POLYHEDRAL OXABORANE CHEMISTRY. SOME COMPARATIVE ^{11}B NMR SHIELDING PATTERNS WITHIN THE TWELVE-VERTEX NIDO-TYPE GEOMETRY

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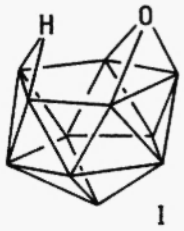
Summary

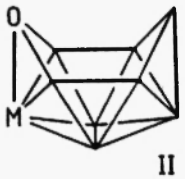
Comparative NMR spectroscopy among $[OB_{11}H_{12}]^-$, $[MeNB_{11}H_{11}(OMe)]^-$ and $[Me_2CHMe_2C)B_{11}H_{13}]^-$ supports the view that the twelve-vertex oxaborane anion $[OB_{11}H_{12}]^-$ is a contiguous *nido*-type twelve-vertex cluster species. Parallels with twelve-vertex *nido*-type oxametallaboranes are also discussed.

Contiguous oxaborane species are rare, but constitute a potentially fascinating area of chemistry. Only one simple-cluster oxaborane has so far been reported, the twelve-vertex $[OB_{11}H_{12}]^-$ anion **1**. [1,2,3] This has a *nido* twelve-vertex geometry (schematic cluster structure **I**), reasonably established as such by NMR spectroscopic analysis. [3] Very recently, a double-cluster macropolyhedral oxaborane, the $[OB_{18}H_{21}]^-$ anion, has been identified crystallographically. [4] The remaining three examples are all metallaoxaboranes. These are ten-vertex $[(\eta^6\text{-}C_6H_3Me_3)FeOB_8H_{10}]$ **2**, [5] twelve-vertex $[(\eta^5\text{-}C_5Me_5)RhOB_{10}H_9Cl(PMe_2Ph)]$ **3** [6] and twelve-vertex $[(\eta^5\text{-}C_5Me_5)RhOB_{10}H_{10}(NEt_3)]$ **4** [7] (schematic cluster structures **II**, **III**, and **IV** respectively). Of these three, the structures of **3** and **4**, as established by single-crystal *X*-ray diffraction analysis, [6,7] are clear analogues of the structure of the pure oxaborane anion **1**. The twelve-vertex *nido* azaborane anion, $[MeNB_{11}H_{11}(OMe)]^-$ **5**, is also closely related (schematic cluster structure **V**),[8] as is the recently reported [9] *nido* eleven-vertex alkyl-substituted borane anion $[Me_2CHMe_2C)B_{11}H_{13}]^-$ **6** (schematic cluster structure **VI**). This last anion **6** traces electronically and structurally to **1** by the interchange of *(a)* the two three-centre bonds to the mutually adjacent bridging hydrogen atoms in **6** with *(b)* the two three-centre bonds to the capping oxygen atom in **1**.

There is merit in examining this sequence of related twelve-vertex *nido* compounds for relationships in cluster NMR shielding behaviour, particularly so because *(a)* in the absence of *X*-ray work, the structure of the parent oxaborane **1** is based essentially upon NMR work,[3] and also *(b)* it is important to examine for the effect of incorporation of oxygen vertices on borane cluster shielding properties in anticipation of a growing oxaborane cluster chemistry.



I



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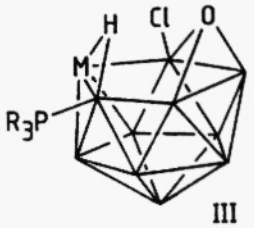

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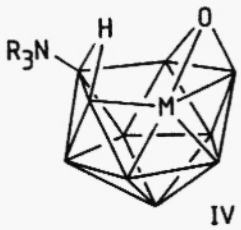

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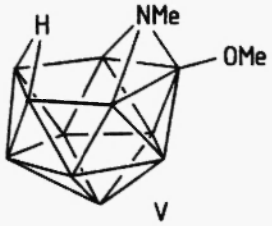

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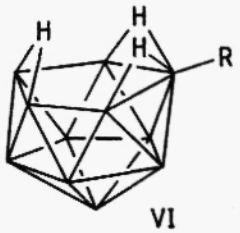
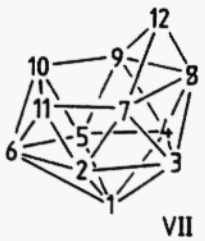


VI

Stick diagrams of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the oxaborane anion **1** together with the non-metallated species **5** and **6** are in Figure 1. Corresponding diagrams to compare **1** with the two metallaoxaboranes **3** and **4** are in Figure 2. The literature references [1-3,6-9] to these compounds have adopted a variety of numberings. Here, for convenience, we use a common scheme as summarised in structure **VII**.



