LIVERSIDGE LECTURE*
Molecular Tectonics: The Construction of Polyhedral Clusters

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1 Introduction

The art of synthesizing new compounds and the determination of their structures and properties has been the central theme of chemistry for over 150 years. In more recent times the *design* of new atomic groupings and the *purposeful synthesis* of target molecules has become increasingly possible as a result of our growing knowledge and understanding of the underlying principles. I have introduced the term 'molecular tectonics' to describe this aspect of our subject since it encapsulates the dominant characteristics of this approach to chemistry. The word tectonics derives from the Greek τεκτονικος and refers to the design and construction of buildings or other structures. In the form of plate tectonics the word has been used during the past few decades by geophysicists interested in continental drift and the structure of the Earth's crust. However, I believe the time is ripe for chemists to take over the term because, of all the sciences, chemistry is pre-eminently concerned with molecular architecture. In this lecture I shall adopt a tectonic approach, as an architect and builder, in describing the design and construction of polyhedral clusters. This presupposes the development of pragmatic bonding theories which enable us to appreciate the factors affecting the stability of polyhedral clusters and which help us to gain some understanding, at least at the phenomenological level, of the mechanistic pathways that permit their construction.

'Clusters', of course, encompass a huge field but I shall concentrate almost exclusively on the boron hydrides since the story of clusters all began with Alfred Stock's boranes [1,2] and these compounds have traditionally been at the forefront of development of cluster chemistry. It is also probably true that the boranes and their derivatives constitute the widest range of cluster structure-types available today. This approach factorizes out electron-precise clusters whose vertices are elements from the Main Groups IV, V, and VI of the Periodic Table. For example, the CH group can act as a three-connected cluster vertex in compounds of stoicheiometry C_nH_n such as tetrahedrane, cubane, cuneane, and most recently the elegant dodecahedrane, $C_{20}H_{20}$.[3] These compounds present no conceptual difficulties in bonding, though of course they present major challenges in synthesis. Likewise,

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* Delivered at a Symposium of the Dalton Division of the Royal Society of Chemistry on 22 March 1984, at Queen Mary College, London E1, and at the Universities of Dundee, Strathclyde, Birmingham, Loughborough, and Exeter

[1] A. Stock, 'The Hydrides of Boron and Silicon', Cornell University Press, Ithaca, 1933.
[2] W. N. Lipscomb, 'Boron Hydrides', W. A. Benjamin, New York, 1963; *Science*, 1977, **196**, 1047.
[3] L. A. Paquette, R. J. Ternansky, D. W. Balogh, and G. Kentgen, *J. Am. Chem. Soc.*, 1983, **105**. 5446.

clusters comprised of elements in Groups V and VI such as P_4, P_4S_3, As_4S_4, P_4O_6, and innumerable others.[4]

Naked-metal clusters of the heavy main-group elements pose greater problems of bonding and electron counting: examples are[4] Sn_5^{2-}, Pb_5^{2-}, Bi_5^{3+}, Bi_8^{2+}, Bi_9^{5+}, Sn_9^{4-}, and As_{11}^{3-}. Of even greater diversity are transition metal-carbonyl clusters and other metal–metal cluster compounds.[5] Indeed, there are many connections between these clusters and those of the boron hydrides and there has been a particularly fruitful and rewarding interaction between these two broad classes of compound at both the conceptual and the experimental level.[6]

2 The Structure of Boranes and Borane Anions

We now know that the parent boranes and their anions form three main series of compound:[7,8] *closo*-borane anions of stoicheiometry $B_nH_n^{2-}$; *nido*-boranes B_nH_{n+4} (and their anions formed by successive deprotonation, $B_nH_{n+3}^-$ *etc.*); and *arachno*-boranes B_nH_{n+6} and related anions $B_nH_{n+5}^-$. The geometrical structure of these compounds can be summarized in what might be called our **First Tectonic Principle**:

Closo-*borane anions feature closed triangulated polyhedral clusters (sometimes called deltahedra)*;

Nido-*borane clusters are formed by removal of one vertex from a* closo *cluster*;

Arachno-*borane clusters are formed by removal of two adjacent vertices from a* closo *cluster.*

Extensions are possible, hypothetically, to *capped-closo* boranes of stoicheiometry B_nH_n and to *hypho*-boranes B_nH_{n+8} and *klado*-boranes B_nH_{n+10}; examples of these series are not known for binary borane species B_nH_m or their anions, though they do occur amongst derivatives.[4]

The construction of these various clusters implies that each BH vertex contributes its remaining three orbitals and two valence electrons to the skeletal bonding of the cluster. This can be generalized as a **Second Tectonic Principle**: *The cluster geometries typified by the boranes can be generated by using as vertices atoms which contribute three orbitals in conical array to the cluster bonding.*

The perceptions embodied in these two tectonic principles find their most elegant codefication in a set of rules first enunciated by Wade in 1971.[9] For our present purpose these may be paraphrased as follows: (a) *closo*-borane anions, $B_nH_n^{2-}$, feature closed triangulated polyhedra (deltahedra) having n vertices and $(n + 1)$ skeletal bonding electron pairs; (b) *nido*-boranes, B_nH_{n+4}, have n vertices of an $(n + 1)$-vertex deltahedron occupied and involve $(n + 2)$ skeletal bonding electron pairs—the four supernumerary H-atoms form $BH_{\mu}B$ bridge bonds around the open face; (c) *arachno*-boranes, B_nH_{n+6}, have n vertices of an $(n + 2)$-vertex deltahedron occupied and involve $(n + 3)$ skeletal bonding electron pairs—some of the six

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[4] N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', Pergamon, Oxford, 1984.

[5] 'Transition Metal Clusters', ed. B. F. G. Johnson, Wiley, Chichester, 1980.

[6] K. Wade, Chapter 3, p. 193, in ref. 5, and references therein.

[7] R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.

[8] K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

[9] K. Wade, *J. Chem. Soc., Chem. Commun.*, 1971, 792.

supernumerary H-atoms form $BH_{\mu}B$ bridge bonds and the rest contribute the second H-atom in BH_2 groups in the open face.

Starting from this basis, which is now to be found in most modern textbooks of inorganic chemistry, we can ask several questions aimed at extending the range of cluster geometries so far encountered. First, what *closo* polyhedral clusters are possible, *e.g.* are they limited to a maximum of 12 vertices as in the icosahedral anion $B_{12}H_{12}^{2-}$; and second, are alternative geometric arrangements of the deltahedral vertices possible? Recent parameterized molecular-orbital calculations by Lipscomb's group[10] have shown that supraicosahedral *closo*-borane anions up to $n = 22$ have apparent overall stabilities comparable with that of $B_{10}H_{10}^{2-}$. Indeed, $B_{14}H_{14}^{2-}$ (D_{6d}) and $B_{17}H_{17}^{2-}$ (D_{5d}) have even greater stability than $B_{10}H_{10}^{2-}$ (D_{4d}) and are surpassed only by the extremely stable anion $B_{12}H_{12}^{2-}$ (I_h) itself. The calculations further suggest that certain hypothetical neutral *closo*-boranes with only $2n$ skeletal electrons might also be stable, *e.g.* $B_{16}H_{16}$ (T_d), $B_{19}H_{19}$ (C_{3v}), and $B_{22}H_{22}$ (T_d). The computational procedures that were used restricted detailed calculations to deltahedra with no more than 24 vertices, though certain even larger clusters with very high symmetry might also have considerable stability. One such structure for $n = 32$ is the elegant omnicapped dodecahedron of I_h symmetry shown in Figure 1—this has 20 seven-co-ordinate and 12 six-co-ordinate boron atoms if the 32 terminal H-atoms are also included.

