 Å, which is similar to the value found in a B<sub>4</sub>N<sub>2</sub>C<sub>2</sub> sandwich complex (5.52 Å).<sup>44</sup> In the X-ray structure there are two THF molecules per potassium center (not shown in Figure 5), but only one solvent molecule remains coordinated when the crystals are dried under vacuum. Similar to compound 1K2, the C1-B1 (1.479(4) Å) and C1-C1' (1.466(3) Å) bond distances are indicative of a double and single bond character respectively. As anticipated, the C1-C1' bond distance in 2Co is of intermediate length between the C1-C1' double bond shown in 2 (1.367(5) Å)<sup>27</sup> and the single bond in  $2K_2$  (1.466(3) Å). Likewise, the B1-C1 bond distance is between that of the B1-C1 single bond for 2  $(1.571(4) \text{ Å})^{27}$  and the double bond in  $2K_2$  (1.479(4)) Å. This clearly illustrates how changing the electronic structure of the molecule upon one and two electron reductions impacts the physical structure of the  $\pi$  system in 2.



Figure 5. Thermal ellipsoid (30%) diagram of the molecular structure of  $2K_2$ . Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1-B1 1.479(4), C1-C1' 1.466(3), C3-B1 1.586(4), C2-C3 1.408(3), C2-C1' 1.479(3); C1-B1-C3 102.2(2); C3-B1-C8-C13 -67.7(3), C7-C2-C1-C1' 179.5(2). Hydrogen atoms and THF molecules have been removed for clarity.





Whereas the ladder diborole 2 is a 14  $\pi$  aromatic system, introduction of another electron pair should give the 16  $\pi$ 

electron dianion  $2\mathbf{K}_2$  antiaromatic character. To evaluate this notion, we carried out NICS calculations (B3LYP/6-311+G(d,p))<sup>45</sup> on the dianion of  $2\mathbf{K}_2$  and dibenzopentalene V.<sup>46</sup> The central five-membered rings possess antiaromatic character (NICS(0) = 6.1, NICS(1) = 1.3) and the flanking benzene rings (NICS(0) = -0.9, NICS(1) = -3.9) are considerably less aromatic than benzene itself (NICS(0) = -9.7). Interestingly, dibenzopentalene V possesses a stronger antiaromatic character on the central rings (NICS(0) = 10.4, NICS(1) = 5.8), and a stronger aromatic character on the benzene rings (NICS(0) = -2.6, NICS(1) = -5.6). This suggests that dibenzopentalene has a more localized  $\pi$  system than  $2\mathbf{K}_2$ ; nonetheless, it is clear that these two isoelectronic  $\pi$  systems are closely related.

With dianions  $1K_2$  and  $2K_2$  in hand, we set out to test our initial hypothesis that  $1K_2$  might be thermally isomerized to the more stable  $2K_2$  using Brønsted acid catalysis. Upon dissolution of compound  $1K_2$  in degassed "wet" THF-*d8*, the solution immediately changed from dark brown to deep red; the <sup>1</sup>H NMR spectrum clearly shows formation of substantial quantities of  $2K_2$ , along with other hydrolysis products. The reaction was therefore performed under more controlled conditions in dry solvents using measured amounts of various 2,6-dimethylphenol as the proton source. After optimization of the conditions, it was determined that a 20% loading of 2,6dimethylphenol at 75°C in THF solution gave compound  $2K_2$ , which could be isolated in 84% yield after stirring for 8 hours under these conditions. However, measureable amounts of a



Scheme 4. Isomerization of  $1K_2$  to  $2K_z,$  synthesis of 3 and generation of 2 via oxidation of  $2K_z.$ 

contaminant were always present and this species was determined to be the doubly protonated neutral compound 3, which can be separately synthesized by treating  $2K_2$  with stoichiometric quantities of the acid. Thus, when two equivalents of 2,6-dimethyl phenol are added to a THF solution

of  $2K_2$ , the solution changes from red to light yellow, forming the air and moisture stable **3** (Scheme 4). After removal of the solvent and extraction/crystallization from hexanes, this compound was isolated as a white solid in 72% yield. The <sup>1</sup>H NMR spectrum only shows formation of only one isomer; DFT calculations (M062X/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE)<sup>47</sup> show that the *cis* isomer is 17.6 kcal/mol more stable than the *trans* isomer, and further characterization via NMR spectroscopy and X-ray crystallography indicates that it is the *cis* isomer that is formed exclusively (Figure 7).

The bridgehead hydrogens alpha to boron appear as a singlet at 4.16 ppm and the downfield <sup>11</sup>B chemical shift of 77.1 is consistent with a three coordinate borane moiety. The patterns observed for the *iso*-propyl groups on the Tipp group in the <sup>1</sup>H NMR suggest that the planarity of the system has been breached, since six sets of signals for the *iso*-propyl methyl protons and three multiplets for the *iso*-propyl methyne protons are now apparent. One of these methyne resonances is significantly upfield shifted compared to the other two (1.29 ppm vs 2.93 and 2.65 ppm), due to the situation of one of the *iso*-propyl groups under the flanking benzene rings (see Figure 7). The methyl signals of this *iso*-propyl group are also shielded due to the influence of the benzene ring.



