

The Structural Significance of the Number of Skeletal Bonding Electron-pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition-metal Carbonyl Cluster Compounds

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Summary The skeletal structures of carboranes, the higher boranes and borane anions, and many transition-metal carbonyl cluster species are related to the number of skeletal bonding electron-pairs they contain; species with n skeletal atoms adopt *closo*-structures if held together by $(n + 1)$ pairs, *nido*-structures if held together by $(n + 2)$ pairs, and *arachno*-structures if held together by $(n + 3)$ pairs of skeletal bonding electrons.

THREE classes of structure are known for carboranes, higher boranes and borane anions.¹ (i) *Closo*-structures are adopted by compounds $C_aB_mH_{m+2}$ ($a = 0-2$). Their n ($n = a + m$) skeletal carbon and boron atoms occupy all the corners of the following polyhedra: $n = 5$, trigonal bipyramid; 6, octahedron; 7, pentagonal bipyramid; 8, dodecahedron; 9, tricapped trigonal prism; 10, bicapped Archimedean antiprism; 11, octadecahedron; and 12, icosahedron. (ii) *Nido*-structures are adopted by compounds $C_aB_mH_{m+4}$ ($a = 0-4$). Their n skeletal atoms occupy all but one of the corners of the $(n + 1)$ -cornered polyhedron. (iii) *Arachno*-structures are adopted by compounds $C_aB_mH_{m+6}$ ($a = 0-6$). Their n skeletal atoms occupy all but two of the corners of the $(n + 2)$ -cornered polyhedron.

All these species can be regarded as having the general formula $[(CH)_a(BH)_mH_b]^{c-}$ and as being built up from a CH and m BH units, held together by the skeletal bonding electrons they themselves provide (three from each CH unit, two from each BH unit), together with an electron apiece from the extra b hydrogen atoms, and a further c electrons in the case of anions.^{2a} The total number of skeletal bonding electron-pairs is then $\frac{1}{2}(3a + 2m + b + c) = n + \frac{1}{2}(a + b + c)$. The following generalisations hold. (i) Species with $(n + 1)$ pairs of skeletal bonding electrons ($a + b + c = 2$) adopt *closo*-structures. (ii) Species with $(n + 2)$ pairs of skeletal bonding electrons ($a + b + c = 4$) adopt *nido*-structures. (iii) Species with $(n + 3)$ pairs of skeletal bonding electrons ($a + b + c = 6$) adopt *arachno*-structures.

These generalisations are valid because the symmetries of the fundamental polyhedra are such that, in each case, $(n + 1)$ bonding skeletal MOs result from interactions between the three AOs contributed by each of the n skeletal atoms located at their corners, as has been shown by MO treatments^{2b,3,4} and because, if, when one or two BH^{2+} (or CH^+) units are removed from a *closo*-species and replaced by two or four H^+ ions, the number and symmetries of the skeletal bonding molecular orbitals will be unaffected if the H^+ ions are located in sites that reflect the skeletal symmetry. These sites are generally BHB bridging sites, occasionally terminal sites, generating BH_2 groups (as in B_4H_{10} or B_5H_{11}) or CH_2 groups (as in $C_2B_7H_{13}$).

The progressive cage-opening that accompanies formal addition of electron-pairs to a *closo*-species $B_mH_m^{2-}$ occurs because one pair of electrons is precisely the contribution made to skeletal bonding by a neutral BH unit or a cationic

CH^+ unit. Formally adding BH (or CH^+) to $B_mH_m^{2-}$ to convert it into $B_{m+1}H_{m+1}^{2-}$ (or $CB_mH_{m+1}^-$) has the same effect on the positions of the original m boron atoms as has the addition of a pair of electrons to $B_mH_m^{2-}$ to convert it into $B_mH_m^{4-}$. In each case, the original m boron atoms move to m of the $m + 1$ corners of the next higher polyhedron.

Species incorporating cage atoms other than carbon and boron can be treated similarly. For example, a Group V atom (P, As, or Sb as in $CB_{10}H_{11}P$) with no terminal hydrogen attached contributes three electrons for skeletal bonding, retaining a lone pair; accordingly, $CB_{10}H_{11}P$ adopts a *closo*-structure.

