## Formation and X-ray structure of a seven-membered C<sub>4</sub>OBN heterocycle by a THF ring-expansion process<sup>†</sup>

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The reaction of BCl<sub>3</sub> with two equivalents of LiN(H)Dipp (Dipp = 2,6-diisopropylphenyl) in THF produces DippN-(H)BO(CH<sub>2</sub>)<sub>4</sub>NDipp, which contains a puckered sevenmembered C<sub>4</sub>OBN ring.

Examples of THF ring-opening promoted by Lewis acidic transition-metal,<sup>1</sup> lanthanide<sup>2</sup> or actinide complexes<sup>3</sup> are more common than those that are initiated by electrophilic main group element centres. In the latter category, ring-opening occurs when dimethylethylamine-alane reacts with three equivalents of 2,6-diisopropylphenol in THF.<sup>4</sup> The combination of TeBr<sub>4</sub> with triphenylphosphine in THF has also produced a ring-opened product.5 We have reported that cooperative ring-opening occurs when the tellurium diimide dimer 'BuNTe(µ-N'Bu)2 TeN'Bu is added to a solution of  $B(C_6F_5)_3$  in THF; the 1:1 adduct of these two reagents also initiates this process.<sup>6</sup> More recently, Stephan and co-workers have demonstrated that sterically bulky phosphines react with the adduct (THF) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in a ringopening fashion to give phosphonium-borate zwitterions.7 In all of these examples the THF molecule appears as an acyclic fragment in the final product. The THF molecule can also be incorporated as part of a ring in the final product, however this behaviour is limited to a single example. Sekiguchi and co-workers recently reported that seven-membered rings (1,3,2-oxasila- and germaborepanes) are formed by insertion of in situ >E=B- (E = Si, Ge) doubly bonded species into a C-O bond of THF.8

The cleavage of ethers by boron trihalides  $BX_3$  (X = Cl, Br) occurs readily, and organoboron halides, *e.g.* Me<sub>2</sub>BBr, are known to cleave cyclic ethers such as 2-methyltetrahydrofuran regioselectively.<sup>9</sup> By contrast, the reaction of Ph<sub>2</sub>BCl with a THF solution of tetralithiated tetra-*tert*-butyl calix(4)arene produces the simple adduct Ph<sub>2</sub>BCl·THF, indicating that the replacement of two chlorine atoms in BCl<sub>3</sub> by two phenyl groups substantially reduces the reactivity of the remaining B–Cl bond towards C–O bond cleavage.<sup>10</sup> In this Communication we report that the *in situ* generation of DippNH boron halides (Dipp = 2,6-diisopropylphenyl) in THF results in the formation of a seven-membered C<sub>4</sub>OBN ring (1,3,2-oxazaborepane), the first example of THF ring-opening promoted by aminoboron halides (RNH)<sub>3-n</sub>BCl<sub>n</sub> (n = 1, 2).

The reaction of BCl<sub>3</sub> with two equivalents of LiN(H)Dipp in THF produces a colourless solid **1a**<sup>‡</sup> and a minor, unidentified oily product. Compound **1a** is isolated as a pure crystalline solid from a concentrated solution of *n*-hexane and toluene at *ca.* -30 °C in 37% yield. In addition to the characteristic resonances for the Dipp substituents, the <sup>1</sup>H NMR spectrum of **1a** reveals four sets of equally intense multiplets (at 3.82, 3.14, 1.69 and 1.52 ppm) with relative intensities that correspond to two protons each and the <sup>13</sup>C NMR spectrum contains resonances at 64.9, 53.5 28.9 and 28.8 ppm. A single broad resonance is observed in the <sup>11</sup>B spectrum at 23.8 ppm indicative of a three-coordinate boron centre. Taken together, the NMR data indicate the presence of four inequivalent CH<sub>2</sub> groups in **1a**, two of which are linked (on the basis of chemical shifts) to electronegative atoms.

