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Boron-based stepwise dioxygen activation with 1,4,2,5-diazadiborinine†

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Activation of dioxygen (O_2) by 1,4,2,5-diazadiborinine **1** is reported. Two boron centers in **1** undergo a formal [4 + 2] cycloaddition with O_2 at room temperature affording a bicyclo[2.2.2] molecule **2** featuring a B–O–O–B unit. Treatment of **2** with an additional equivalent of **1** leads to the cleavage of the O–O bond in **2** concomitant with the formation of two B–O bonds to yield **4** involving the extremely rare $B_4C_2N_2O_2$ ten-membered rings. A series of these reactions demonstrate the stepwise scission of the O=O π-bond and the O–O σ-bond of O_2.

Introduction

Oxygen activation is of paramount importance in biological systems as represented by catalytic redox processes using oxidase and oxygenase enzymes.[1] Significantly, the Fe center in the enzymes exhibits versatility in bonding with the O atom derived from O_2 activation.[2] To mimic such biological processes artificially, considerable attention has been paid to the isolation of metal complexes that correspond to the key intermediates in the enzyme-O_2 activation process. To date, various transition metal–oxygen species such as superoxide,[3] peroxide[4] and metal μ-oxo species[5] have been synthesized through O_2 activation, and structurally characterized.

Over the past decade, it has been demonstrated that main group elements serve as if they are transition metals in the activation of small molecules.[6–9] Dioxygen activation has also been described by using various p-block molecules on the basis of group 13,[10,11] 14,[12–14] and 15 [15] elements. However, in stark contrast to the extensive and detailed studies of diverse products from O_2 activation by transition metals,[2–5] only a handful main group protocols have achieved a complete scission of the O=O bond of O_2 in distinct stepwise reactions concomitant with the isolation and full characterization of the initial and final products.[10f,11i,12c,h,13a,15c] Recently, a few boron compounds featuring the BOO unit were successfully isolated through the O_2 activation reaction (**I–VI**, Fig. 1A),[10] among which only **III** and **VI** possess the dibora-peroxide (B–O–O–B) moiety. To the best of our knowledge, the reactivity of dibora-peroxides **III** and **VI** has never been realized thus far.

Recently, we have reported that 1,4,2,5-diazadiborinine **1** readily reacts with unsaturated bonds (C=C, C=O, C≡C, and C≡N) and σ-bonds (C–O, B–H, Si–H, and P–H) in small molecules.[16] We reasoned that the boron-centered reactivity of **1** would allow for oxygen activation only at the boron centers. Herein, we report that indeed both the O=O π-bond and the O–O σ-bond of O_2 can be cleaved by **1** in a stepwise manner (Fig. 1B).

Results and discussion

By a freeze–pump–thaw method, O_2 was introduced into a Schlenk tube containing a benzene solution of **1**. Within five

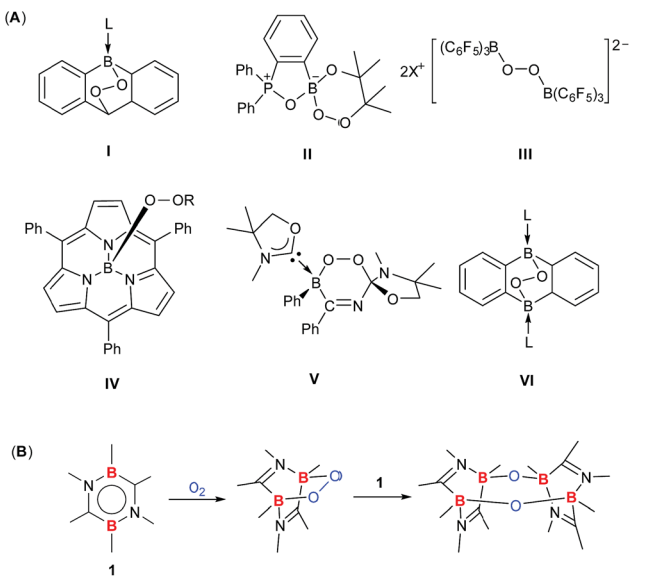

Fig. 1 (A) Reported boron peroxides obtained through oxygen activation; (B) this work: O_2 activation at the boron centers in two distinct steps.