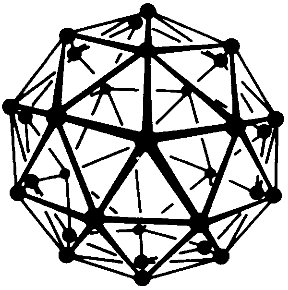


Figure 1 *The 32 vertex structure of I_h symmetry envisaged for a hypothetical* closo-*borane (anion?)* $B_{32}H_{32}$[10]

The question of alternative geometrical arrangements for the BH vertices of *closo*-borane anions has been considered by Kepert and his group.[11] For example Figure 2 shows 17 polyhedra with 12 vertices. On the basis of an admittedly oversimplified procedure, it appears that no fewer than ten of these might have a stability intermediate between those of the observed icosahedral $B_{12}H_{12}^{2-}$ (a), and the frequently invoked cuboctahedral rearrangement intermediate (b). Note, however, that very few of the structures in Figure 2 are fully triangulated polyhedra, many having faces with four, five, or even six edges. The synthetic implications of these geometrical considerations are intriguing and we shall return to them shortly.

[10] J. Bicerano, D. S. Marynick, and W. N. Lipscomb, *Inorg. Chem.*, 1978, **17**, 3443.

[11] D. J. Fuller and D. L. Kepert, *Inorg. Chem.*, 1982, **21**, 163; *Polyhedron*, 1983, **2**, 749.

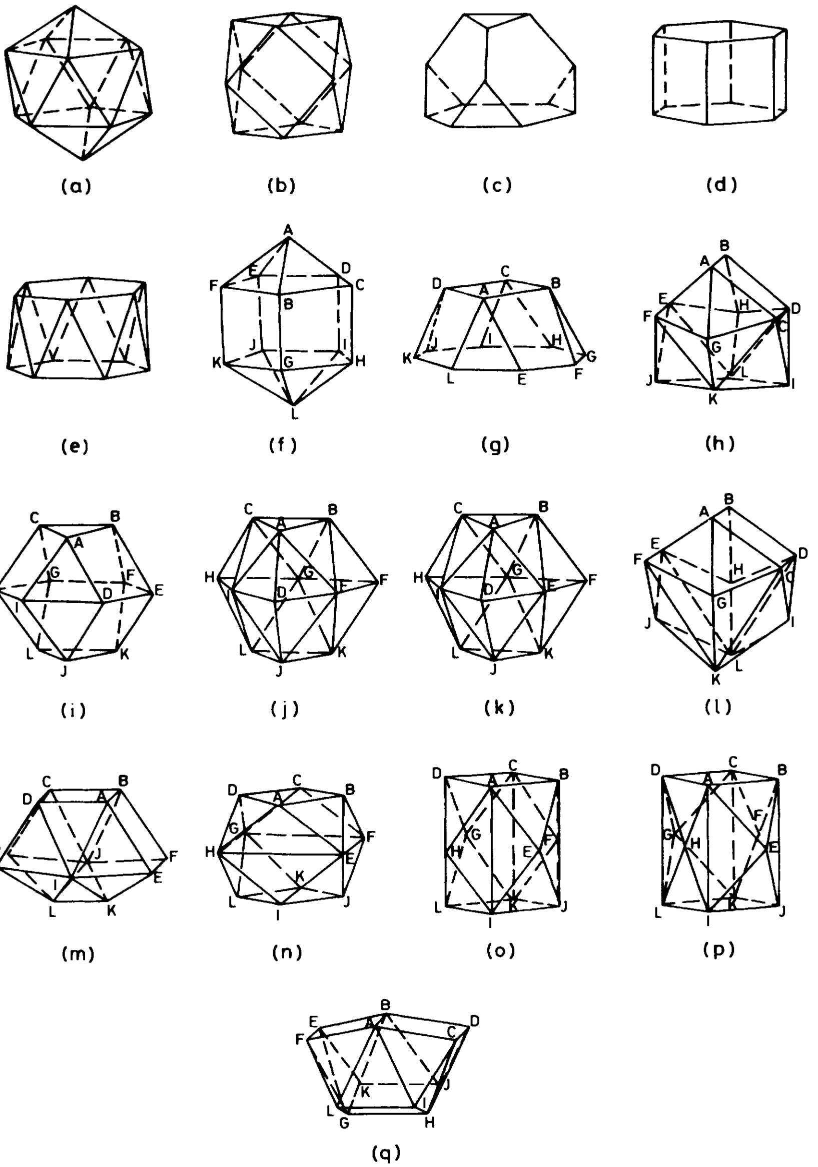


Figure 2 *Polyhedra with twelve vertices:*[11] (a) *regular icosahedron,* (b) *cuboctahedron,* (c) *truncated tetrahedron,* (d) *hexagonal prism,* (e) *hexagonal antiprism,* (f) *bicapped pentagonal prism,* (g) *square cupola,* (h) *sphenomegacorona,* (i) *anticuboctahedron,* (j) D_{3h} *icosahedron,* (k) C_{3h} *icosahedron,* (l) *tetracapped kite prism,* (m) *hebesphenocorona,* (n) *compressed cuboctahedron,* (o) *elongated cuboctahedron,* (p) *orthorhombically distorted cuboctahedron,* (q) *disphenohedron*

A third type of structural question arises when we think of the formation of *nido* and *arachno* species by the notional removal of vertices from the parent *closo* species. As can be seen in Figure 3, the skeletal connectivities of BH vertices in the anion $B_nH_n^{2-}$ range from three to six and, with the exception of $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$, each anion features two or more different types of vertex. Usually a *nido* cluster is formed by the notional removal of the most highly connected vertex. Clearly, however, a different *nido* cluster geometry would arise if a vertex of lower connectivity were removed. Whilst this particular type of geometrical isomerism is not yet known among the binary borane species themselves, it is becoming increasingly common among heteroatom boranes. An example is in Figure 4, which

