Ring expansion reactions of electron-rich boron-containing heterocycles

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ABSTRACT: The potassium salts of the dianions of isomeric compounds bis-benzocycloborabutylidene, **1**, and the ladder diborole **2** were reacted with carbon dioxide (CO₂) and carbon monoxide (CO) and the ring expansion products fully characterized. Both dianions **1** and **2** react rapidly with carbon dioxide to form the same insertion product, **3**, in which the boron containing rings are expanded to six membered rings. Compound **3** is a B-O analog of binaphtholate. Only dianion **2** reacts cleanly with the weaker electrophile CO, producing a product (**4**) in which only one of the boron containing rings is expanded through formal insertion of CO into a B-C bond. The X-ray structures of both **3** and **4** are reported and reasonable paths to their formation are proposed.

INTRODUCTION

The chemistry of 4 π antiaromatic boroles **I** (Chart 1) has been rapidly expanded in the past several years, leading to a more sophisticated understanding of the properties of these molecules, better synthetic methods for their preparation, and incorporation of the borole core into more complex systems.¹⁻¹⁰ In terms of reaction chemistry, their strong Lewis acidity and electron affinity are at the root of two of the more obvious reaction modes, namely Lewis base coordination and reduction. A more recently emphasized area of exploration involves using boroles in reactions that expand the antiaromatic five-membered ring to larger ring heterocycles. In these processes, the alleviation of both ring strain and antiaromaticity provide the driving force, while the strong Lewis acidity associated with the borole boron center delivers a kinetic path by facile binding of the reagents that lead to expanded rings.

The first ring-expansion of this five-membered boracycle was reported¹¹ as part of the series of pioneering studies by Eisch on the synthesis and reactivity of pentaphenylborole. Suspensions of **I** and diphenylacetylene led to a Diels-Alder cycloaddition that triggered a series of rearrangements leading to the 7-membered borepin, **II**, a bright yellow solid.¹¹⁻¹³ Similar ring

expansion chemistry was observed in the perfluorinated pentaphenylborole,¹⁴ yielding perfluoroborepin-**II**.¹⁵ More recently, the Braunschweig group reported the synthesis of 1,2-azaborirines (**III**)¹⁶⁻¹⁷ by ring expansion of boroles.¹⁸ The compounds were prepared by direct reaction between organic azides and the borole derivatives with the concomitant release of nitrogen. When pentaphenylborole **I** was treated with trimethylsilylazide, TMSN₃, the reaction proceeded slowly at room temperature, while use of the bulkier mesityl substituent on the boron center also significantly decreased the rate of the reaction, suggesting coordination of the azide reagent to the boron center was a key first step in the reaction. Shortly thereafter, Martin and co-workers investigated the mechanism of the borole ring expansion using computational methods¹⁹ and found a low energy path that supported this postulate. Subsequent to coordination, formation of a bicyclic intermediate, leads to nitrogen release, yielding the 1,2-azaboririne product. Finally, Martin *et al.* have also shown that pentaphenylborole reacts with isocyanates, ketones and aldehydes to yield²⁰ seven-membered ring boron-containing heterocycles exemplified by **IV**.

Most of these borole ring expansion studies have involved the neutral pentaphenylborole **I**, or its derivatives; few if any examples of ring expansion chemistry have been identified out using reduced species or more extended π frameworks with borole subunits. We recently reported the synthesis and characterization of the first benzoborole-fused benzoborole, (**V**),²¹ which was prepared by a light-driven photoisomerization of bis-benzocycloborabutylidene **VI**. Since it was necessary to employ the extremely bulky 2,4,6-tri-isopropylaryl "Tipp" group in order to successfully construct these frameworks, it was hardly surprising, given the discussion above, that ring expansion reactions involving reagents like azides were unsuccessful. When **V** and TMSN₃ were mixed, no reaction was observed under any conditions we explored, presumably due to the blocked access to the boron center afforded by the Tipp group.

Chart 1

Both compounds accept two electrons under reducing conditions, which allowed us to characterize their dianions **1** and **2**²² (depicted in Scheme 1). We hypothesized that by using the direduced compounds **1** and **2**, which have HOMO and LUMO orbitals of quite different character, might give cleaner chemistry and so explored the ring-expansion chemistry of these compounds using carbon dioxide (CO₂) and carbon monoxide (CO) as the agents of expansion. This turned out to be the case and herein we describe the results of this study.