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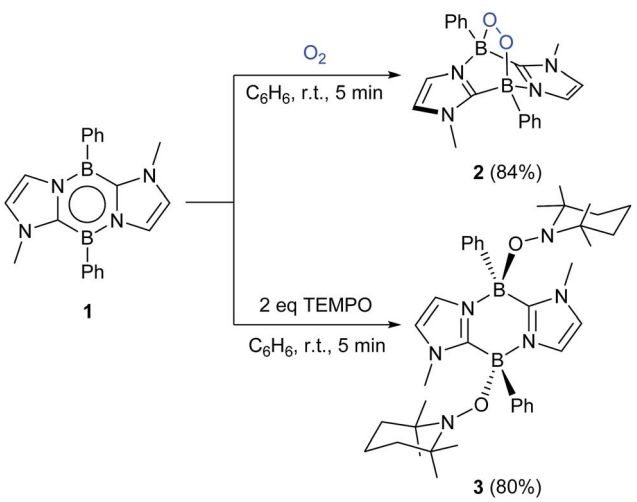
minutes at room temperature, a white precipitate appeared concomitant with disappearance of the orange colour of **1**. After work-up, **2** was obtained as a white powder in 84% yield (Scheme 1). **2** exhibits a poor solubility in benzene, acetonitrile and tetrahydrofuran but dissolves well in dichloromethane and chloroform. In the ^{11}B NMR spectrum of **2**, a sharp singlet appears at −0.4 ppm, which is shifted upfield with respect to that (18.3 ppm) of **1**,[16] indicating the formation of four-coordinate boron centers. The ^{1}H NMR spectrum shows a singlet at 3.24 ppm for the methyl groups on the nitrogen atoms and two doublets at 6.60 ppm and 6.98 ppm for the CH of the imidazole rings, indicative of the center of symmetry of **2**. The solid-state IR spectrum of **2** showed a characteristic peak at 964 cm^{-1} for the B–O stretching vibration (Fig. S20†) whereas the O–O stretching mode was detected at 953 cm^{-1} in the Raman spectrum (Fig. S21†), confirming the presence of B–O and O–O bonds in **2**, which was further revealed by an X-ray diffraction analysis (Fig. 2).

The solid-state molecular structure of **2** shows a bicyclo [2.2.2] geometry involving an endocyclic O–O unit bound to two boron atoms, indicating that **1** underwent a formal [4 + 2] cycloaddition reaction with O_2. The O–O bond distance (1.507(4) Å) is slightly longer than those (1.4733(2)–1.487 (2) Å) reported for molecules featuring a B–O–O–B unit.[10c,f,h] The B–O bond distances (B1–O1 1.505(6) Å and B2–O2 1.495(6) Å) are similar to the related compound (1.5029(19) and 1.492(2) Å).[10h] The B–O–O-angles (B1–O1–O2 113.2(3)° and B2–O2–O1 112.9(3)°) are nearly identical to those (109.48(10)° and 112.41(10)°) in the endoperoxide.[10h] Compound **2** represents one of the rare examples of diboraperoxide derivatives.[10c,f,h] Note that inorganic peroxides (B–O–O) are proposed not only as the key intermediate in organic synthesis,[17–19] but also as the active sites in oxidative dehydrogenation of propane catalyzed by boron nitrides.[20] Moreover, recently, Linker *et al.* reported that an aromatic endoperoxide has proved to be a useful precursor for the generation of singlet oxygen.[21]

We also carried out the reaction of **1** with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). In benzene, **1** and two equivalents of TEMPO were mixed at room temperature, which led to a fast disappearance of the orange colour of **1**, and concomitantly a white precipitate appeared. After work-up, **3** was obtained in 80% yield and fully characterized by NMR spectroscopy and X-ray diffractometry (Fig. 3). Each boron center in **3** forms a B–O bond with TEMPO, and the B–O bond distances (B1–O1: 1.500(4) Å and B2–O2: 1.480(4) Å) are similar



Scheme 1 Reactions of **1** with O_2 and TEMPO.