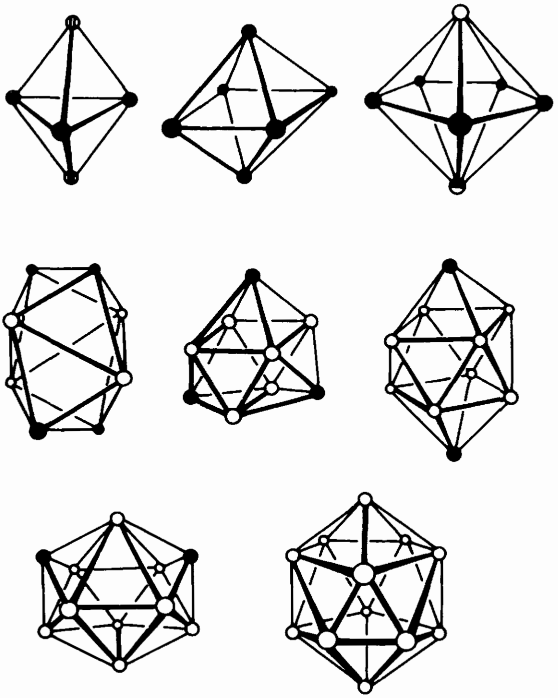
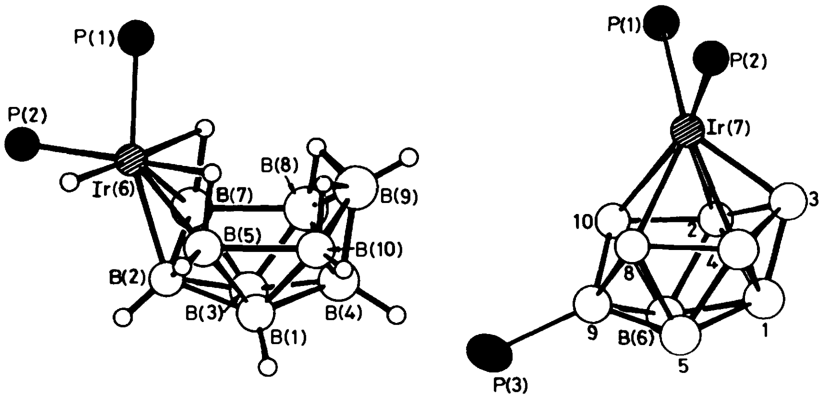


Figure 3 *Cluster geometries for the* closo-*borane anions* $B_nH_n^{2-}$ *showing the various skeletal connectivities of the* BH *vertices* (◍ = 3; ● = 4; ○ = 5; ◒ = 6). *Note: the anion* $B_5H_5^{2-}$ *is not known but the isoelectronic carbaborane* $C_2B_3H_5$ *is well characterized*

shows two *nido*-type ten-vertex structures formed by the notional removal of the six-connected and four-connected vertices respectively from the eleven-vertex *closo* polyhedron shown in Figure 3. Considerations of this sort lead to a refinement of the first tectonic principle enunciated above. This refinement can be expressed as the **First Tectonic Corollary**: *If a* closo *cluster has more than one type of vertex* (e.g.

vertices with differing connectivities to the cluster) then the geometrical shape of related nido *clusters will depend on which vertex is removed. Likewise for* arachno *clusters.*

A fourth type of structural question concerns the possibility of clusters of clusters. So far we have considered only individual clusters but these in turn may be incorporated as the subunits of larger *conjuncto*-boranes. Several possibilities can be envisaged, all of which have been observed in practise.[4] Thus, *conjuncto*-boranes or *conjuncto*-heteroatom-boranes may feature:



(a) (b)

Figure 4 *The decaborane-like structure of* nido-$[H(PPh_3)_2IrB_9H_{13}]$[12] (a) *compared with the structure of the deep purple* iso-nido-$[(PPh_3)_2Ir(B_9H_{10}{\cdot}PPh_3)]$[13] (b) *In this latter compound the* B–B *distances are in the range* 177 ± 10 pm *except for* B(8)–B(10) *which is* 222 pm (i.e. *essentially non-bonding*)

(*a*) two (or more) clusters linked by direct B–B bonds;
(*b*) clusters fused at a *commo*-B or *commo*-M atom;
(*c*) edge-fusion *via* a common pair of B or M atoms;
(*d*) confacial-fusion *via* a common triangle of B or M atoms;
(*e*) more complex conjunctions.

An excellent example of the structural subtlety that can arise amongst even the simplest—type (*a*)—*conjuncto*-boranes is afforded by our recent work on the isomers of $B_{20}H_{26}$ *i.e.* *conjuncto*-$(B_{10}H_{13})_2$ or bi(*nido*-decaboranyl).[14–16] There are four geometrically distinguishable types of B atom in *nido*-$B_{10}H_{14}$ and this

[12] S. K. Boocock, J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1982, 713.

[13] J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, unpublished work, 1982.

[14] N. N. Greenwood, J. D. Kennedy, T. R. Spalding, and D. Taylorson, *J. Chem. Soc., Dalton Trans.*, 1979, 840.

[15] S. K. Boocock, Y. M. Cheek, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1981, 1430.

[16] S. K. Boocock, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 2573.

leads to the possibility of eleven geometrical isomers of $(B_{10}H_{13})_2$, see Figure 5. Furthermore, since B(5) and B(7) are not contained within either of the molecular mirror planes of $B_{10}H_{14}$, bonding to either of them generates enantiomeric pairs; there are four such pairs in addition to the unique 5,7′ *meso*-diastereoisomer, making 15 distinct isomers in all. As expected, many of these show markedly different chemical reactions, particularly when comparison is made between isomers where the intercluster bonding involves atoms in the six-membered open face of decaborane rather than the 'hinge' (1,3) or 'apical' (2,4) boron atoms. Numerous other examples of B–B bonded *conjuncto*-boranes are known, *e.g.* $[(closo\text{-}B_{10}H_9)_2]^{4-}$, $(nido\text{-}B_5H_8)_2$, and $(arachno\text{-}B_4H_9)_2$.[4]

An example of conjunction *via* a boron atom common to two subclusters is *conjuncto*-$B_{15}H_{23}$:[17] as shown in Figure 6 this comprises a B_7 plus a B_9 unit fused

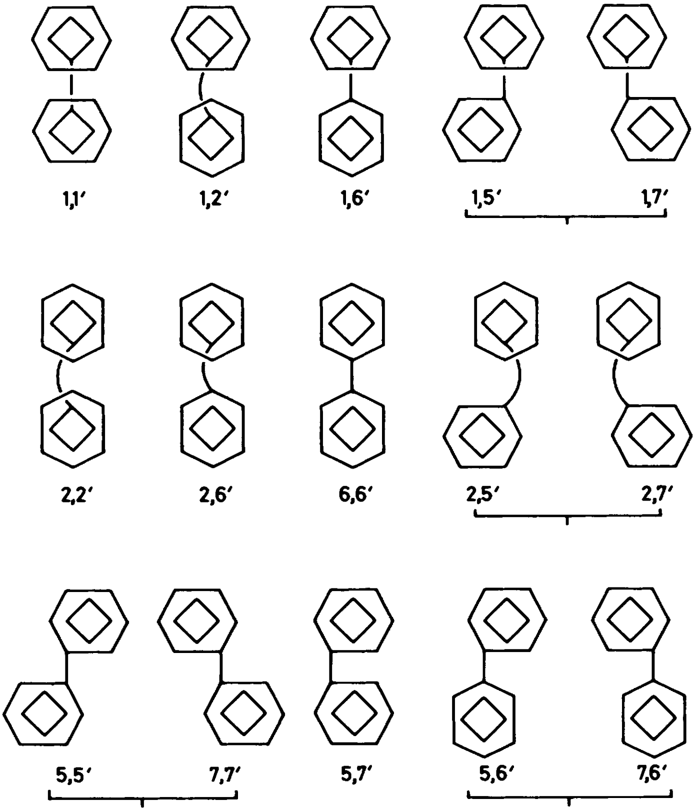


Figure 5 *Schematic representation of the eleven geometrical isomers of* $(\text{nido-}B_{10}H_{13})_2$ *using the conventional numbering system of decaborane*(*14*). *The positions* 5, 7 (*and* 8, 10) *are chiral and intercluster bonding involving one of these positions leads to enantiomeric pairs as shown. The* 5,7′ *isomer is the unique* meso-*diastereoisomer of the* 5,5′ *and* 7,7′ *enantiomeric pair*[15]

