Bonding in Clusters. Part 12.[1] A Reinterpretation of the Bonding of *arachno*-Boranes†

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A series of MNDO (minimum neglect of differential overlap) calculations have been used to assess the standard relationship between *arachno*- and *closo*-boranes, namely that the *arachno*-boranes are related both structurally and in their bonding to a *closo*-borane with two adjacent boron atoms deleted. It is found that there is no evidence from the calculations to support this description but that a far more valuable correlation is that between *arachno*- and *nido*-boranes with the same number of boron atoms. These are inter-related by chemical reduction and oxidation. One of the $n + 2$ cluster orbitals of the corresponding *nido* compound is destroyed by the reduction, and two additional *exo*-hydrogen bonds (or lone pairs in the anions) are created. The *arachno*-borane B_nH_{n+6} has $n + 1$ cluster-bonding orbitals and not $n + 3$ as proposed in the standard description.

The accepted correlation of the borane structural types is that *arachno*-boranes and *nido*-boranes are derived from a *closo*-$B_nH_n^{2-}$ geometry by deletion of one and two adjacent BH apices respectively. The cluster bonding-electron count of the parent *closo*-borane is 're-established' by the addition of bridging and *endo*-hydrogens to the structure so created. This convenient correlation has its origin in Williams' 1976 review of borane and carborane geometries[2] and has been part of borane chemistry ever since. It was justified on the grounds of geometry comparison and electron count, but in fact carries no additional value. There is no corresponding similarity of chemistry or physical properties between the molecules connected by the correlation and in no case is there a preparative route from one member of the *closo*, *nido*, *arachno* triad to another.

In an earlier paper we investigated the first step of this correlation,[3] *closo–nido*, through MNDO (minimum neglect of differential overlap) calculations on a variety of *closo*, hetero-*closo* and *nido* sets of molecules. We determined that *nido* compounds can best be regarded as *closo* compounds with an unusual heteroapex, four bridging hydrogens, $4H_b$. This 'apex' replaces a BH^{2-} apex of *closo*-boranes (or CH^- apex of *closo*-monocarboranes, or the S atom of thiaboranes) whilst maintaining the contributions of the apex to the occupied molecular orbital set and hence the bonding of the molecule. This was very much in agreement with the standard, geometric correlation between the *closo* and *nido* structural types. In this paper we report an extension of that work to *arachno*-boranes, in which we do not find that the standard description is supported by the electronic structure calculations. In fact we propose that *arachno*-boranes are just chemically reduced *nido*-boranes, and that the structural correlation is fortuitous, not very persuasive and, to some extent, misleading.

Computational Method

The calculations discussed in this paper are MNDO calculations run using the AMPAC suite of programs.[4] The geometries were optimized with no restriction on the $(3N - 6)$ degrees of freedom of the molecules. If the results of this produced a slightly asymmetric geometry for what is clearly a symmetric molecule then the final result was symmetrized to ease the analysis of molecular orbitals. This symmetrization did not cause a significant increase in the total energy of the molecule.

The validity of applying MNDO calculations to the analysis of borane bonding has been established in many of the earlier papers in this series. The calculations have been used in comparison with structural, photoelectron spectroscopic and protonation energy data,[1] all with good agreement. The only property that has required higher-level methods is infrared absorption frequencies.[5] In the following we proceed in the manner of ref. 3 and will make particular use of the localized orbitals calculated for the molecules. These are derived from the usual, canonical set of molecular orbitals and are a representation of the chemical bonding as described in valence-bond terminology. The actual localized orbitals are of little interest or use in the following, but the calculation also provides a 'number of centres' index for each localized orbital which corresponds fairly closely to the concept of two-, three-centre, *etc.*, bonding in the valence description. Thus the B–H–B three-centre bonds of B_5H_9 are calculated to be 50% on the H atom and 25% on each of the B atoms and have an index of 2.7, those of $B_{10}H_{14}$ an index of 2.8; the B–B–B bonds of $B_6H_6^{2-}$ are found 36% on two borons, 20% on the third and have an index of 3.2. Indices of 2.5 are 90% on two atoms, 10% on a third (or distributed over other centres) and cannot be seriously considered as multi-centre bonding orbitals. This index will be used extensively in the discussion below.