RESULTS AND DISCUSSION

When a THF solution of dianion **1** was exposed to one atmosphere of CO₂ gas, the dark brown solution, characteristic of **1**, rapidly turned yellow, even at low temperature. Upon warming to room temperature, the ¹H NMR spectrum showed clean formation of a new species, **3** (Scheme 1). The resonances of the aromatic protons moved downfield (6.55–7.45 ppm) compared to the starting material (4.20–5.57 ppm) while an upfield shift of the *ortho*-isopropyl methine resonances, from 3.58 ppm in **1** to 2.86 ppm in the new species, provided another clear indication that the electronic properties of the starting material were significantly modified.⁶ The chemical shift of the carbon derived from CO₂ was observed at 165.6 ppm, shifted significantly downfield compared to free carbon dioxide (125.7 ppm). The resonance for the bridging carbon appears at 85.2 ppm, drastically upfield from the analogous carbon in **1** (129.4 ppm). Interestingly, the insertion product did not show a signal in the ¹¹B or ¹⁰B NMR spectrum despite numerous attempts at detection.²³ However, MALDI-TOF mass spectrometry confirmed the presence of two boron atoms in the molecule by a good match in the expected isotopic distribution for the parent peak (Figure S6).

Scheme 1. Reactions of **1** and **2** with CO₂

X-ray quality crystals of **3** were obtained by slow evaporation of a dichloromethane solution and depictions of the structure are given in Figures 1 and 2. The X-ray crystallographic analysis confirmed the product **3** to be the six-membered ring insertion product (Figure 1) and shows that three of the insertion product molecules assemble into a cluster bridged by six potassium ions (Figure 2). The cluster also contains two molecules of THF coordinated to the potassium centers K1 and K1'

(the solvent molecules are omitted in Figure 2). The THF atoms were disordered, but their positions were located from a difference Fourier map and were included in the least squares refinements at fixed positions. The core of the structure was free of disorder and unequivocally establishes the connectivity of the molecular structure of the compound. The atoms of the B-O naphthyl fused rings are essentially coplanar, but the C3-C2-C2'-C3' dihedral angle of 91.6(7)^o is as expected in a binaphthyl-type framework. The boron centers adopt a slightly distorted trigonal planar geometry, with C-B-C angles close to the ideal 120^o. The intraring B-C bond length in **3** (1.506(9) Å) is shorter than the exocyclic B-C bond (1.574(8) Å), and it is also shorter than the average B-C bond length found in Ph₃B (1.577(6) Å).²⁴ Furthermore, this bond is very similar to the B=C bond found in **1** (1.504(3) Å),²² slightly shorter than the analogous distance found in a related 2-oxa-boranaphthalene derivative reported in 1993.²⁵ The pendant aryl ring is not coplanar with the fused rings but is almost perpendicular with a torsion angle of -93.1(9)^o. The C1-O2 bond distance is considerably longer than the distance reported in products of carbon dioxide insertion into FLP systems (1.2081(15) Å and 1.209(4) Å),²⁶ consistent with a single bond character and a carboxylate structure. The C1-C2 (1.373(7) Å) and C2-C2' (1.494(7) Å) bond distances are indicative of double and single bonds, respectively.²⁷ The potassium centers are located between the anionic oxygen atoms and the heteroacene ring of the other bridged fragment (Figure 2). Therefore, the potassium centers are not only stabilized by the anionic oxygen centers, but also by π -electrons of the heteroacene rings.

Interestingly, when dianion **2** was subjected to the same reaction conditions, a rapid red to yellow color change was observed upon exposure to CO₂ and NMR spectroscopy showed that this reaction also afforded **3** in very good yield. This result was somewhat of a surprise since we expected a seven-membered ring expansion-product related to a borepin derivative^{20, 28–30} to form via the insertion of CO₂ into **2** as shown in Scheme 1. Density Functional Theory calculations (M062X/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE)³¹ showed that a six-membered ring insertion product is ≈ 43 kcal mol⁻¹ more stable than a seven-membered ring isomer (See SI for details).