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[17] J. C. Huffman and R. Schaeffer, personal communication of unpublished work, 1981.

at a common boron atom (shaded). The structure may alternatively be regarded as a derivative of the ligand adduct LB_9H_{13} (*cf.* *arachno*-$B_9H_{14}^-$) in which the ligand is replaced by *nido*-B_6H_{10} which donates the electrons in its basal B–B bond to form a three-centre BBB bond. We shall return to this structure-type in a later section. Examples of edge-shared cluster fusion are afforded by $B_{14}H_{20}$ and the two isomers of $B_{18}H_{22}$ whereas confacial cluster fusion is found in $(MeCN)_2B_{20}H_{16}$ (triangulo) and *closo*-$B_{20}H_{16}$ (4B conjunction). Other more complex conjunctions will emerge in later sections.

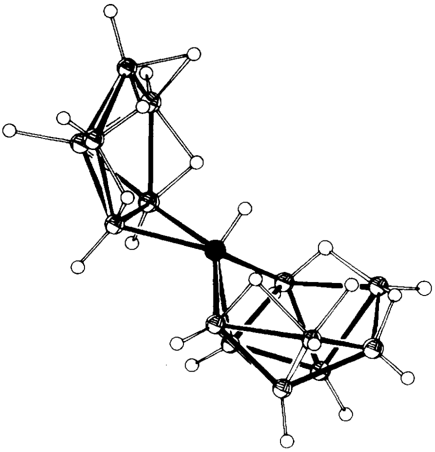

Figure 6 *Structure of* conjuncto-$B_{15}H_{23}$ *showing the* commo-B *atom shaded (see text)*[17]

So far we have been dealing with polyhedral boranes, in which the cluster vertices are occupied exclusively by boron atoms. In seeking to extend the treatment we next consider the possibility of incorporating other elements as deltahedral vertices.

3 Heteroatom Boranes

It has been known for over 20 years that carbon can be incorporated into borane clusters and that the resulting carbaboranes are often extremely stable compounds.[18] More recently it has become apparent that numerous other elements, both non-metals and metals, can act in this way and to date some 40 elements have been incorporated as heteroatoms in borane clusters.[19] As implied by Wade's rules, each boron atom contributes three frontier orbitals in conical array and two electrons to the cluster bonding.[8] With carbon the bonding can still be described in terms of the same conical array of three frontier orbitals but the heteroatom now contributes three electrons rather than two to the cluster bonding. Other possibilities can easily be envisaged and examples are known in which

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[18] R. N. Grimes, 'Carboranes', Academic Press, New York, 1970.

[19] N. N. Greenwood, *Pure Appl. Chem.*, 1983, **55**, 77 and 1415.

heteroatoms contribute 0, 1, 2, 3, or 4 electrons to the cluster bonding. Such examples fall within the original concept of Wade's rules. More drastic extensions can, however, be imagined. For example, the heteroatom might contribute 1, 2, 3, or 4 frontier orbitals and, even with three frontier orbitals, the arrangement might be for example T-shaped rather than conical. Indeed, one can envisage the possibility that some transition metals could individually contribute a variable number of electrons, a variable number of orbitals, and a variable geometrical arrangement of orbitals to the cluster bonding. This diversifies the tectonic possibilities, and extends enormously the range of structures that can be synthesized. The position can be summarized in a **Third Tectonic Principle**: *Cluster geometry depends on both the number and the mutual arrangement of the frontier orbitals contributed by each atomic vertex.*

One of the first structurally characterized examples of a 1-orbital contributor was the *nido*-pentaborane derivative $[(PPh_3)_2CuB_5H_8]$;[20] as shown in Figure 7 the copper(I) centre $\{L_2Cu–\}$ replaces a bridge-hydrogen with which it is isobobal.[21]

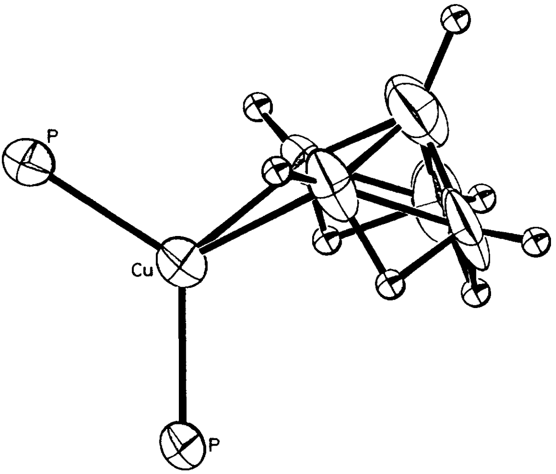

Figure 7 *Molecular structure of* $[(PPh_3)_2Cu(\eta^2\text{-}B_5H_8)]$ *with the six phenyl groups omitted for clarity. Note the similarity to the structure of* nido-B_5H_9, *one* H_μ *having been replaced by the* $\{(PPh_3)_2Cu\text{-}\}$ *moiety*

Numerous other 1-orbital contributors can act in this way *e.g.*,[22] $\{L_2Ag^I\text{-}\}$, $\{L_2Au^I\text{-}\}$, $\{L_2XNi^{II}\text{-}\}$, $\{L_2XPd^{II}\text{-}\}$, $\{L_2XPt^{II}\}$, $\{LXCd^{II}\text{-}\}$, $\{(\eta^5\text{-}C_5H_5)Be\}$, $\{Me_2B\text{-}\}$, $\{R_3Si\}$, $\{R_3Ge\text{-}\}$, $\{Me_3Sn\text{-}\}$, $\{Me_3Pb\text{-}\}$, and $\{Me_2P^{III}\text{-}\}$.

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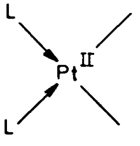
[20] V. T. Brice and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1970, 1312; *J. Chem. Soc., Dalton Trans.*, 1975, 334; G. G. Outerson, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, 1976, **15**, 1456.

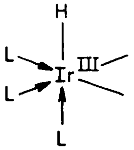
[21] N. N. Greenwood, J. A. Howard, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1976, 37.

[22] N. N. Greenwood and J. D. Kennedy in 'Metal Interactions with Boron Clusters', ed. R. N. Grimes, Plenum Press, New York, 1982, Chapter 2, p. 43.