Discussion

arachno-B_nH_{n+6} *from closo*-$B_{n+2}H_{n+2}^{2-}$.—We first consider the merits of the standard *arachno–closo* relationship in terms of very simple bonding diagrams, in the same manner that was a successful starting point for the consideration of the *nido–closo* pairs. From the parent *closo*-$B_{n+2}H_{n+2}^{2-}$ a $B_2H_2^{2-}$ unit is deleted and replaced by six 'extra' hydrogens, a 6H ($4H_b$,$2H_{wt}$, where wt indicates a wing-tip) apex, to form the structurally related *arachno*-B_nH_{n+6}. As each BH unit contributes two electrons to the cluster bonding of the *closo* compound then clearly the electron count is maintained. The BH units also contributed three 'atomic' orbitals, one axial σ and two perpendicular π, to the cluster-orbital basis set. As the two BH units deleted are always adjacent then these basis orbitals can be recast as shown in Fig. 1. In essence the reduction from the $C_{\infty v}$ symmetry of BH to the C_{2v} symmetry of B_2H_2 requires that the group orbitals of each BH unit be rehybridized from sp to sp^2 as

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† *Non-SI unit employed*: eV ≈ 1.60×10^{-19} J.

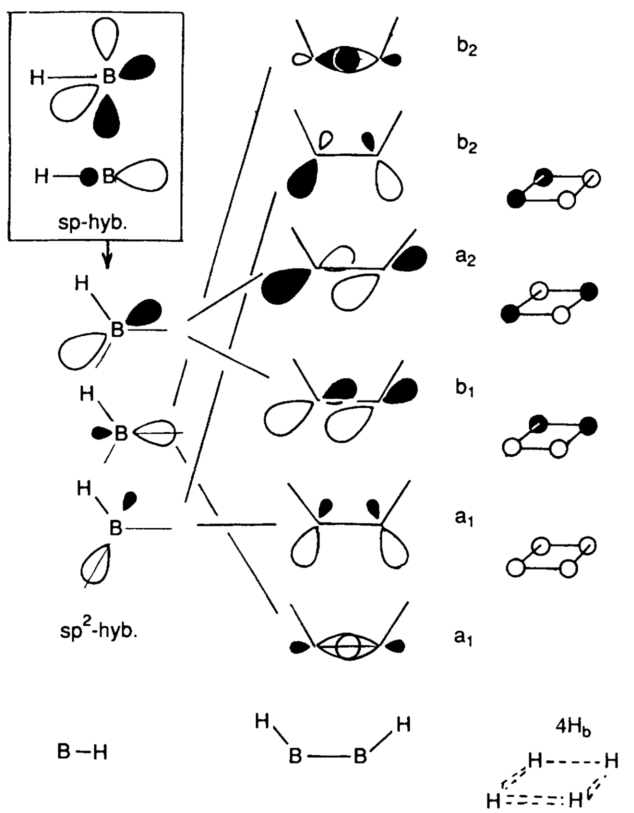

Fig. 1 Comparison of the group orbitals of the B_2H_2 unit, as constructed from the orbitals of two BH groups, and those of the $4H_b$ group shown, and then combined to form to molecular orbitals of the moiety, which includes as a matter of course the B–B connection.

In order to test whether the six hydrogen atoms can adequately replace this unit, which is the fundamental implication of the standard comparison of the two structural types, we have to make some assumptions about their physical arrangement. This is a problem as very few *arachno*-boranes have been structurally characterized, and those that have are not always the neutral species that are real comparitors with the *closo*-boranes. The known *arachno* geometries offer a variety of arrangements of these hydrogen atoms and there is no value in studying each individually as we are looking for general relationships. We decided to limit our considerations to the arrangement derived from $B_6H_6^{2-}$ and B_4H_{10}. This is clearly a good model for other known *closo–arachno* pairs, $B_{12}H_{12}^{2-}$ and $B_{10}H_{16}$ (where, of course, only $B_{10}H_{14}^{2-}$ is known but the location of the other two hydrogens is clear), $B_8H_8^{2-}$ and B_6H_{12}, $B_{11}H_{11}^{2-}$ and B_9H_{15} (again only the monoanion is known but the geometry of the neutral compound is fairly obvious). In fact the model pair will serve quite well for all known pairs except $B_7H_7^{2-}$ and B_5H_{11}. Fig. 2 compares the geometries of $B_6H_6^{2-}$ and B_4H_{10}, and highlights a major problem with the standard comparison of the two types of molecules. Two of the hydrogens, the wing-tip hydrogens, are located nowhere near the space originally occupied by the B_2H_2 unit. The four bridging hydrogens are well distributed about the space, rather lower than the boron atoms, but the wing-tips are on a line perpendicular to the original B–B connection and a long way from it. It is already difficult to see how they can possibly provide bonding contributions comparable to those of the boron atoms, but we persist with the comparison as proposed.