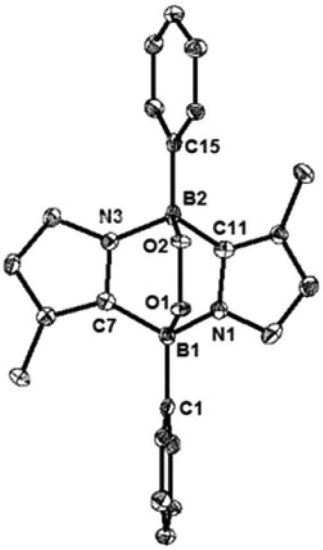


Fig. 2 The solid-state molecular structure of **2** (All hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: B1–O1 1.505(6), B1–N1 1.582(7), B1–C7 1.611(6), C7–N3 1.345(6), B2–O2 1.495(6), B2–N3 1.583(7), B2–C11 1.623(6), C11–N1 1.354(6), O1–O2 1.507(4), O1–B1–N1 103.9(4), O1–B1–C7 104.1(4), N1–B1–C7 104.6(4), N3–C7–B1 115.6(4), O2–B2–N3 104.7(4), C7–N3–B2 114.0(4), O2–B2–C11 104.1(3), N3–B2–C11 104.7(4), N1–C11–B2 114.7(4), C11–N1–B1 114.3(4), B1–O1–O2 113.2(3), and B2–O2–O1 112.9(3).

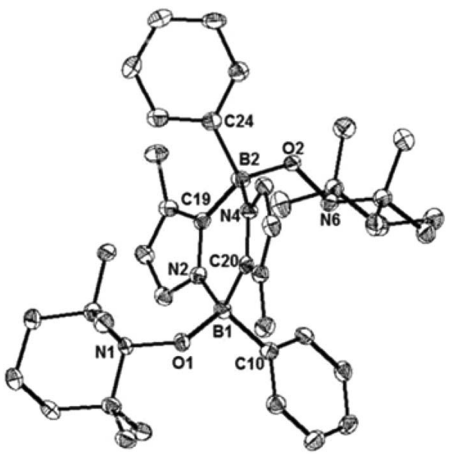
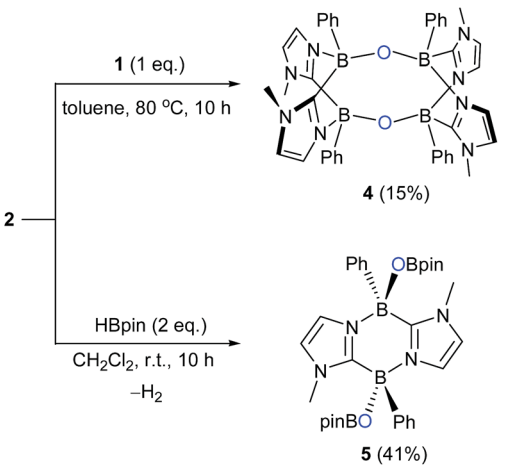


Fig. 3 The solid-state molecular structure of **3** (all hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: B1–O1 1.500(4), B1–N2 1.574(5), B1–C20 1.628(5), B1–C10 1.639(5), C19–N2 1.357(4), B2–C19 1.636(5), B2–N4 1.581(5), B2–O2 1.480(4), N1–O1 1.445(4), N6–O2 1.456(3), O1–B1–N2 114.4(3), O1–B1–C20 105.7(3), N2–B1–C20 104.7(3), and O1–B1–C10 108.9(3).

to that of the B–O bond (1.500(4) Å) of $C_2H_2(NCH_2C_6H_4)_2CB$-TEMPO.[22] Two TEMPO units are located in opposite sides with respect to the central $B_2C_2N_2$ plane, probably due to the steric repulsion between the two bulky TEMPO units. This result proposes that the formation of **3** would proceed in a stepwise manner.[22,23]