Figure 1. Thermal ellipsoid (50%) diagram of the molecular structure **3**. Hydrogen and potassium atoms and THF molecules have been removed for clarity. Selected bond lengths (Å) and angles (°): C9-B1 1.574(6), B1-C8 1.506(9), B1-O1 1.355(6), C1-O1 1.395(6), C1-O2 1.257(5), C1-C2 1.373(7), C2-C3 1.413(5), C3-C8, 1.396(8) C2-C2' 1.494(7), O1-C1-C2 118.7(4), C1-C2 1.373(7), O2-C1-C2 128.0(5)

Figure 2. POV-ray depiction of the cluster structure of dianion **3**. Hydrogen atoms and THF molecules have been removed for clarity. C: gray, B: orange, O: red, K: purple.

The observation that both **1** and **2** react with CO_2 to yield the same product suggests that a common intermediate is involved in these processes. We have previously observed that **1** is thermally isomerized to **2** by catalytic amounts of a weak Brønsted acid.²² The simplest explanation for the above observation is that CO_2 acts as a *Lewis* acid catalyst for the rearrangement of **1** to **2** via unobserved intermediates **I_A** and **I_B**, Scheme 2a, which then undergoes a double ring expansion process to give the observed product **3**. Since activation of CO_2 invariably requires the cooperative interaction of Lewis bases and acids,^{32–34} the electrophilicity of the CO_2 carbon is likely enhanced by the potassium ions present and

is thus sufficiently acidic to catalyze the highly thermodynamically favorable isomerization of **1** to **2**.²² The mechanism of formation of compound **3** is unknown, but since the 7 membered ring product depicted in Scheme 1 is not observed it implies that upon addition of CO_2 to the nucleophilic carbons of **2**, anionic oxygen attacks the opposing boron center rather than the adjacent boron (Scheme 2b), which would lead to borepin-like products.²⁰ The intermediates **I_{C-E}** depicted are plausible but their precise nature and the path followed must be regarded as speculative at this point.

Scheme 2. Proposed mechanism for the formation of 3 from 1 and 2. a) CO_2 catalyzed isomerization of 1 to 2. b) Ring expansion to 3.

The reactions of **1** and **2** with carbon monoxide were also explored. Addition of CO to compound **1** resulted in a complex mixture of intractable products and this chemistry was not pursued further. In contrast, compound **2** underwent clean conversion to a new species in a very slow reaction when a THF solution was sealed under one atmosphere of CO (Scheme 3). At

room temperature, the formation of the new species took 4 days, but at 70°C the entire process takes approximately 17 hours. The formation of the new species is accompanied by a color change in the solution from red to dark blue and can be followed by ^1H NMR spectroscopy (Figure 3). The ^1H NMR spectrum of the final product, compound **4**, indicates that the B_2C_{14} ring

system has undergone desymmetrization, suggesting that only one of the

Figure 3. ^1H NMR spectra of the reaction of **2** with carbon monoxide (70 °C, THF-*d*8, 600 MHz).

two borole rings has undergone expansion. Prolonged heating (5 days, 70 °C) did not change the appearance of the NMR spectrum and therefore, the reactivity of **2** towards CO is quenched after the first insertion. Compound **4** was isolated as brittle, dark blue crystals in 65% yield after crystallization from THF and hexanes.

Figure 4. Left: Thermal ellipsoid (50%) diagram of the molecular structure **4**. Hydrogen atoms and THF molecules have been removed for clarity. Selected bond lengths (Å) and angles (°): C16-B1 1.587(2), B1-C8 1.520(3), B1-C1 1.570(2), C1-C6 1.423(3), C7-C8 1.449(2), C8-C9 1.442(2) C9-C14, 1.437(3) C14-B1, 1.521(3) B1-C15 1.553(3), O1-K2 2.614(2), C8-K1 2.870(2), C8-B1-C1 103.9(2), C15-B2-C14 118.7(2). Right: POV-ray depiction of **4**.