Fig. 1 shows that the four group orbitals of the four bridging hydrogen atoms have the same symmetries and are a good match in their distributions to four of the orbitals of the B_2H_2 moiety. These are also the four orbitals of the moiety that are capable of being involved in cluster bonding with the rest of the *closo* structure. The other two are the bonding and antibonding orbitals of the B–B connection and are not directed towards the rest of the molecule. If the two wing-tip hydrogens are included in the diagram then the two additional orbitals created will have symmetries a_1 and b_1 as the atoms are disposed perpendicular to the B–B connection orbitals. Thus they can never replace the antibonding orbital, an unimportant fact as it is never occupied. They could create an additional a_1 orbital, which whilst having no similarity to the original B–B bonding orbital may play a part in cluster bonding; and they introduce a b_1 orbital that has no counterpart in the B_2H_2 moiety. This last orbital may be important. In B_5H_9 the $4H_b$ apex provides one more orbital to the cluster-bonding set than does the BH^{2-} it replaces and this extra orbital was found to be very important in the effectiveness of $4H_b$ as a pseudo-apex. It is possible that the additional b_1 orbital has a similar role here.

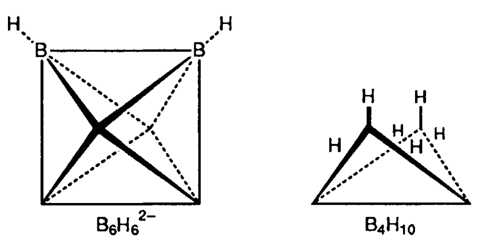

Fig. 2 Comparison of the physical positioning of the B_2H_2 group in $B_6H_6^{2-}$ and the ($4H_b$, $2H_{wt}$) atoms of B_4H_{10}

The simple picture above is supported by MNDO calculations on the isolated B_2H_2 unit. The calculated orbitals are found to be similar to those of Fig. 1 in distribution, and the energy order and spread are as expected (it is not an exact comparison because of mixing with the B–H orbitals, ignored above). At this level the comparison is not quite as good as that which we found for BH^{2-} and $4H_b$, but is certainly not bad enough to discount the possibility that the $B_2H_2^{2-}$ and 6H are equivalently effective cluster-bonding units.

Evidence for this effectiveness operating inside the electronic structure of the molecules is now sought from the computational details on pairs of molecules. The terminology used in this process is that of *closo*-borane bonding in which the $n + 1$ occupied cluster-bonding orbitals are described by atomic orbital labels owing to the approximate spherical geometry of the molecules.[6] The labels S^σ, P^σ, D^π (F^π) refer to the usual atomic distributions and degeneracies (but only as far as the total number of basis functions and the symmetry of the molecule will allow) and the superscripts refer to the basis orbitals of BH of which the molecular orbitals are predominantly composed.

arachno-B_4H_{10} *and nido*-B_5H_9.—The low symmetry of B_4H_{10} makes mixing of orbitals of distinct types (cluster σ or π, B–H bonding) a problem in analysing and comparing the electronic structure of the molecule. Hence we start with the most broad description of the structure, the localization indices, and work back to the details contained in the molecular orbitals. The numerical results of the localized-orbital calculations for B_4H_{10} and its related *closo* and *nido* compounds are: seven orbitals of 2.9–3.1-centre cluster bonding and six of two-centre BH bonding for $B_6H_6^{2-}$, exactly as expected from this perfect cluster; two of 3.18 and five of 2.73 cluster and five 2.02 BH for B_5H_9; one 3.15-centre and four 2.79-centre cluster and six BH in B_4H_{10}. Clearly the *arachno* compound is found to have two less cluster orbitals than its partners; the wing-tip hydrogen atoms are found to be involved in perfectly standard two-centre, two-electron bonds.