VII

For the non-metallated compounds **1**, **5** and **6** (Figure 1) there are clear trends in shielding behaviour that are consistent with a replacement of the two three-centre bond to the μH(7,8) and μH(8,9) hydrogen atoms in compound **6** with two three-centre bonds to the single heteroatoms in compounds **1** and **5**. Thus, as the

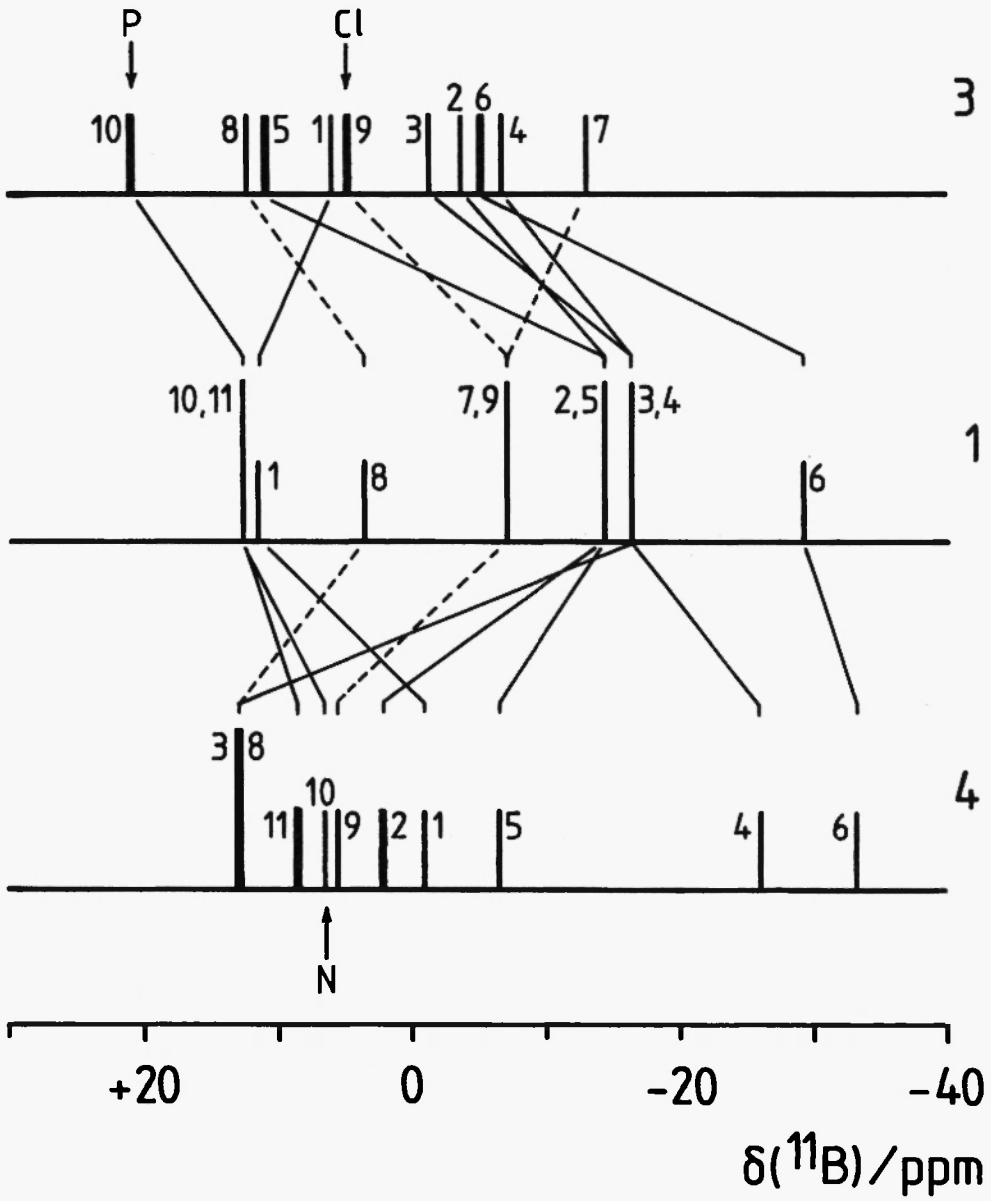


Figure 2. Stick diagrams of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the oxaborane anion $[OB_{11}H_{12}]^-$ **1** (data from references 1 and 3) and of the two neutral metallaoxaboranes $[(\eta^5\text{-}C_5Me_5)RhOB_{10}H_9Cl(PMe_2Ph)]$ **3** and $[(\eta^5\text{-}C_5Me_5)RhOB_8H_{10}(NEt_3)]$ **4** (data from references 5 and 6). For numbering scheme, relate structures **I**, **III** and **IV** to structure **VII**. Lines join equivalent positions in the three species; hatched lines are associated with the oxygen-bound boron positions. Heavier vertical lines in the schematic spectra for **3** and **4** designate boron positions adjacent to rhodium atoms. In compound **3** the 9- and 10-positions are substituted by Cl and PMe_2Ph respectively, and in **4** the 10-position is substituted by NEt_3.