**Figure 7.** Thermal ellipsoid (30%) diagram of the molecular structure of **3.** Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1-B1 1.589(7), C1-C1' 1.551(6), C3-B1 1.548(7), C2-C3 1.388(6), C2-C1' 1.508(6); C1-B1-C3 105.4(4), B1-C1-C9 115.4(4); C2-C1'-C1-C9 131.2(4), C3-B1-C8-C13 95.7(6). Hydrogen atoms (except for the central protons) have been removed for clarity.

The X-ray structural analysis (Figure 7) confirms that the polycyclic ring framework is significantly bent as a result of the addition of the two hydrogen atoms. C1 adopts a distorted tetrahedral geometry, with B1-C1-C9, C9-C1-C1', C1'-C1-B1 angles of 115.2(4)°, 105.4(3)° and 105.5(4)° respectively, and the torsion angle C2-C1'-C1-C9 is 131.2(4)°. The C1-C1' bond distance is considerably longer (1.551(6) Å) than for 2 (1.367(5) Å) and  $2\mathbf{K}_2$  (1.466(3) Å), reflecting the Csp<sup>3</sup>-Csp<sup>3</sup> single bond character.

Attempts to doubly deprotonate compound 3 using potassium 2,6-dimethyl phenoxide to regenerate  $2K_2$  did not succeed, indicating protonation by phenol is irreversible. However,

addition of potassium *tert*-butoxide to **3** did generate  $2K_2$  essentially quantitatively, and this salt was stable in the presence of <sup>t</sup>BuOH. Thus, the more weakly acidic alcohol was used in excess to convert  $1K_2$  to  $2K_2$  on a preparative scale, avoiding contamination by **3** and providing  $2K_2$  in excellent yield. As shown in Scheme 4, the dianion can be oxidized using silver triflate to furnish **2** in 65% yield upon work up, successfully completing a thermal synthesis of **2** from **1** as planned.

This type of isomerization is new for a boron containing heterocycle, but we have proposed an analogous mechanism to the one proposed for the carbon analogue (II). However, instead of a carbocation as the key species in the rearrangement, the Lewis acidic boron center triggers the bond migrations that occur upon protonation of the framework (Scheme 5). Intermediate  $I_A$  is formed after protonation of one of the benzylic carbons in  $1K_2$  by the alcohol. Nucleophilic attack on the borane by the electron rich carbanion of the other borabenzocyclobutene induces ring opening to generate  $I_{B}$ , positioning the carbanion for attack on the other boron center to expand the remaining four membered ring, giving  $I_{C}$ , which is monoprotonated  $2K_2$ . When the acid is a phenol, this species can be irreversibly protonated to give 3; thus we surmise that  $I_{C}$ is itself acidic enough to protonate 1K<sub>2</sub> or phenoxide to induce further ring expansion rearrangements, or the reaction would stop at this point in the phenol catalysed processes. For the <sup>t</sup>BuOH mediated process, this is not an issue, since the alcohol is not acidic enough to protonate  $2K_2$ . Attempts to generate  $I_C$ through protonation of  $2K_2$  with one equivalent of a strong acid such as HNTf<sub>2</sub> were not successful, producing only half an equivalent of 3; this indicates that  $I_C$  is a very reactive species, both as an acid and a base.



Scheme 5. Proposed mechanism for the rearrangement of 1K<sub>2</sub>.

#### Conclusions

We have described the synthesis, characterization and reactivity studies of  $1K_2$ , which was synthesized by direct reduction of 1 with potassium naphthalenide. In the course of these studies, we found that the persistent radical anions 1K, 2K and  $2C_0$ , formed upon one electron reduction, could be generated and characterized. In the case of  $2C_0$ , an X-ray structural

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determination was possible, allowing for a detailed analysis of the bond length changes in the conjugated framework upon sequential one and two electron reduction. Dianion  $1K_2$ undergoes a Bronsted acid mediated isomerization to form  $2K_2$ , confirming out hypothesis. Tert-butanol is the best reagent for inducing this skeletal rearrangement since more acidic phenols can doubly protonate  $2K_2$  to form the compound 3 as an air and moisture stable white solid. Compound  $2K_2$  can be oxidised using silver triflate, providing a more reliable and efficient preparative route to the ladder diborole complex 2 from 1.

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#### Notes and references

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Electronic Supplementary Information (ESI) available: Crystallographic data files for 2Co (CCDC 997324), 1K<sub>2</sub> (997321), 2K<sub>2</sub> (997322), and 2H<sub>2</sub> (997323), additional experimental and spectroscopic details and the full citation for reference 32. See DOI: 10.1039/b000000x/

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