Fig. 3 shows the correlation of the cluster orbitals of *closo*-$B_6H_6^{2-}$, *nido*-B_5H_9 and *arachno*-B_4H_{10}, using the same symmetry axes as in Fig. 1. The correlation between the first two molecules has been analysed in detail before.[3] The orbitals of B_5H_9 and B_4H_{10} are correlated by changing the symmetry

Table 1 Distribution of the occupied orbitals of B_4H_{10} between the various groups of atoms involved in cluster bonding

Energy/eV	Symmetry	B_{hin}*	B_{wt}*	$4H_b$	$2H_{wt}$	Assignment
−31.1	a_1	45.4 (2.4)	25.7 (4.0)	13.7	1.8	S^σ
−23.6	b_1	14.6	45.9 (8.0)	13.0	9.6	P_y^σ
−21.9	b_2	41.8 (8.0)	9.3	32.0		P_x^σ
−18.9	a_1	13.8 (12.9)	17.8 (18.0)		5.8	
−15.5	a_1	9.1 (10.1)	33.0	3.9	32.0	B_{wt}–H_{wt}
−14.8	a_2	24.9	23.8	50.9		D^π
−14.3	b_1	11.5	(42.0)	5.7		B_{wt}–H_t
−13.4	a_1	20.7 (18.3)	(16.5)	5.3	4.3	
−13.1	b_1	12.6	32.5	14.9	38.9	B_{wt}–H_{wt}
−13.0	b_2	7.0 (36.0)	6.4	14.4		B_{hin}–H_t
−12.5	a_1	38.1	5.6 (4.4)	29.6	4.4	

* The total percentage on the two atoms is the sum of these two numbers. The numbers in parentheses are the percentages attributable to bonding to the terminal hydrogen atoms (equal to the percentages on those hydrogen atoms which are not included in the table, see text)

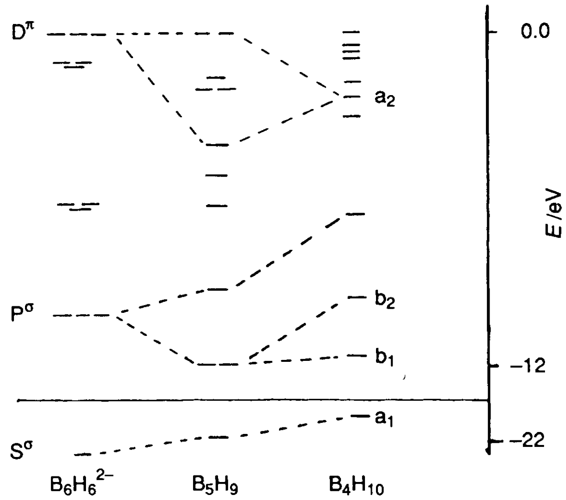

Fig. 3 Correlation of the occupied molecular orbitals of $B_6H_6^{2-}$, B_5H_9 and B_4H_{10}. The calculated orbital energies have been shifted by adding −0.61, 11.47 and 12.50 eV respectively

axis from its C_4 direction in the former to the C_2 direction of the latter. This requires some mixing of D^π orbitals as shown in Fig. 4 (and similar mixing of P^σ orbitals) to determine the orbital symmetries expected in the *arachno* compound. The results of the calculation, Fig. 3, show that just these symmetry orbitals are found and further that they have energies reasonably similar to those of the *nido* compound. There is nothing in the broad comparison of orbital symmetries and energies to account for the fewer cluster-bonding orbitals of B_4H_{10}.

Table 1 shows the composition of the 11 occupied molecular orbitals, partitioned between the symmetry-related groups of atoms (B_{hin} denotes the pair of borons on the hinge of the butterfly shape), excluding the four terminal hydrogens. In the analysis we have used a technique employed in ref. 1 to share boron atom density between B–H terminal bonding and cluster bonding. The localized orbitals of the four B–H_t bonds show these to be almost exactly equally distributed on the B and H_t atoms; therefore, in any one molecular orbital, B atom density equal to that on the attached H_t atom is attributed to B–H_t bonding and is shown in parentheses in Table 1, the remainder of the B atom density being attributed to cluster bonding. Four cluster-bonding orbitals are then readily identifiable, S^σ, P_y^σ, P_x^σ and $D^\pi(a_2)$ the latter involving the a_2 orbital of $4H_b$ of Fig. 1 and that of the boron atoms of Fig. 4. Two orbitals of a_1 and b_1 symmetry, which could on purely symmetry grounds be mistakenly counted as cluster bonding, are predominantly B–H_{wt} bonding and are the prime source of the two-centre, two-electron bonding of the H_{wt} atoms and two more of b_1 and b_2 symmetry are B–H_t bonding. The only real problem lies with three a_1 symmetry orbitals which have no clear individual assignment but between them must account for two B–H_t bonding pairs and the P_z^σ orbital. The one at −18.9 eV clearly has the right energy to be the P_z^σ and is so indicated in Fig. 3, but in fact the highest-energy orbital at −12.5 eV has a boron composition most similar to the a_1 orbital of Fig. 4. There is nothing further that can be said about these three orbitals; the localized-orbital calculation shows that they produce one cluster bonding and two B–H_t densities between them.