While the formation of the B–O–O–B endoperoxide **2** is reminiscent of the addition of O_2 to NHC-stabilized boranthrene reported by Harman *et al.*,[10h] further examination of the complete scission of the O–O bond, in particular with the boron system, has never been achieved, which prompted us to investigate further reaction of **2** with **1**. First, we observed no reaction between **2** and **1** (1 eq.) in toluene under ambient conditions. When the reaction mixture was heated at 80 °C, the orange colour of **1** disappeared gradually. After 10 h, formation of a major product **4** (Scheme 2) was detected by NMR spectroscopy, which was isolated after work-up as a light-yellow powder in 15% yield. The poor isolated yield of **4** is due to the formation of insoluble unidentified byproducts during the reaction (Fig. S8 and S9†). The ^{11}B NMR spectrum of **4** exhibits only one singlet at −2.4 ppm, which is nearly identical to that (−0.4 ppm) of **2**. The ^1H NMR spectrum of **4** shows a singlet at 3.03 ppm for the Me groups on the N atoms and two doublets at 6.41 ppm and 6.15 ppm for the CH moieties of the imidazole rings. The solid-state molecular structure was unambiguously identified by an X-ray diffraction analysis (Fig. 4). Two diazadiborinine units are bridged *via* two B–O–B linkers, confirming that the O–O σ-bond in **2** was cleaved by **1**, concomitant with the formation of two B–O bonds.



Scheme 2 Reactions of **2** with **1** (1 eq.) and HBpin (2 eq.).

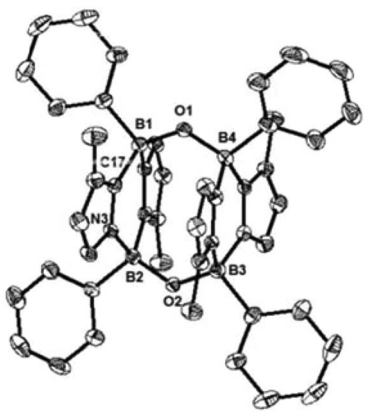


Fig. 4 Solid-state molecular structure of **4** (all hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: B1–O1 1.435(3), B1–C17 1.632(4), C17–N3 1.346(3), B2–N3 1.601(3), B2–O2 1.436(3), B3–O2 1.444(3), B4–O1 1.440(3), B1–O1–B4 128.2(2), and B2–O2–B3 129.8(2).

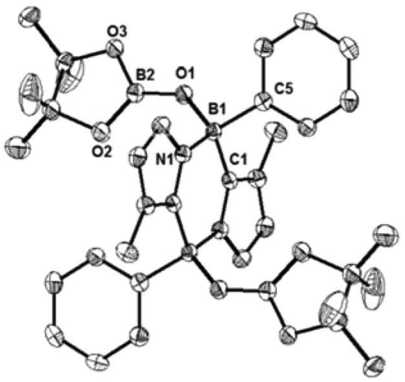


Fig. 5 Solid-state molecular structure of **5** (all hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: B1–O1 1.467(3), B1–N1 1.577(3), B1–C1 1.622(3), B1–C5 1.628(3), B2–O1 1.340(3), O1–B1–N1 110.76(17), O1–B1–C1 112.39(18), N1–B1–C1 105.10(17), O1–B1–C5 107.59(16), N1–B1–C5 109.58(17), and C1–B1–C5 111.43(17).

We found that compound **2** reacted with pinacolborane (HBpin) as well under ambient conditions, generating product **5** with the release of hydrogen gas. The solid-state structure of **5** revealed that along with the cleavage of the O–O bond in **2**, two OBpin units were formed (Fig. 5). Interestingly, the two OBpin units are at opposite sides with respect to the central $B_2C_2N_2$ ring.

Conclusions

We have shown that the two B centers of 1,4,2,5-diazadiborinine **1** readily capture O_2 under ambient conditions to furnish a formal [4 + 2] cycloaddition product **2** featuring an O–O bond. The reaction of **1** with TEMPO afforded **3** bearing two B-TEMPO units. Further treatments of **2** with **1** and HBpin led to **4** and **5**, respectively, *via* a cleavage of the O–O bond in **2**. The former demonstrates complete O_2 activation at the B center in two distinct steps. These results show the potential of the boron-based system for the development of a metal-free strategy to mimic metalloenzymes. The oxygen transfer reaction from **2** to other substrates is underway in our laboratory.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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