The structures of many transition-metal carbonyl cluster compounds which are difficult to describe in other terms can be rationalised simply using this approach. For example, consider the octahedral anion $Ru_6(CO)_{18}^{2-}$, effectively the parent species from which the carbonyl hydride $H_2Ru_6(CO)_{18}$, containing six terminal $Ru(CO)_3$ groups, is derived.⁵ If we allocate eighteen electron-pairs to localized two-centre Ru-C bonds resulting from overlap of 18 carbonyl carbon *sp* orbitals with 18 suitably directed metal orbitals (three on each metal) we are left with 36 metal orbitals (six on each metal), and 25 electron-pairs, for cluster metal-metal bonding. Since not all 25 electron-pairs can be accommodated in orbitals that are strongly cluster *bonding*, it is realistic to allocate three electron-pairs per metal atom to essentially *nonbonding* atomic orbitals (chosen to have appropriate symmetry for dative π -bonding to the terminal carbonyl groups). This leaves seven electron-pairs for cluster bonding orbitals derived from interactions between the remaining three AOs on each metal atom. The picture this gives of the cluster bonding of $Ru_6(CO)_{18}^{2-}$ is directly analogous to that given by Longuet-Higgins³ for the anion $B_6H_6^{2-}$. Each $Ru(CO)_3$ unit of $Ru_6(CO)_{18}^{2-}$, like each BH unit of the *closo*-borane anion, effectively contributes two electrons, and three orbitals, to the cage bonding, for which seven electron-pairs are needed to fill the seven bonding molecular orbitals.

A similar treatment is possible for the related carbonyl carbide $Ru_6(CO)_{17}C$,⁶ with the modifications that two 2-centre bonds to a doubly bridging carbonyl group replace two terminal Ru-CO links, and the central carbide carbon contributes four electrons for skeletal bonding. For $Rh_6(CO)_{16}$, the environment of the metal atoms is different, each being co-ordinated to two terminal carbonyl groups and two triply bridging carbonyl groups in a distorted tetrahedron.⁷ Allocation of an electron-pair to each of the 24 Rh-C links uses four orbitals on each metal atom and leaves altogether 30 atomic orbitals, and 19 electron-pairs, for use in cluster bonding. An apt allocation⁸ is of two electron-pairs per metal to 'nonbonding' (metal-carbonyl dative π -bonding) orbitals, leaving again three atomic orbitals on each metal, and altogether seven electron-pairs, for cluster bonding.

The analogy between these *closo*-octahedral carbonyl complexes and the borane anion $B_6H_6^{2-}$ can be extended by considering the compound $Fe_5(CO)_{15}C$, which has a square pyramidal arrangement of five $Fe(CO)_3$ units, the carbide carbon being located below the centre of the base of the pyramid.⁹ Removing this carbon atom without the electrons it contributes to the cluster bonding, *i.e.* as C^{4+} , one is left with the square pyramidal anion $Fe_5(CO)_{15}^{4-}$, the *nido*-structure of which (*cf.* $B_5H_5^{4-}$ as represented by B_5H_9) is that appropriate for a cage species with five cage atoms and seven cage bonding electron-pairs.

Other *nido*-species based on an octahedron, and incorporating both main group and transition elements as skeletal atoms, are the iron carbonyl complexes $Fe_3(CO)_9S_2$,¹⁰ $Fe_3(CO)_9Se_2$,¹¹ and $Fe_3(CO)_9(NN:CPh_2)_2$,¹² while the complex $Co_4(CO)_{10}(C_2Et_2)$ ¹³ is a further example of a *closo*-octahedral species. An extensive range of *closo*-species is of course represented by metallocarboranes with seven [*e.g.*

$(C_2B_4H_6)Fe^{II}(CO)_3$],¹⁴ nine [*e.g.* $(C_2B_6H_8)Co^{III}(\pi-C_5H_5)$],¹⁵ ten [*e.g.* $(C_2B_7H_9)Co^{III}(\pi-C_5H_5)$],¹⁶ or twelve [*e.g.* $(C_2B_9H_{11})Fe^{III}(\pi-C_5H_5)$]¹⁷ skeletal atoms, the examples cited showing the group $M(\pi-C_5H_5)$, like $M(CO)_3$, to be capable of contributing three metal orbitals of appropriate symmetry for cluster bonding. Significantly, when fewer orbitals are available, as in bis(dicarbollide) complexes $M(C_2B_9H_{11})_2^{2-}$, in which M has eight (*e.g.* Ni^{II})¹⁸ or nine (*e.g.* Cu^{II})¹⁹ electrons to accommodate in 'non-bonding' orbitals, the metal is displaced from the normal icosahedral position.

These examples illustrate the value of a common approach to the skeletal bonding of cluster species in which the cluster bonding orbitals result from interactions between three atomic orbitals of each cluster atom. Further structural examples can be found in recent reviews.^{8,20}

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