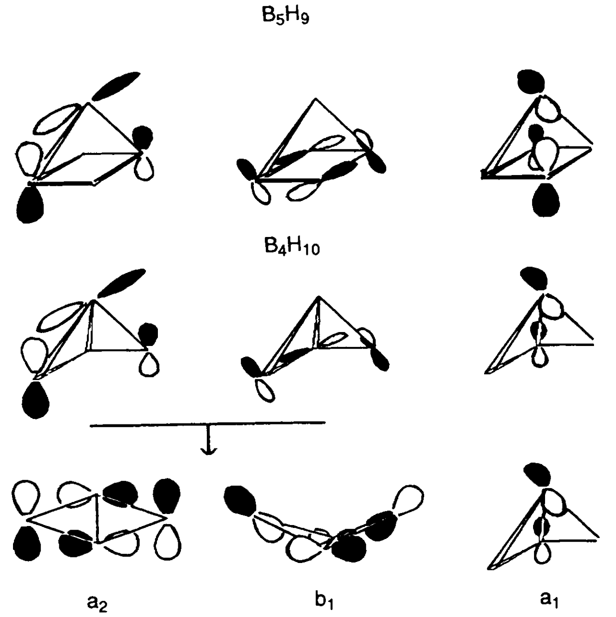

Fig. 4 Conversion of the D^π orbitals of B_5H_9 into those of B_4H_{10} by first deleting an apex and then resymmetrizing the resultant orbitals

The main point is that the calculation finds that the $4H_b$ group is involved in cluster-bonding molecular orbitals, whilst the $2H_{wt}$ is not. Even though the wing-tip hydrogens do appear in orbitals that might nominally be considered to be cluster bonding insofar as they have the expected symmetries, summing over the full set of molecular orbitals shows that they make *no net contribution* to the cluster bonding of the molecule. In many respects this is not too surprising a result; the structure 'looks' to have six *exo*-hydrogens, but it is not the way that the bonding is generally described. The two wing-tip *exo*-hydrogens are supposed/expected to contribute to cluster bonding. The question now becomes at what point does the *closo* bonding model break down.

Comparison with other Hetero-nido-*boranes*.—We first consider the stability of the *nido*-B_5H_9 structure to substitution of an apex by other heteroapices as this was the successful method in the earlier study. Calculations on CB_4H_8 with the carbon atom in the apical position produce a geometry recognizably related to the square-based pyramid but distorted by having only three basal bridging hydrogens. The calculation finds six multicentre localized orbitals, three B–H–B of 2.8 order and three C–B–B but these are closer to two- than to three-centre being of only 2.4 order which cannot be counted as seriously multicentred. This is one less multicentre bond than true *nido*, the seventh pair of electrons having gone to form the unbridged basal B–B bond. Starting the calculation with the carbon in the basal plane produces a highly distorted geometry with a CH_2 group and only four reasonable multicentre bonds, two B–H–B (2.7 order) and two B–B–B (2.8 order), whilst the two C–B bonds are close to ordinary two-centre bonding. The same is true of the geometry found by starting with a S atom in the basal plane; in fact the structure is very similar in shape and bonding with the S atom replacing the CH_2 group. Other substitutions involving the NH group or O atoms produce highly distorted geometries with very little multicentre bonding; these substitutions are too extreme to be useful.

In the previous study a comparison of *closo*-borane bonding with that of associated carborane and thiaborane molecules was the most persuasive evidence for *nido*-boranes being simply unusual hetero-*closo*-boranes. The evidence of the above is that the $4H_b$ group is essential for the correlation and that any perturbation to it breaks down the relationship. This seems highly reasonable from Fig. 1; the $4H_b$ apex does effectively substitute four of the 'missing' orbitals from the parent *closo* structure, but there are problems with the other two, so any perturbation to the $4H_b$ apex is likely to undermine the integrity of the cluster bonding.