Two-orbital contributors are exemplified by planar $\{L_2Pt^{II}\}$ (1) and octahedral $\{L_3HIr^{III}\}$ (2):



(1)



(2)

Metallaboranes that are thought to incorporate at least some contribution of this sort to the metal–boron bonding include $[(PMe_2Ph)_2PtB_8H_{12}]$,[23] $[\{(PMe_2Ph)_2Pt\}_2B_8H_{10}]$,[23] $[(CO)(PMe_3)_2HIrB_8H_{11}Cl]$,[24] $[(S_2CNEt_2)AuB_8H_{12}]$,[25] and $[\{(S_2CNEt_2)Au\}_2B_8H_{10}]$.[25] Indeed, very recently a heterobimetalladecaborane cluster has been synthesized which contains both these structure/bonding features within the one cluster *viz.* $[\{(PMe_3)_2Pt\}B_8H_{10}\{IrH(PMe_3)_2(CO)\}]$, (see Figure 8).[26]

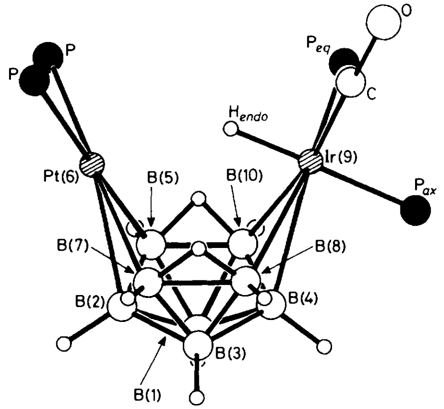


Figure 8 *Molecular structure of* $[\{(PMe_3)_2Pt\}B_8H_{10}\{IrH(PMe_3)_2(CO)\}]$ *as deduced from detailed multi-element single- and multiple-resonance n.m.r. spectroscopy. (Remember that lines within the deltahedral cluster delineate the polyhedral geometry and do not represent two-electron two-centre bonds.)*

Three-orbital contributors include the classic conical borane and carbaborane vertices $\{BH\}$ (3) and $\{CH\}$ (4) as well as isolobal groups such as $\{L_3Fe\}$ (5) and $\{(\eta^5\text{-}C_5H_5)Co\}$ both of which, like $\{BH\}$, contribute two electrons to the cluster. T-Shaped two electron contributors such as $\{LPt\}$ (6) can also be envisaged:

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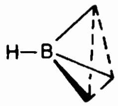
[23] S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.

[24] J. Bould, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 1903.

[25] M. A. Beckett, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 1427.

[26] J. Bould, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 2477.

Conical:



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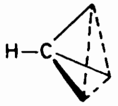

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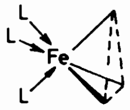
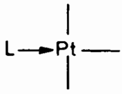


(5)

T-shaped



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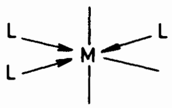

(7)

A T-shaped disposition would also result if three meridionally grouped octahedral orbitals (7) were used for cluster bonding, but examples of this have not yet been synthesized.

As an example of a compound containing a conical three-orbital metal contributor we can cite the *nido*-metallaborane $[(CO)_3FeB_4H_8]$ (Figure 9) which was first obtained in a hot/cold tube reaction (at 220/20 °C) between *nido*-B_5H_9 and $[Fe(CO)_5]$.[27] The structural analogy with *nido*-B_5H_9 is obvious, the apical $\{BH\}$ unit having been replaced by the isolobal $\{Fe(CO)_3\}$ group. When the reaction is carried out at 60—70 °C in dimethoxyethane in the presence of $LiAlH_4$, the *nido*-diferraborane $[\{(CO)_3Fe\}_2B_3H_7]$ is obtained in which a second (basal) $\{BH\}$ has also been subrogated.[28] If all five $\{BH_t\}$ vertices in B_5H_9 are notionally replaced by $\{Fe(CO)_3\}$ vertices and the four H_μ are replaced by the four-electron equivalent C, then the well-known carbidopentairon carbonyl $[Fe_5(CO)_{15}C]$ is obtained (Figure 10).[29]

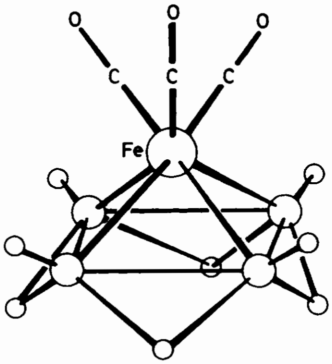

Figure 9 *The structure of* nido-$[(CO)_3FeB_4H_8]$, *an analogue of* nido-B_5H_9 *with the apical* $\{BH\}$ *group subrogated by the isolobal* $\{Fe(CO)_3\}$ *group*

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[27] N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 1974, 718.

[28] E. L. Andersen, K. J. Haller, and T. P. Fehlner, *J. Am. Chem. Soc.*, 1979, **101**, 4390.

[29] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, 1962, **84**, 4633.

Two further aspects of the structure of *nido*-$[(CO)_3FeB_4H_8]$ of great significance emerge if we rewrite the formula more explicitly as $[(CO)_3Fe\{\eta^4\text{-}B_4H_4(H_\mu)_4\}]$; replacement of the four $\{BH_\mu\}$ units by isoelectronic C atoms then generates the formula $[(CO)_3Fe(\eta^4\text{-}C_4H_4)]$, *i.e.* *tetrahapto*-cyclobutadiene iron tricarbonyl. This introduces in explicit form not only the concept of boranes as ligands but also the possibility of stabilizing fugitive species such as cyclo-C_4H_4 or cyclo-B_4H_8 by co-ordination to the metal centre. These examples and many others,[22,30] show that there is an almost continuous gradation of isostructural compounds between the polyhedral boranes, the metallaboranes, organometallic compounds, and metal carbonyl clusters. The power of Wade's rules in systematizing such apparently diverse families of compound is clear. When conical three-orbital contributors are involved these perceptions are also extremely helpful in assigning preliminary structures to compounds, perhaps obtained initially in small yields, before more effective syntheses have been devised. A good illustration of this approach concerns the iridaborane $[(CO)(PMe_3)_2IrB_4H_9]$ which was first unexpectedly obtained in milligram amounts as a by-product of the reaction of $B_4H_4(H_\mu)_4\}]$; replacement of the four $\{BH_\mu\}$ units by isoelectronic C atoms then conventional elemental analysis but the detailed n.m.r. properties indicated that the compound could reasonably be formulated as the apex-subrogated derivative of *arachno*-pentaborane, B_5H_{11}. This conviction was strengthened by the realization that the complex has two more electrons available for cluster bonding than does *nido*-$[(CO)_3FeB_4H_8]$, since it contains one more H atom and Ir is in the group following iron in the Periodic Table. The structure was confirmed by a crystal

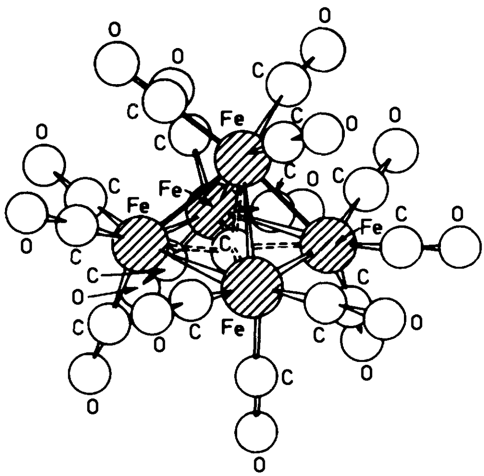

Figure 10 *The structure of* $[Fe_5(CO)_{15}C]$, *see text*

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[30] C. E. Housecroft and T. P. Fehlner, *Adv. Organomet. Chem.*, 1982, **21**, 57.

