Oxygen in an Electron-deficient Borane Skeleton: the Oxa-*nido*-dodecaborate Anion $[OB_{11}H_{12}]^-$

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$B_{11}H_{14}^-$ in aqueous sodium hydroxide reacts with oxygen to give $OB_{11}H_{12}^-$, the first example of an oxaborane species where oxygen is part of the boron–hydrogen cluster.

In a previous report,[1] the reaction of $[B_{11}H_{14}]^-$ with M_2O_3 (M = As, Sb, Bi) was investigated in the two-phase system 10 mol dm^{-3} $NaOH–CH_2Cl_2$ and was shown to lead to the expected, previously described,[2] icosahedral species $[MB_{11}H_{11}]^-$ with good yields. A by-product was also obtained and tentatively characterized as the *B*-hydroxy compound $[B_{11}H_{13}(OH)]^-$, a derivative of the parent anion $[B_{11}H_{14}]^-$ and closely related to the recently prepared $[B_{11}H_{13}(Me_2S)]$.[3] This paper is concerned with the reexamination of the structure of this hydroxy derivative in solution by NMR techniques. From this study it is concluded that this compound actually is an oxaborane species $M[OB_{11}H_{12}]$ **1a–c** (M = NEt_4, $PhCH_2NEt_3$, Na) and it appears to be the first example of a boron cluster with an oxygen atom within the boron framework.

The constitution of **1** can be deduced from NMR data.† Thus the ^{11}B NMR spectrum of **1a** displays a pattern for a boron framework of C_s symmetry (intensity ratio 2:1:1:2:2:2:1; three B atoms on the mirror plane), with each hydrogen atom being attached to one boron atom. The ^1H NMR spectrum reveals the presence of only one bridge hydrogen per cage (0.95, 0.99 and 0.89 for **1a**, **1b** and **1c**, respectively). The 2D $^1H–^{11}B$ correlation spectrum allows the exact location of the bridge hydrogen atoms, in agreement with the results of a selective $^{11}B-\{^1H\}$ irradiation experiment that resulted in an enhancement of the signal of the relevant boron atoms. The 2D $^{11}B–^{11}B$ COSY spectrum enables the straightforward assignment of all boron atoms. Two points deserve further comments: (*i*) no correlation could be observed between B(2) and B(4,5); (*ii*) a very weak cross-peak was observed between B(7,8) and B(4,5). These two facts, in addition to the deshielding observed for the ^{11}B chemical shifts and T_1 measurements of B(2), B(4) and B(5), strongly support the presence of a strongly electronegative atom bonded to these three boron atoms. From elemental analysis (C, H, N, B for **1a** and **1b**) and mass spectrometric data for **1b**, this atom is reasonably concluded to be oxygen and so the correct formula is $M[OB_{11}H_{12}]$. Thus this compound is a *nido*-12-vertex 28-electron oxaborane (assuming four electrons for the oxygen atom according to classical electron counting rules) and it is the first example of an oxaborane, *i.e.* of a cluster with boron, hydrogen and oxygen within the framework. Oxametallaboranes are known, *e.g.* $[OB_8H_{10}\{Fe(C_6H_3Me_3)\}]$,[4] $[(C_5Me_5Rh)OB_{10}H_9Cl(PMe_2Ph)]$[5] and $[\{C_5Me_5Rh\}OB_{10}H_{10}(NEt_3)]$,[6] the last two derivatives being isoelectronic with $[OB_{11}H_{12}]^-$ described in this paper. Another closely related isoelectronic, anionic species $[MeNB_{11}H_{11}(OMe)]^-$, obtained by methanolysis of *closo*-$NMeB_{11}H_{11}$, has been reported recently.[7] Other 12-vertex 28-electron clusters such as $[(C_5H_5Co)Se_2B_9H_9]$[8] or $Et_4C_4B_8H_8$ are also known.[9] In spite of our failure to obtain crystallographic data for this compound, it is reasonable that the structure of the anion [Fig. 1(*a*)] can be derived from that of the hypothetical *closo*-tridecaborate $[B_{13}H_{13}]^{2-}$ [Fig. 1(*b*)][10] by removal of the B(3) atom. Thus, removal of B(3) from the *closo*-skeleton eliminates the unfavourable connectivity $k = 6$ of B(4) and B(5) in the boron framework. Simultaneously, an optimal place is made available for the electronegative oxygen atom in position 1 with $k = 3$. Atoms B(7) and B(8) attain the connectivity $k = 4$ and are thus able to accommodate a bridging hydrogen whereas all the other boron atoms with $k = 5$ are not likely to form H bridges.[11] Thus the three B–O bonds in the skeleton might be normal (2 centre–2 electron) bonds representing an oxonium-type, 'classical,' O atom. Surprisingly, the structure of the anion $[OB_{11}H_{12}]^-$ appears to be very stable since it does not react with water, alcohols, MeI, NaOMe, I_2, NaH or HBF_4. The above results are similar to those observed with the anion $[MeNB_{11}H_{11}(OMe)]^-$.[7]

The synthesis of **1a** was reported earlier;[1] an improved method (11% yield of **1a**) was used now.‡ The mechanism of the formation of $[OB_{11}H_{12}]^-$ from $[B_{11}H_{14}]^-$ is not clear. However (*i*) on account of the strongly basic medium required, $[B_{11}H_{13}]^{2-}$ is most likely to be the reacting species; (*ii*) the oxygen atom is provided by atmospheric oxygen present in the solvents used, the added KH_2PO_4 probably behaving as a catalyst. Thus, when aqueous NaOH solutions and solvents are