Comparison with Anions derived from B_4H_{10}.—As it appears that the $4H_b$ apex is necessary for the *nido* electronic structure, we now consider the possibility that the *arachno* compound is simply suffering from the excessive demand of so many additional hydrogen atoms. To this effect we performed calculations on the anions $B_4H_9^-$ and $B_4H_8^{2-}$ and the results can be compared after shifting the orbital energies to account for the effect of the charges. Adding −6 and −12 eV to the calculated orbital energies of $B_4H_9^-$ and $B_4H_8^{2-}$ respectively results in orbital energy levels in which no orbital energy has changed by more than 0.8 eV (most by only ≈0.2 eV) with the exceptions of one and two orbitals, respectively, which are lone pairs on the wing-tip boron atoms corresponding to the deleted hydrogen. There is no tendency for the geometry to close up and involve these electrons in cluster bonding; in fact, except for slight angle changes involving the other two wing-tip hydrogens, the three geometries are essentially identical.

The localized orbitals also show that the three molecules are inherently very similar. In all cases there are five multicentre bonding orbitals, the degree of multicentre bonding decreasing as the charge increases, and as well defined lone pairs replace the deleted hydrogens. This argues strongly that the two extra hydrogens of the *arachno* compound are not demanding too much of the cluster-bonding system of B_4H_{10}; the molecule really does support five cluster orbitals, and four of these involve the $4H_b$ apex. From these calculations on our model system we can now predict that an *arachno*-B_nH_{n+6} molecule has $n + 1$ cluster-bonding orbitals and not $n + 3$ as expected from the standard description of their bonding.

A point rather off the main theme of this paper, but one worth noting, is the result of the localized-orbital calculation on the isoelectronic hydrocarbon anion $C_4H_4^{2-}$. This compound, which on Hückel rules should be a planar aromatic having 6π electrons, is often cited as an example of an *arachno*-hydrocarbon, as all calculations on the isolated molecule find it to have a butterfly geometry similar to that of B_4H_{10}. Our calculations also finds this geometry, and the localized orbitals are eight two-centre two-electron orbitals corresponding to the eight bonds in the molecule and two lone pairs, one on each wing-tip carbon, exactly comparable to $B_4H_8^{2-}$. We would suggest that the reason it is non-planar is that there simply is not room for six π electrons on such a small ring without the presence of an electron-withdrawing species such as a transition metal.

Other arachno-B_nH_{n+6} *Systems.*—The next question is whether this observation on a small *arachno*-borane is general or a particular feature of the size of the system. To this end we have calculated the localized orbitals of other *arachno*-boranes of known geometries, as neutral molecules and/or anions if these are the most stable form. For B_5H_{11} the calculation finds six cluster-bonding localized molecular orbitals, one of 2.67 order, two of 2.75, one of 2.80 and two of 3.2; for $B_{10}H_{16}$ 10 cluster localized orbitals in the range 2.7–3.2 and one of 2.54 index which can be counted as just making up the expected count of 11 cluster bonds. On forming the known $B_{10}H_{14}^{2-}$ anion the bonding is little affected; the lowest bond index reduces somewhat making for a rather tenuous count of eleven cluster-bonding pairs, but overall the differences are minimal and the geometry very similar. These two systems are behaving in the same manner as B_4H_{10}; even the reduction in cluster bonding between the neutral and the anion is expected from smaller systems.

The compound B_3H_9 and its anion $B_3H_8^-$ both show a significant difference from the above being found to have three cluster-bonding orbitals of 2.75 index (the three B–H–B bridges) in the neutral molecule, and two of 2.54 index (being 50% on the bridging hydrogen, 30% on the singly bridged boron atom, 12% on the doubly bridged one) and one of 3.0 index in the anion. There is a size effect prohibiting the realization of the full set of $n + 1$ cluster-bonding orbitals in these small molecules, but B_4H_{10} is large enough to avoid it.

The compound B_5H_{11} is a peculiar case meriting separate consideration. On the logic of the above we would expect it to have six cluster-bonding molecular orbitals and in fact have listed it as such above. However it is a distinctive system, known to have three bridging hydrogens and three *endo*-hydrogens, unlike any other neutral *arachno*-borane; and, importantly, the *endo*-hydrogens are arranged over an open face, not away from one as in other molecules. Taking the B_5H_9 geometry as the starting point there is clearly a problem with attaching the extra two hydrogens. Connecting these to basal B atoms, which is reasonable, will either weaken all four bridged bonds if the boron atoms are not connected, or weaken one bridged bond dramatically if they are. In practice the latter occurs and one bridged bond is lost and the hydrogen atom migrates to the apical boron atom.