[31] J. Bould, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1982, 481.

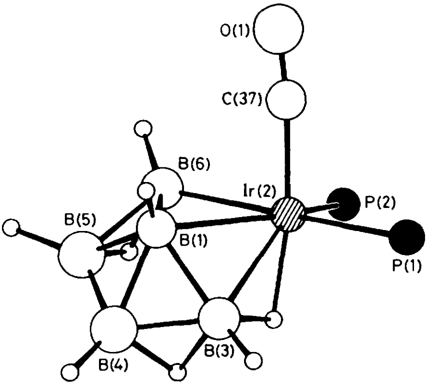

Figure 11 *The structure of the metallahexaborane cluster in* nido-[(CO)(PPh$_3$)$_2$IrB$_5$H$_8$]. *The* Ir *atom is almost coplanar with the four basal boron atoms* B(3—6) *in contrast to the position of the* Cu *atom in* [(PPh$_3$)$_2$CuB$_5$H$_8$] (*Figure* 7) *which superficially has similar stoicheiometry*

structure determination on the closely related compound *arachno*-[(CO)(PMe$_2$Ph)$_2$IrB$_4$H$_9$].[32]

Another (much higher yield) route to metallaborane clusters involving a conical three-orbital metal contributor is the oxidative insertion of an iridium(I) complex into *nido*-B$_5$H$_8^-$ to give an expanded six-vertex *nido*-cluster:[33]

$$nido\text{-}B_5H_8^- + trans\text{-}[Ir(CO)Cl(PPh_3)_2] \longrightarrow nido\text{-}[(CO)(PPh_3)_2IrB_5H_8] + Cl^-$$

As can be seen in Figure 11, the compound is a direct structural analogue of *nido*-B$_6$H$_{10}$.

The development of various high-yield routes to metallaboranes invites speculation that successive reactions might produce polymetallaboranes, and several examples of interesting and potentially useful compounds are now known. Thus, cluster expansion by oxidative insertion of [Os(CO)ClH(PPh$_3$)$_3$] into *nido*-B$_5$H$_8^-$ affords the six-vertex *nido*-[(CO)(PPh$_3$)$_2$OsB$_5$H$_9$] in 80% yield and this can then be deprotonated and reacted with *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] to give the seven-vertex *nido*-[{(CO)(PPh$_3$)$_2$Os}H$_\mu${PtCl(PMe$_2$Ph)}B$_5$H$_7$] (Figure 12).[34] The compound is notable for the presence of an OsH$_\mu$Pt grouping which exerts a stabilizing influence, since seven-vertex clusters are conspicuous by their complete absence among binary borane species themselves. The compound also illustrates the first tectonic *corollary* mentioned above since the *nido*-OsPtB$_5$ cluster (8) can be notionally generated by removal of a five-connected vertex from the parent dodecahedral *closo*-B$_8$ structure (9) and is thus a cluster isomer of the known *nido*-

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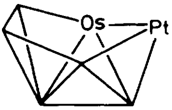
[32] S. K. Boocock, M. J. Toft, and S. G. Shore, 182nd Chem. Soc. National Meeting, New York, 23—28 August 1981, Abstract INOR 149.

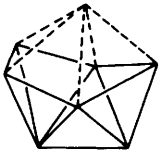
[33] N. N. Greenwood, J. D. Kennedy, W. S. McDonald, D. Reed, and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1979, 117.

[34] J. Bould, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 951.

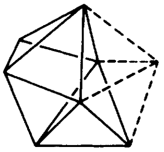
$[\{(\eta^5\text{-}C_5Me_5)Co\}_2B_5H_9]$ (11)[35] which can be notionally generated by removal of a four-connected vertex (10):



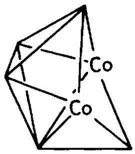
(8)



(9)



(10)



(11)

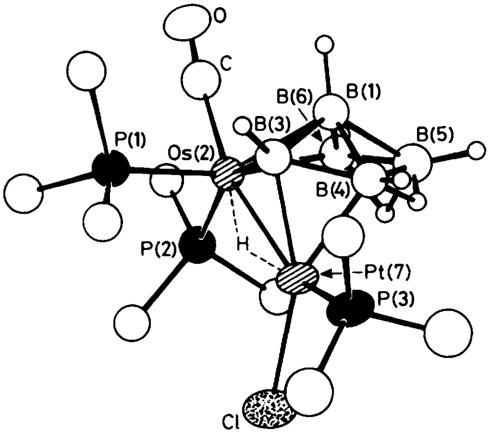


Figure 12 *The structure of the seven-vertex* nido-*heterobimetallaborane* $[\{(CO)(PPh_3)_2Os\}\text{-}H_\mu\{PtCl(PMe_2Ph)\}B_5H_7]$

As an alternative to the *nido*→*nido*→*nido* tectonic sequence just considered it is also possible to generate *nido*-metallaborane clusters in high yield by adding a vertex to an *arachno*-cluster (*i.e.* by reversing the sequence implied by the first tectonic *principle* mentioned above). An example is afforded by the reaction[36] of *arachno*-$B_9H_{14}^-$ with $[IrCl(PPh_3)_3]$ which gives an 85% yield of *nido*-$[H(PPh_3)_2IrB_9H_{13}]$ plus small amounts of the isomeric cluster *iso-nido*-$[(PPh_3)_2Ir(B_9H_{10}.PPh_3)]$; these two compounds have already been illustrated in Figure 4.

4 Novel *Closo* Deltahedral Geometries

Within the context of the Williams–Wade formalism,[7,8] *closo* structures are formally derived by capping the open face of a *nido* cluster with a conical three-orbital contributor such as {BH} or one of its many isolobal analogues. If a four-orbital contributor could be devised, then it would be possible to imagine the generation of a *closo*-type structure by the direct capping of an *arachno*-cluster with

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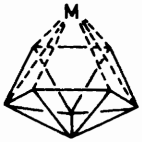
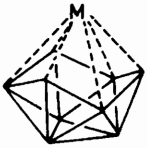
[35] T. L. Venable and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 887.

[36] J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 465.