X-Ray quality crystals of 1a§ were obtained by recrystallisation from an *n*-hexane and toluene solvent mixture. An X-ray structural determination revealed the formation of DippN(H)BO(CH<sub>2</sub>)<sub>4</sub>NDipp comprised of a seven-membered  $C_4OBN$  (1,3,2-oxazaborepane) ring with a Dipp group attached to nitrogen and a DippNH substituent on the boron atom. The heterocycle 1a is the first structurally characterised example of a seven-membered ring containing nitrogen, boron and oxygen, in which three-coordinate nitrogen and boron atoms are covalently bonded. A single example of a 1,3,2-oxazaborepane with an alkyl substituent on boron has been reported. It was obtained from the reaction of 1-hydroxymethyl-2-aminomethylbenzene with dibutyl isopropylboronate as a red oil and characterised only by <sup>1</sup>H NMR and IR spectra and by MS.11 Other heterocycles containing the OBN unit within smaller rings are known, including the wellstudied 1,3,2-oxazaborolidines, which are used as catalysts for numerous organic transformations,12 and the tricyclic borazine 2 (Chart 1).<sup>13</sup> The molecular structure of 1a is shown in Fig. 1 and selected structural parameters are presented in Table 1.



Carbon atoms C26 and C27 are disordered over two atomic sites resulting in two superimposed seven-membered rings with chairand boat-like conformations in a 60 : 40 ratio, respectively (Fig. 2), with dihedral angles of 57.1° for C25–C26–C27–C28 and 39.7° for C25A–C26A–C27A–C28A. The C28–N1–B1–O1 torsion angle is 22.4°, comparable to that of a related seven-membered heterocycle

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B1O1	1.381(3)	N1-C28	1.478(2)
B1-N2	1.421(3)	N1-C1	1.440(2)
B1-N1	1.428(3)	O1-C25	1.431(3)
O1-B1-N2	116.5(2)	B1-N1-C28	123.9(2)
O1-B1-N1	122.9(2)	C1-N1-C28	113.9(2)
N2-B1-N1	120.6(2)	B1-N1-C1	120.8(2)
C28–N1–B1–O1	22.4(3)	C28A-C27A-C26A-C25A	39.7(8)
C28-C27-C26-C25	57.1(4)		



Fig. 1 Molecular structure of one conformation of DippN(H)BO- $(CH_2)_4$ NDipp (1a). Hydrogen atoms omitted and only  $\alpha$ -carbon atoms of Dipp groups are shown for clarity.



Fig. 2 Molecular conformations of the  $C_4NBO$  ring in 1a (hydrogen atoms omitted for clarity).

containing nitrogen, boron and oxygen where the boron atom is four-coordinate.<sup>14</sup> The boron–oxygen bond length of 1.381(3) Å is in agreement with those in structures containing a nitrogen– boron–oxygen fragment, which typically range from  $1.35^{15}$  to 1.43 Å;<sup>16</sup> specifically, the distance is indistinguishable from that observed for the tricyclic borazine, **2**,<sup>13</sup> which provides a comparable cyclic environment to that of **1a**. The endocyclic and exocyclic B–N bond lengths in **1a** are equal and intermediate between single and double bond values. The endocyclic C–N bond is slightly elongated compared to that of the exocyclic one, however, the latter is identical, within experimental error, to the N–C bond of the NHDipp substituent (1.431(2) Å). The geometry about the three-coordinate boron and nitrogen atoms is planar ( $\sum \angle B = 360^{\circ}$  and  $\sum \angle N1 = 358.6^{\circ}$ ).

The formation of the C<sub>4</sub>OBN heterocycle **1a** can be envisaged to involve the initial coordination of THF to a Lewis acidic chloroborane (DippNH)<sub>n</sub>BCl<sub>3-n</sub> (n = 1 or 2; shown for n = 1in Scheme 1), followed by concomitant N–C bond formation and ring-opening (C–O bond cleavage) with the elimination of HCl to give the observed product.