Of the six localized cluster orbitals found in the calculation of the one of 2.67 index is 85% on the apical boron atom and its attached *endo*-hydrogen, the other 15% being on the other two boron atoms of the open face. This is not a good cluster orbital but is quite different to the localized orbitals involving the other two '*endo*' hydrogens which are found to be bonded by perfectly standard two-centre two-electron bonds to the basal borons. This result is in agreement with recent experimental[7] and theoretical[8] results on the geometry of B_5H_{11} which show that the apical *endo*-hydrogen has a cluster-bonding role. The molecule does not exist in the C_s symmetry that we have used but is asymmetric as this *endo*-hydrogen is bridging to one of the basal borons. It is involved in cluster bonding to the extent that the geometry will allow whilst the other two are simple terminal hydrogens. This is a different arrangement of atoms to that which we have been considering but with the same result.

Conclusion

It appears that for any *arachno*-borane with $n \geqslant 4$ boron atoms there are $n + 1$ cluster bonding pairs of electrons, not $n + 3$ as proposed in the standard view of the bonding of these molecules. If geometry follows the number of cluster-bonding pairs of electrons then *arachno*-B_nH_{n+6} should be related to *closo*-$B_nH_n^{2-}$ and *nido*-$B_{n-1}H_{n+3}$ which is obviously not the case. Alternatively one can be guided by the number of boron atoms in the molecule in establishing a pattern and the only one that we can identify that makes any consistent sense is $B_nH_{n+4} \xrightarrow{2H} B_nH_{n+6}$ in which the reduction reaction, adding two hydrogens to the *nido* structure destroys one of the $n + 2$ cluster orbitals of the *nido* system to leave $n + 1$ in the *arachno* compound. The four electrons (two from the reducing hydrogens and two for the disrupted cluster orbital) are used to form the two additional *exo*-B–H bonds.

Thus our opinion, based on a large number of calculations on a variety of compounds, is that *arachno*-boranes are simply reduced *nido*-boranes and are not electronically or structurally related in any direct manner to the ideal cluster-bonded *closo*-boranes. The structural aspect is the important one as it was this that formed the basis of the original relationship. The known structures of *arachno*-boranes does not cover the complete set of proposed molecules. However in all known cases the structure of *arachno*-B_nH_{n+6} bears as much similarity to that of *nido*-B_nH_{n+4} as it does to that of *closo*-$B_{n+2}H_{n+2}^{2-}$. It is only an accident of history that the latter similarity was emphasized to the exclusion of the former. The reduced *nido* description of *arachno*-boranes has a number of advantages in that it carries chemically sensible content. It does not require what are quite obviously *exo*-B–H bonds to be counted in the cluster-bonding system of the molecule (or in a Wade's rules manner, that BH_2 be considered to contribute four electrons to the cluster-bonding electron count). It agrees with the known structures, requiring the addition of two extra B–H bonds to the open face of the *nido* structure with, at most, the breaking of a B–B connection. However, possibly most important, it agrees with the known chemistry of the compounds.

Wermer and Shore[9] have shown that *nido*- and *arachno*-boranes with the same number of boron atoms can be interconverted by oxidation/reduction reactions. Thus $B_5H_9 \xrightarrow{Na} B_5H_9^{2-} \xrightarrow{HCl} B_5H_{11}$ is a chemical realization of our discussion, whereas $B_3H_8^- + BBr_3 \longrightarrow HBBr_3^- + (B_3H_7)$ and other similar reactions are the reverse oxidation process.[10]

We would suggest that geometry, the property that underpins the established description of the borane types, is not a sufficiently sensitive indicator to use when trying to establish trends in bonding. In the case of *closo–nido* comparisons, geometry gives the correct relationship but when this is extrapolated to *nido–arachno* comparisons it does not, although the arguments are very persuasive until one inspects them carefully. We have also found that the *nido* cluster bonding is extremely sensitive to any perturbation, rapidly decaying from multicentred bonding to a collection of two-centre bonds and partial bonds and it is probably misleading to pronounce on the overall geometry type from a consideration of the overall electron count and the structure alone. We would go further and suggest that this situation must be even more applicable to the cases of metallaboranes and metal clusters. They undoubtably have geometries similar to boranes and the electron-counting methods of Wade's rules[11] and their explanation in the isoelectronic/isolobal description of Hoffmann and Mingos[12] are very useful; but we suspect that these work largely due to the insensitivity of geometry to differences in bonding in these systems and do not really imply any genuine similarity of electronic structure. This would explain why 'anomalous', or 'non-Wadian', structures are as common in metallo-cluster chemistry as those which obey the rules.