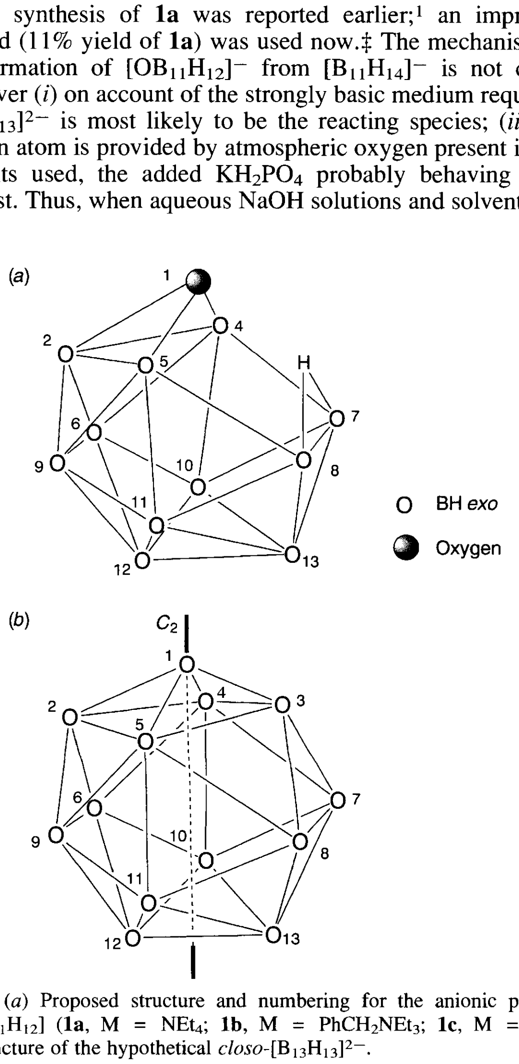

Fig. 1 (*a*) Proposed structure and numbering for the anionic part of $M[OB_{11}H_{12}]$ (**1a**, M = NEt_4; **1b**, M = $PhCH_2NEt_3$; **1c**, M = Na). (*b*) Structure of the hypothetical *closo*-$[B_{13}H_{13}]^{2-}$.

carefully deoxygenated prior to use, no $[OB_{11}H_{12}]^-$ is obtained. Conversely, boiling solutions of $Na[B_{11}H_{14}]$ in 10 mol dm^{-3} NaOH in presence of air resulted in significant recovery (*ca.* 10%) of pure **1c** whose ^{11}B NMR spectra were identical to those of **1a** and **1b**. Furthermore, even at room temperature it appears that $[B_{11}H_{13}]^{2-}$ itself is readily converted to $[OB_{11}H_{12}]^-$ either in strongly basic solution or in the solid state, provided air is present.

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Footnotes

† *Spectroscopic data*: **1a** NMR spectra in CD_3CN: ^1H NMR (300.13 MHz, $SiMe_4$); δ 3.9 [B(7,8)], 3.5 [B(12)], 2.75 [B(2)], 2.05 [B(4,5)], 1.7 [B(6,9)], 1.05 [B(10,11)], 0.3 [B(13)], −2.1 (bridge hydrogen). One cross-peak in the 2D ^1H-^{11}B spectrum between the bridge hydrogen and B(7,8). ^{11}B NMR (96.28 MHz, BF_3–Et_2O); δ 12.8 [d, *J* 151 Hz, B(7,8); cross-peaks in 2D ^{11}B–^{11}B NMR with B(10,11,13) and very weak with B(4,5)] 11.3 [d, *J* 141 Hz, B(12); cross-peaks with B(10,11), B(6,9) and B(13)], 4.35 [d, *J* 163 Hz, B(2); cross-peaks with B(6,9) but not with B(4,5)], −7.0 (d, *J* 156 Hz, B(4,5); cross-peaks with B(10,11), B(6,9) and a very weak one with B(7,8)], −14.15 [d, *J* 134 Hz, B(10,11); cross-peaks with B(7,8), B(12), B(4,5), B(6,9) and B(13)], −16.4 [d, *J* 139 Hz, B(6,9); cross-peaks with B(12), B(10,11), B(2), B(4,5)], −29.1 [d, *J* 139 Hz, B(13); cross-peaks with B(10,11), B(7,8), B(12)]. T_1/ms; 8.4 [B(7,8)], 10.8 [B(12)], 6.6 [B(2)], 8.2 [B(4,5)], 11.5 [B(10,11)], 9.0 [B(6,9)] and 10.2 [B(13)]. **1b**, Negative fast atom bombardment (observed) m/z = 147.188 for the anion; Calc. m/z = 147.198 for $[^{11}B_9{}^{10}B_2{}^1H_{12}{}^{16}O]^-$.

‡ $NMe_3H[B_{11}H_{14}]$ (1.2 g, 6.22 mmol) in 10 mol dm^{-3} NaOH (20 cm^3) was briefly heated and KH_2PO_4 (0.15 g) in H_2O (10 cm^3 1.1 mmol) was added with vigorous stirring for 6 h. An aqueous solution of NEt_4Br in excess gave a white precipitate extracted by small portions of CH_2Cl_2 to give 0.48 g of a mixture containing **1a** with 15% of $NEt_4[B_3H_8]$ (from ^{11}B NMR). After treatment by MeI and recrystallization from MeOH–hexane 0.30 g of analytically pure **1a** was recovered (yield 11%). Addition of $PhCH_2NEt_3Cl$, instead of NEt_4Br, gave 0.34 g of **1b** (yield 16%).

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