In an attempt to obtain evidence for this reaction pathway, the disubstituted chloroborane ClB(NHDipp)<sub>2</sub> (3)<sup>17</sup> was stirred in THF for 18 h: however, the heterocycle 1a was not formed. In the light of this observation, we considered that the monosubstituted dichloroborane Cl<sub>2</sub>B(NHDipp) (4) (a stronger Lewis acid than 3) may be responsible for initiating the ring-opening. Consequently, the reaction depicted in Scheme 1 was carried out using a BCl<sub>3</sub>: LiN(H)Dipp molar ratio of 1:1 in THF in order to generate 4 in situ. The <sup>1</sup>H NMR spectrum of the product of this reaction reveals a major species that exhibits equally intense multiplets at 3.69, 3.13, 1.56 and 1.48 ppm; a singlet is observed at 26.8 ppm in the <sup>11</sup>B NMR spectrum. The similarity of the chemical shifts for -CH<sub>2</sub>- groups in the <sup>1</sup>H NMR spectrum to those observed for 1a together with the small downfield shift of 3.0 ppm in the <sup>11</sup>B NMR resonance with respect to 1a is consistent with the formation of the ring-opened derivative 1b with an exocyclic Cl substituent attached to boron (Scheme 1). The reaction mixture also contained [DippNH<sub>3</sub>]Cl (<sup>1</sup>H NMR spectrum), which is presumably formed by the reaction of eliminated HCl with LiN(H)Dipp in a 2:1 molar ratio. Further evidence that the oily product is 1b was garnered from the observation that the addition of an excess of LiN(H)Dipp produces 1a (<sup>1</sup>H and <sup>11</sup>B NMR spectra). As with the synthesis of 1b, crystals of [DippNH<sub>3</sub>]Cl were also isolated from the reaction of BCl<sub>3</sub> with 2 equivalents of LiN(H)Dipp, which suggests that the yield could be increased by adding excess amide to scavenge the HCl by-product. However, carrying out this reaction in a 2:5 molar ratio of BCl<sub>3</sub>: LiN(H)Dipp produced lower yields of 1a (by <sup>1</sup>H NMR).

In summary, the reaction of BCl<sub>3</sub> with LiN(H)Dipp in THF generates the first structurally characterised example of a 1,3,2oxazaborepane. Variation of the stoichiometry of this reaction indicates that this THF ring-opening process is initiated by the dichloroborane  $Cl_2B(NHDipp)$ .<sup>18</sup> Although the formation of this seven-membered ring formally involves the insertion of the iminoborane ClB=NDipp into a C–O bond of the THF molecule, the generation of an iminoborane under the reaction conditions employed here is unlikely as these compounds are typically obtained from gas phase thermolysis reactions.<sup>19</sup> Recently, it has been shown that iminoboranes can also be formed by inducing HX elimination from sterically bulky aminoboranes using Na[N(SiMe<sub>3</sub>)<sub>2</sub>] in THF,<sup>20</sup> demonstrating a contrast in reactivity to the chloro-aminoboranes presented here.