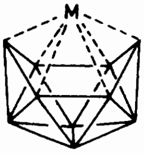
a single vertex. The process is illustrated schematically below for *arachno*-B_8, -B_9, and -B_{10} clusters leading to the closed deltahedral structures $\{MB_8\}$ (12), $\{MB_9\}$ (13), and $\{MB_{10}\}$ (14).[37]



(12)



(13)



(14)

It is notable that structure (12) differs from the tricapped trigonal pyramidal structure of $B_9H_9^{2-}$ (Figure 3) and that the structure of (13) differs from the familiar bicapped Archimedian antiprismatic structure of $B_{10}H_{10}^{2-}$ (Figure 3). However, because the skeletal structures of *arachno*-$B_{10}H_{14}^{2}$ and *nido*-$B_{10}H_{14}$ are very similar, it follows that structure (14) for $\{MB_{10}\}$ is essentially the same as that for $B_{11}H_{11}^{2-}$ (Figure 3), with the unique six-connected {BH} vertex subrogated by the metal centre. These observations can be expressed as a **Second Tectonic Corollary**: *The capping of an* arachno *cluster with a single additional vertex may result in a* closo *structure differing in geometrical shape from that formed by the capping of a* nido-*structure*. Examples of all three *iso-closo* structure types (12), (13),

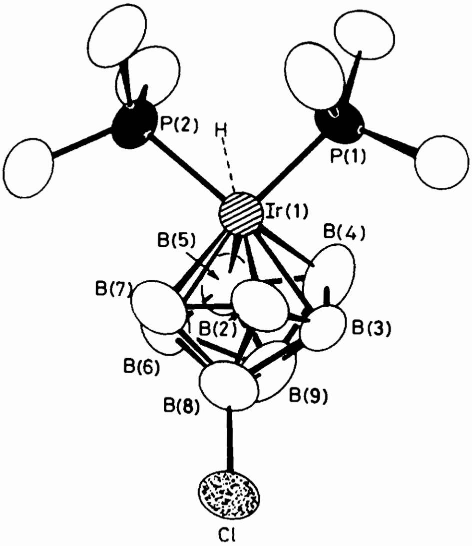


Figure 13 *The structure of* iso-closo-$[H(PMe_3)_2IrB_8H_7Cl]$ *showing the* 2,2,4,1 *stack of the central deltahedron. The* Ir–B(2,4,5,7) *distances are* 218.5 (± 1.0) pm *and* Ir–B(3,6) *are* 231 pm; *there is no significant bonding between* B(2)–B(4) *or* B(5)–B(7) (307 *and* 304 pm *respectively*)

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[37] J. E. Crook, M. Elrington, N. N. Greenwood, J. D. Kennedy, and J. D. Woollins, *Polyhedron*, 1984, 3, 901.

and (14) are now known and will be described in the ensuing paragraphs.

The first example of a nine-vertex *iso-closo* deltahedron was obtained by the mild thermolysis of *arachno*-$[H(CO)(PMe_3)_2IrB_8H_{11}Cl]$:[38] at *ca.* 80 °C there is quantitative elimination of H_2 to give *nido*-$[(CO)(PMe_3)_2IrB_8H_{10}Cl]$ and this, at 135 °C, eliminates a further mole of H_2 plus CO to give a 45% yield of the poppy red *iso-closo*-$[H(PMe_3)_2IrB_8H_7Cl]$. As can be seen in Figure 13, the central deltahedron comprises a 2,2,4,1 stack $\{B_2B_2B_4Ir\}$ rather than the usual 3,3,3 stack of a tricapped trigonal prism (Figure 3). The iridium atom is thought to contribute four orbitals and four electrons to the cluster bonding, *i.e.* it is formally in the +5 oxidation state. The facile, thermally-induced *arachno*→*nido*→*closo* cluster closure is also particularly noteworthy as the first experimental demonstration of a sequence which is implicit in the familiar Williams–Wade cluster formalism (albeit to give an *iso-closo* deltahedron as end product).

A good example of a ten-vertex *iso-closo* deltahedron is afforded by the mild thermolysis of *nido*-$[H(PPh_3)_2IrB_9H_{13}]$ (Figure 4): heating this compound at 85 °C results in the elimination of $3H_2$ and the quantitative formation of the novel, bright orange, orthocycloboronated *iso-closo*-$[(HPPh_3)(Ph_2P\overline{C_6H_4)IrB}_9H_8]$ shown in Figure 14.[36] Several other examples are also known. The 3,3,3,1 stack of the *iso-closo* deltahedron [B(8,9,10),B(3,5,7),B(2,4,6)Ir(1)] is immediately apparent and the idealized local C_{3v} symmetry of the cluster contrasts with the D_{4d} symmetry of the more familiar 1,4,4,1 stack of $B_{10}H_{10}^{2-}$ (Figure 3), or the closely

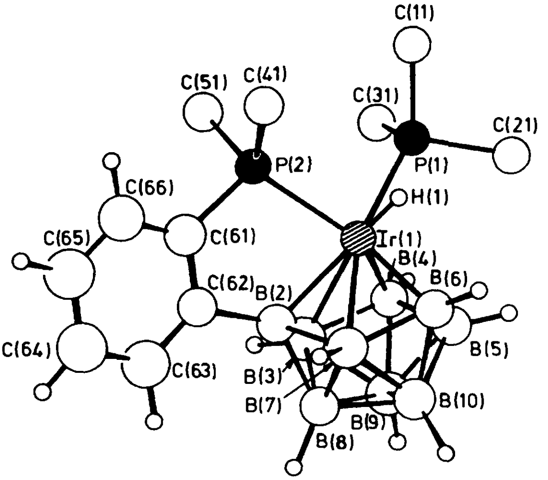

Figure 14 *The structure of* iso-closo-$[H(PPh_3)(Ph_2P\overline{C_6H_4)IrB}_9H_8]$ *showing the* 3331 *stack of the central deltahedron. Distances from* Ir(1) *to* B(2,4,6) *are in the range* 214.8–218.8 pm *and to* B(3,5,7) *are in the range* 237.8–246.0 pm

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[38] J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 346.

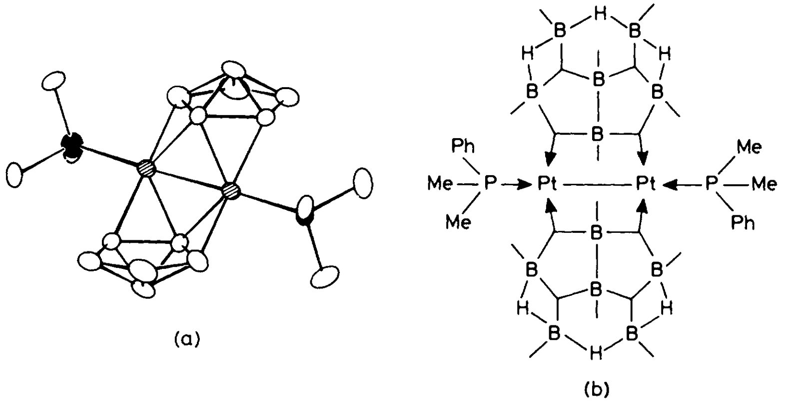
related C_{4v} local cluster symmetry of the 1,4,4,1 stack in $[(PMe_2Ph)_2NiB_9H_7Cl_2]$.[39] Again the iridium atom can be considered to be an Ir^V four-orbital, four-electron contributor to the cluster bonding.