(1.449(2) Å) bond distance is slightly shorter than the distance observed in **1** (1.466(3) Å),²² and the C7-C15 (1.414(3) Å) bond distance is significantly longer than the C-C double bond in **V** (1.367(5) Å).²¹ This data suggests that the B1-C8 double bond in **4** is more delocalized into the π -system than the double bond in **2**. The exocyclic B-C distances are similar to those reported in other boracyclic compounds,^{5, 36-37} for example 9-phenyl-9-borataanthracene (1.582(3) Å).³⁷ The C15-B2-C14 angle (118.7(2)°) is significantly larger than the C1-B1-C8 (103.9(2)°) angle due to the release of angle strain by the expansion from a 5- to a 6-membered ring. One of the potassium centers is η^4 -coordinated to the six-membered heterocycle, which can be seen in the difference between the K1-C8 and K1-B1 bond distances (2.870(2) and 3.467(2) Å

Scheme 3. Reaction of **2** with CO

X-ray quality crystals were obtained by slow diffusion of hexanes into a THF solution of **4** and the structure is depicted in Figure 4. This confirms the notion that only one ring has expanded via formal insertion of an equivalent of CO into one of the B-C bonds. The molecule crystallizes as a dimer, where two potassium centers are bringing the molecules. The bridging potassium atoms are solvated by one molecule of THF each and the non-bridging potassium centers are solvated by two molecules of the solvent. The B1-C1 bond distance is in agreement with previously reported B-C single bonds.^{28, 35-36} However, the B1-C8 (1.520(3) Å) bond distance is significantly longer than other B=C bonds.³⁷⁻³⁹ In fact, the distance is of intermediate length between the B-C double bond shown in **2** (1.479(4) Å)²² and the single bond in **V** (1.571(4) Å).²¹ Likewise, the C8-C7

respectively). The other potassium center is coordinated to the anionic oxygen O1 with a distance of 2.614(2) Å, but also stabilized by an interaction with the B-aryl ring.⁴⁰⁻⁴¹

It is typically assumed that insertion of CO into B-C bonds proceeds via initial coordination of the carbon monoxide to the boron center.⁴²⁻⁴⁴ However, given the sterically imposing Tipp group guarding the boron centers in **2**, it is not clear that this path is viable in this reaction. Although less common, the carbon center in CO can also react with strong nucleophiles.⁴⁵ For instance, it is well-known that CO reacts with sodium hydroxide to form sodium formate at moderately high temperatures.⁴⁶⁻⁴⁷ Such reactivity is perhaps enhanced by the presence of strongly Lewis acidic cations; in **2**, the presence of potassium counteranions could play a role in

which a reaction path involving interaction of the CO with the nucleophilic bridged-carbon in **2** might be operative. When CO is attacked by a nucleophile, the σ -withdrawing, π -donating oxygen favors a singlet ground-state multiplicity⁴⁸⁻⁴⁹ and attack of this carbene-like species on the electrophilic boron center could lead to formation of a three-membered boracycle en route to the product **4** via a bond rearrangement (Scheme 4). Alternatively, the transformation to product **4** can be considered as an intramolecular 1,2-migration, which is a well-established process for singlet carbenes.⁵⁰⁻⁵¹ Whether CO interacts with **2** as a nucleophile or, less conventionally, as an electrophile, either option is likely to be a high barrier process, which accounts for the slow reactivity observed in the formation of compound **4** and the lack of further ring expansion chemistry with this small molecule.

Scheme 4. Formation of **4**

CONCLUSIONS

The reactions of the potassium salts of dianions **1** and **2** with CO₂ and CO have been shown to lead to ring expansion products of the ladder diborole framework we reported recently. In the case of the CO₂ reactions, both **1** and **2** produced the same product, a dipotassium salt of a 1,1'-bi-2-naphtholate derivative with potential applications as a novel ligand. Interestingly, in contrast to the studies reported by Martin *et al.*,²⁰ we did not observe any formation of seven-membered boron heterocycles after ring expansion with CO₂. In the CO reactions, only one of the 5-membered rings in **2** underwent expansion, a reflection of the lower electrophilicity of this reagent.

EXPERIMENTAL SECTION

General Methods. See the Supporting Information. Note that, due to the sensitivity of these compounds, satisfactory elemental analyses for were not obtained despite duplicate attempts. Thus, bulk purity has been established using high resolution mass spectrometry and/or NMR spectroscopy.