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## Notes and references

<sup>‡</sup> Synthesis of 1a: A solution of LiN(H)Dipp (1.10 g, 6.0 mmol) in THF (15 mL) was added to a solution of BCl<sub>3</sub> (3 mL, 1 M, 3.0 mmol) in nhexane at ca. -80 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. Volatiles were removed in vacuo and the oily product was extracted with n-hexane and filtered. After removal of solvent, a sticky solid was isolated and colourless, X-ray quality crystals of 1a were grown from an n-hexane-toluene solution (0.488 g, 1.12 mmol, 37%) (Found: C, 76.68; H, 10.02; N, 6.28. Calc. for C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>BO: C, 77.41; H, 9.98; N, 6.45%). <sup>1</sup>H: δ (399.45 MHz; C<sub>6</sub>D<sub>6</sub>; 25 °C): 7.18–7.09 (m, 6 H, Dipp groups), 3.82 (m, 2 H, ring -CH<sub>2</sub>-O), 3.66 (sept, 2 H, -CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{\text{H-H}} = 6.9 \text{ Hz}$ ), 3.40 (sept, 2 H,  $-CH(\text{CH}_{3})_2$ ,  ${}^{3}J_{\text{H-H}} = 6.9 \text{ Hz}$ ), 3.40 (sept, 2 H,  $-CH(\text{CH}_{3})_2$ ,  ${}^{3}J_{\text{H-H}} = 6.9 \text{ Hz}$ ), 3.14 (m, 2 H,  $-CH_2-N$ ), 2.92 (1 H, br s, -NH), 1.69 (m, 2 H,  $O-CH_2-CH_2-$ ), 1.52 (m, 2 H,  $-CH_2-CH_2-N$ , 1.35 (d, 6 H,  $-CH(CH_3)_2$ ,  ${}^{3}J_{H-H} = 6.8$  Hz), 1.23 and 1.22 (overlapping d, 18 H,–CH(CH<sub>3</sub>)<sub>2</sub>). <sup>11</sup>B:  $\delta$  (128.16 MHz; C<sub>6</sub>D<sub>6</sub>; 25 °C): 23.8 (s). <sup>13</sup>C:  $\delta$  (100.45 MHz; C<sub>6</sub>D<sub>6</sub>; 25 °C): 147.7 (Dipp), 145.8 (Dipp), 144.6 (Dipp), 138.1 (Dipp), 127.5 (Dipp), 125.6 (Dipp), 124.9 (Dipp), 123.3 (Dipp), 64.9 (-CH<sub>2</sub>-O), 53.5 (-CH<sub>2</sub>-N), 30.8 (-CH(CH<sub>3</sub>)<sub>2</sub>), 28.9 (ring CH2-), 28.8 (ring -CH2-), 28.5 (-CH(CH3)2), 26.5 (-CH(CH3)2), 24.5 (-CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 (-CH(CH<sub>3</sub>)<sub>2</sub>). Synthesis of 1b: A solution of LiN(H)Dipp (0.917 g, 5.0 mmol) in THF (15 mL) was added to a solution of BCl<sub>3</sub> (5 mL, 1 M, 5.0 mmol) in n-hexane at ca. -80 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. Volatiles were removed in vacuo and the product was extracted with nhexane and filtered to remove LiCl. After removal of solvent a peachcoloured oil was isolated. <sup>1</sup>H: δ (399.45 MHz; C<sub>6</sub>D<sub>6</sub>; 25 °C): 7.15-6.97 (m, 3H, Dipp), 3.69 (m, 2 H, -CH2-O), 3.36 (sept, 2 H, -CH(CH3)2), 3.13 (m, 2 H, -CH<sub>2</sub>-N), 1.56 (m, 2 H, O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48 (m, 2 H, -CH<sub>2</sub>-CH<sub>2</sub>-N), 1.13 (overlapping d, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>11</sup>B: δ (128.16 MHz; C<sub>6</sub>D<sub>6</sub>; 25 °C): 26.8 (br). The resonances of [DippNH<sub>3</sub>]Cl were also observed in the <sup>1</sup>H NMR spectrum. The product **1b** could not be separated from the by-product [DippNH<sub>3</sub>]Cl. Addition of LiN(H)Dipp (0.288 g, 1.57 mmol) to this oily product (0.258 g) in either hexane or THF gave an oil, which exhibited multiplet resonances at  $\delta$  3.82, 3.14, 1.69, 1.52 in the <sup>1</sup>H NMR spectrum attributable to 1a.

§ Crystal data for **1a**: A single crystal of **1a** suitable for X-ray analysis was covered with Paratone oil and mounted on a glass fibre. Data were collected in a stream of N<sub>2</sub> at 173 K on a Nonius KappaCCD diffractometer (Mo-Kα radiation,  $\lambda = 0.71073$  Å) using COLLECT (Nonius, B.V. 1998) software. The unit cell parameters were calculated and refined from the full data set. All crystal cell refinement and data reduction was carried out using the Nonius DENZO package. After data reduction, the data were corrected for absorption based on equivalent reflections using SCALEPACK (Nonius, B.V. 1998). The structures were solved by direct methods with the SHELXS-97<sup>21</sup> program package and refinement was carried out on *F*<sup>2</sup> against all independent reflections by the full-matrix least-squares method by using the SHELXL-97 program.<sup>22</sup> All non-hydrogen atoms were refined

with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective atoms. Two of the carbon atoms of the former THF molecule (C26, C27) were disordered over two atomic sites; the disorder was refined and the final site occupancy was found to be approximately 60:40.  $C_{28}H_{43}BN_2O$ , M = 434.45, monoclinic, a = 10.839(2), b = 20.360(4), c = 12.049(2)Å,  $\beta = 97.85(3)^\circ$ , V = 2633.8(9)Å<sup>3</sup>, T = 173 K, space group  $P2_1/n$ , Z = 4,  $\mu = 0.065$  mm<sup>-1</sup>,  $R_{int} = 0.0278$  (for 26111 measured reflections),  $R_1 = 0.0597$  [for 4634 unique reflections with  $[I > 2\sigma(I)]$ ),  $wR_2 = 0.1671$  (for all data).

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