pair of bridging hydrogen atoms in compound **6** is successively replaced by the progressively more electronegative centres in compound **5** (nitrogen) and compound **1** (oxygen), there is a progressive decrease in nuclear shielding in general, with the average chemical shifts $\delta(^{11}B)$ changing in the sequence -15.0 → -11.4 → -5.7 for **6** → **5** → **1**. A component of this is in the progressively lower shielding at the B(7,9) sites on which the 2H → NMe → O replacement directly occurs. Interestingly, however, larger progressive contributions occur at the hydrogen-bridged B(10,11) positions that are β to the heteroatom capping position, and there are also significant deshieldings at the B(1) site that is δ to the heteroatom capping position and antipodal to the open face. Both of these last indicate non-localised contributions to the twelve-vertex *nido*-12-heterododecaborane bonding scheme. There may well also be an inherent progressive deshielding at the third site that is also directly bound to the heteroatom cap, *i.e.* the B(8) position, but this cannot be assessed directly because this site is substituted both in compound **6** (by alkyl) and in compound **5** (by alkoxy). However, both alkyl and alkoxy groups are known to induce significant deshielding effects of up to 20-30 ppm or so on the ^{11}B sites to which they are bound. [10] It is therefore reasonable to predict significantly higher shielding for $^{11}B(8)$ in an (as yet hypothetical) $[MeNB_{11}H_{12}]^-$ anion than for $^{11}B(8)$ in the $[OB_{11}H_{12}]^-$ anion **1**. Consequently, a sequence passing from an unsubstituted $[B_{11}H_{14}]^-$ anion (static, and of configuration **VI**), through the $[MeNB_{11}H_{12}]^-$ anion, and thence to the $[OB_{11}H_{12}]^-$ anion, would be expected to show a similar deshielding progression at the B(8) position to that exhibited by the B(7,9) positions for the sequence **6** → **5** → **1**. This general behaviour is therefore all consistent with the contiguous *nido* twelve-vertex cluster structure **I** for the oxaborane anion **1**. In particular, it further discounts an *exo*-hydroxy-substituted eleven-vertex *nido* cluster structure [1] which would be expected to have [2,3] a shielding pattern much more akin to that of the *exo*-$(CHMe_2CMe_2)$-substituted eleven-vertex *nido* species **6**.

The relationship in the shielding patterns among the oxaborane **1** and its metallaoxaborane analogues **3** and **4** (Figure 2) is far less clear-cut. The rhodium sites are off what would be the B(1)B(6)B(8)O(12) symmetry plane in **1**, and can therefore synergically augment any tendency towards electronic asymmetry and thereby accentuate differential NMR shielding behaviour. In addition, both **3** and **4** are asymmetrically substituted, and, in particular, compound **3** has two boron-bound π-active ligands that may also interact synergically with the cluster. On average, the boron sites in both rhodium compounds are less shielded than in the oxaborane anion **1** with $\delta(^{11}B)$(mean) for **3** and **4** at +2.8 and -2.9 ppm being respectively some 8.5 and 2.8 ppm less shielded than $\delta(^{11}B)$(mean) for **1** at -5.7 ppm. However, in contrast to the relationships among **1**, **5** and **6** discussed above, no helpful individual trends can be usefully discerned. Boron sites adjacent to $\{Rh(\eta^5\text{-}C_5Me_5)\}$ centres in rhodaboranes generally exhibit considerable ^{11}B deshielding, [11,12,13] as generally also observed for compounds **3** and **4** compared to **1**. On the other hand, several other sites in the rhodaoxaboranes **3** and **4** also