A General Description of the Reduction Process.—We now try and provide a general explanation for why the two-electron reduction of a *nido*-borane should result in the formation of two additional *exo*-bonded hydrogens. Given the complexity of the molecules involved it is not possible to prove that this is the case but only that it is highly reasonable. We consider the addition of the two electrons to an unoccupied orbital of the *nido* cluster and the localization when these are mixed with the electron density of the highest occupied molecular orbital (HOMO) of the molecule. The model taken is that of the original *closo* molecule as a sphere and the *nido* as a truncated sphere, and we concentrate on the boron atom that is deleted in forming the latter from the former, as shown in Fig. 5. We have made extensive use of the diagrams in Stone's paper[6] on borane cluster bonding.

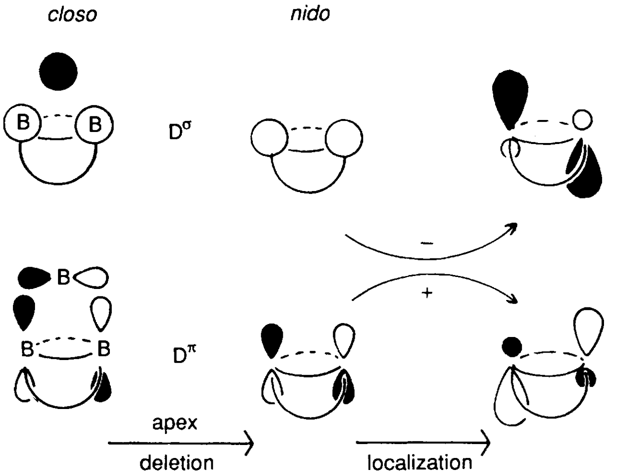

Fig. 5 Schematic orbital representations of the highest-occupied D^π orbital of a *nido* compound and a low-energy D^σ orbital which can mix to give correctly directed localized orbitals for B–H_{wt} bonding

Of the occupied cluster orbitals, those with significant density in the region of interest are destabilized by the deletion. As the D^π (F^π) set are the highest-energy orbitals of the *closo* molecule then one (or two if degeneracy is allowed) will be the HOMO of the *nido* species. The additional two electrons are going to reside in an orbital from one of the $P^{\pi/\sigma}$ (see earlier papers in this series for discussions on the precise description of these; our opinion is that they are predominantly P^π), $P^{\bar\pi}$, $D^{\bar\pi}$ or D^σ sets of orbitals. The deletion will serve to destabilize the P^π orbitals, as they are bonding to non-bonding in character, and stabilize, as they are antibonding, any of the others with significant density on the deleted boron atom. The orientation of the boron 2p atomic orbitals in the $D^{\bar\pi}$ orbitals is standard parallel π-type and therefore not much effected by the deletion, whereas the D^σ orbitals are strongly antibonding and will be stabilized. One of these is shown in Fig. 5 and, after the deletion, can be combined with the HOMO to form two orbitals, 50% of each being exactly as required to form *exo*-hydrogen bonds or lone pairs in the anions. Inspection of Stone's diagrams for P^π, $P^{\bar\pi}$, $D^{\bar\pi}$ and D^σ shows that this is the only way to produce the required result. Admittedly the explanation only accounts for 50% of the observed results of the reduction process and the remainder has to be attributed to unquantifiable effects, such as reduction in symmetry or mixing with occupied cluster orbitals, and we have not explained why this orbital in particular, D^σ, is preferred over the other D^σ or $P^{\bar\pi}$ orbitals. It does, however, show that the result is reasonable and general to all *nido*/*arachno*-B_n pairs.

There is, however, one interesting adjunct to this explanation in that it requires five boron atoms in the original *closo* (four in the *nido*) molecule to generate a D^σ orbital. This could be the reason why the *arachno*-B_3 molecules do not fit into the general pattern identified above, being based on the *nido*-B_3H_7 molecule.

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