Synthesis of **3 from **1**:** In a 25 mL round-bottomed flask compound **1** (40 mg, 0.048 mmol) was dissolved in THF (15 mL). The resulting brown solution was degassed by freeze-pump-thaw cycles. CO₂ was expanded into the flask (1 atm) and the flask was warmed to room temperature and allowed to stand for 30 minutes. The flask was evacuated to remove the solvent, giving a yellow-orange solid. In the glove box, the solid was suspended in cold pentane, filtered and washed with cold pentane twice. Compound **3** was isolated as a yellow solid (28 mg, 71%). ¹H NMR (CD₂Cl₂) δ 7.32 (dd, J = 7.5, 1.5 Hz, 2H), 7.21 (ddd, J = 8.4, 6.8, 1.5 Hz, 2H), 6.98 (s, 4H), 6.81 (d, J = 8.4 Hz, 2H), 6.60 (td, J = 7.1, 1.1 Hz, 2H), 2.88 (hept, J = 6.9 Hz, 2H), 2.73 (hept, J = 6.8 Hz, 2H), 2.66 (hept, J = 6.7 Hz, 2H), 1.36 (d, J = 6.6 Hz, 6H), 1.24 (dd, J = 7.0, 2.1 Hz, 18H), 0.99 (d, J = 6.8 Hz, 6H), 0.79 (d, J = 7.0 Hz, 6H). ¹³C{¹H} NMR (CD₂Cl₂) δ 165.11, 151.97, 151.03, 149.69, 149.23, 139.05, 134.45, 133.92, 123.01, 120.33, 120.22, 120.07, 118.19, 85.20, 53.84, 35.36, 34.81, 34.78, 25.99, 25.66, 25.13, 24.44, 24.07. HRMS: Calcd for C₄₆H₅₅B₂O₄K₂[M]⁺⁺H: 771.3561, Observed: 771.3565.

Synthesis of **3 from **2**.** In a 25 mL round-bottomed flask compound **2** (40 mg, 0.048 mmol) was dissolved in THF (15 mL). The

resulting red solution was degassed by freeze-pump-thaw cycles. CO₂ was expanded into the flask (1 atm) and the flask was warmed to room temperature and allowed to stand for 30 minutes. The flask was evacuated to remove the solvent, giving a yellow solid. In the glove box, the solid was suspended in cold pentane, filtered and washed with cold pentane twice. Compound **3** was isolated as a yellow solid (30 mg, 75%). Spectroscopic data are identical to **3** prepared from **1**.

Synthesis of **4.** In a 25 mL thick-walled glass vessel compound **2** (30 mg, 0.036 mmol) was dissolved in THF (10 mL). The resulting red solution was degassed by freeze-pump-thaw cycles. CO was expanded into the flask (1 atm), the vessel was closed and allowed to reach room temperature. The solution was stirred at 70 °C for 24 h. At room temperature, the vessel was evacuated to remove the solvent. In the glove box, the dark blue solid was dissolved in THF (1 mL), layered with hexanes (1.5 mL) and allowed to crystallize for 6 days at -35 °C. Compound **4** (0.020 g) was isolated as dark blue crystals in 62% yield. ¹H NMR (THF-*d*₈) δ 8.17 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.05 (s, 2H), 6.96 (s, 2H), 6.92 (d, J = 7.8 Hz, 1H), 6.76 (t, J = 6.8 Hz, 1H), 6.69 (d, J = 6.8 Hz, 1H), 6.47 (t, J = 7.2 Hz, 1H), 6.33 (t, J = 7.3 Hz, 1H), 6.09 (t, J = 6.8 Hz, 1H), 3.10 (hept, J = 6.8 Hz, 2H), 3.03 (hept, J = 6.8 Hz, 2H), 2.96 – 2.85 (m, 2H), 1.31 (d, J = 7.0 Hz, 6H), 1.26 (d, J = 6.5 Hz, 12H), 1.09 – 1.02 (m, 18H). ¹³C{¹H} NMR (THF-*d*₈) δ 155.84, 153.03, 151.24, 150.17, 146.98, 146.35, 145.53, 142.48, 137.91, 135.83, 130.24, 127.89, 127.73, 124.51, 122.92, 120.61, 119.64, 119.47, 115.97, 35.17, 35.13, 34.87, 34.47, 26.20, 25.60, 25.47, 25.33, 24.62, 24.58. ¹¹B NMR (THF-*d*₈) δ 46.6.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, NMR spectra, MALDI-TOF data, computational output data and supplementary crystallographic data for **3** (CCDC 1063731) and **4** (1063732) in the form of .cif files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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