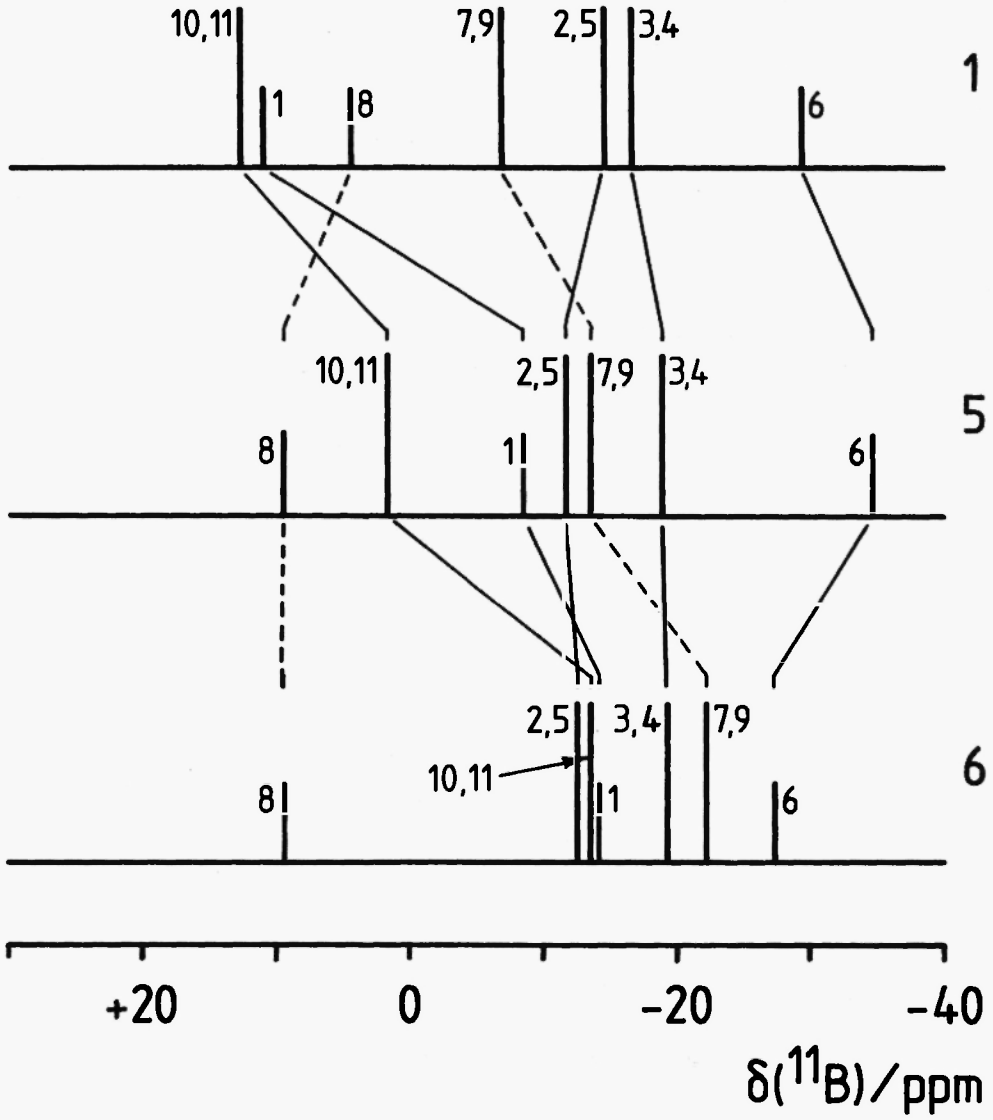


Figure 1. Stick diagram of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the three anionic non-metal-containing species $[OB_{11}H_{12}]^-$ **1** (data from references 1 and 3), $[MeNB_{11}H_{11}(OMe)]^-$ **5** and $[(Me_2CHMe_2C)B_{11}H_{13}]^-$ **6** (data from references 8 and 9). For numbering scheme, relate structures **I**, **V** and **VI** to structure **VII**. Lines join equivalent positions in the three species; hatched lines are associated with the oxygen-bound boron positions of anion **1**. In compounds **5** and **6** the 8-positions are substituted by MeO- and Me_2CHMe_2C- respectively.

exhibit significant deshielding, particularly in **3**, and in compound **4** one site adjacent to rhodium, B(11), exhibits an *increase* in ^{11}B nuclear shielding compared to **1**. The main conclusion here is that the incorporation of the {Rh(η^5-C_5Me_5)} unit into the *nido* 12-oxadecaborane cluster, either in an oxygen-bound position (compound **4**) or in a hydrogen-bridged position (compound **3**), severely and generally affects the entire cluster bonding scheme for this *nido* twelve-vertex oxaborane cluster type. This is in contrast to other systems that have been examined, for example the *nido* ten-vertex one based on *nido*-$B_{10}H_{14}$, [11,12] in which the shielding perturbations have been observed to occur principally at the boron sites directly bound to the rhodium centres, with the rest of the basic cluster electronic structure largely unperturbed. This type of conclusion is again consistent with there being substantial non-localised contributions to the twelve-vertex *nido*-12-heterododecaborane bonding scheme as suggested by the comparative behaviour among **1**, **5** and **6** as discussed above.

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