The eleven-vertex *iso-closo* structure (14) is exemplified by $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$.[37]

5 Macropolyhedral Metallaboranes

The preceding two sections have explored the tectonic implications of replacing the conical three-orbital contributor {BH} with a range of other non-isolobal metal vertices. The perceptions emerging can be summarized as a **Third Tectonic Corollary**: *The range of cluster geometries observed for parent boranes and their anions can be considerably extended by incorporating as vertices metal atoms which differ from boron in the number or mutual arrangement of their frontier orbitals.* In the present section we explore the tectonic consequences of one specific modification of vertex-bonding geometry, namely the replacement of a conical by a T-shaped three-orbital contributor. We can anticipate the detailed results by stating a **Fourth Tectonic Corollary**: *The* T-*shaped distribution of three frontier orbitals facilitates the construction of complex macropolyhedral clusters.*

Perhaps the first indication of this structural effect was the formation of the extremely stable 14-atom cluster $[(PMe_2Ph)_2Pt_2B_{12}H_{18}]$ [Figure 15(a)].[40] The compound is formed in several quite diverse reactions, though often in low



(a)

(b)

Figure 15 (a) *The structure of the macropolyhedral dimetallaborane* $[(PMe_2Ph)_2Pt_2B_{12}H_{18}]$ *comprising two* (η^3-B_6H_9) *subclusters joined in transoid configuration to a central* P–Pt–Pt–P *group* (Pt–Pt distance 264.4 pm). (b) *Simplified bonding scheme showing the* T-*shaped distribution of the three orbitals contributed to the cluster by each of the two* {(PMe$_2$Ph)Pt} *vertices; the bonding in each of the borane subclusters is typical of* nido-$B_6H_9^-$

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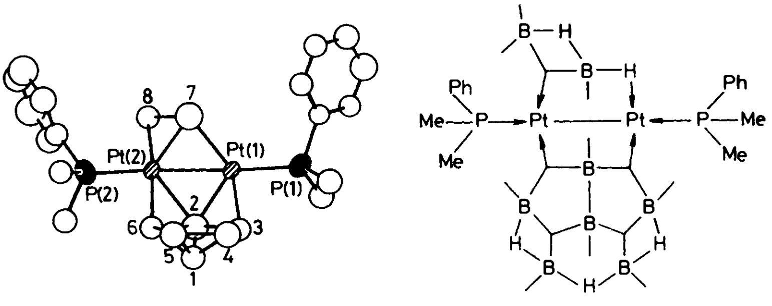
[39] N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, in the press.

[40] N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1980, 37.

yield;[23,40,41] The more open *transoid* centrosymmetrical geometry is notably different from the *cisoid* configuration of the known 'isoelectronic' binary borane, $B_{14}H_{20}$, *i.e.* $[(H_2B_2)B_{12}H_{18}]$.[42] A variant on this theme is the related compound $[(PMe_2Ph)_2Pt_2B_8H_{14}]$ which is shown in Figure 16(a).[41] The central linear P–Pt–Pt–P array is still present as is one of the (η^3-B_6H_9) subclusters, but the second (η^3-B_6H_9) has been replaced by the vestigial (η^3-B_2H_5) group [Figure 16(b)]. A fascinating feature of this latter compound $[(PMe_2Ph)_2Pt_2B_8H_{14}]$ is that it is isoelectronic with the known compound $[\{(PMe_2Ph)_2Pt\}_2B_8H_{10}]$, the two additional phosphine ligands providing the four electrons formerly supplied by the extra four H-atoms; despite this the structures of the two compounds are entirely different as can be seen by comparing the *arachno*-$B_{10}H_{14}^{2-}$-like structure of $[\{(PMe_2Ph)_2Pt\}_2B_8H_{10}]$ (Figure 17)[23] with the macropolyhedral structure of



(a) (b)

Figure 16 (a) *The structure of the diplatinadecaborane* $[(PMe_2Ph)_2Pt_2B_8H_{14}]$ *comprising an* (η^3-B_2H_5) *and an* (η^3-B_6H_9) *subcluster joined to a central linear* P–Pt–Pt–P *group* (Pt–Pt *distance* 262.1 pm); *note the* cisoid *location of the two phenyl rings in contrast to their* transoid *location in Figure* 15(a). (b) *Simplified bonding scheme showing similarity to that in Figure* 15(b)

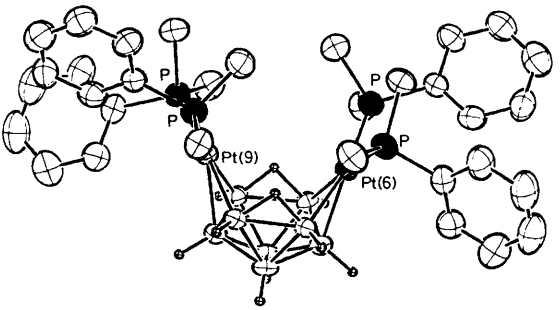


Figure 17 *The* arachno-$B_{10}H_{14}{}^{2}$ *-like structure of the diplatinadecaborane cluster* $[\{(PMe_2Ph)_2Pt\}_2B_8H_{10}]$

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[41] R. Ahmad, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 1019.

[42] J. C. Huffman, D. C. Moody, and R. Schaeffer, *J. Am. Chem. Soc.*, 1975, **97**, 1621.

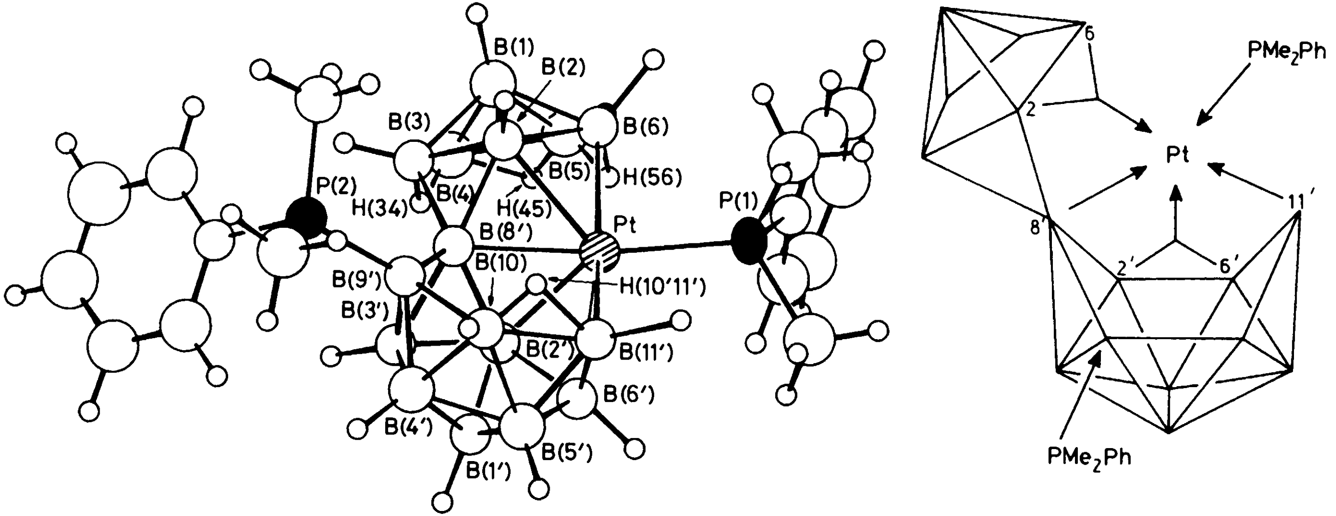
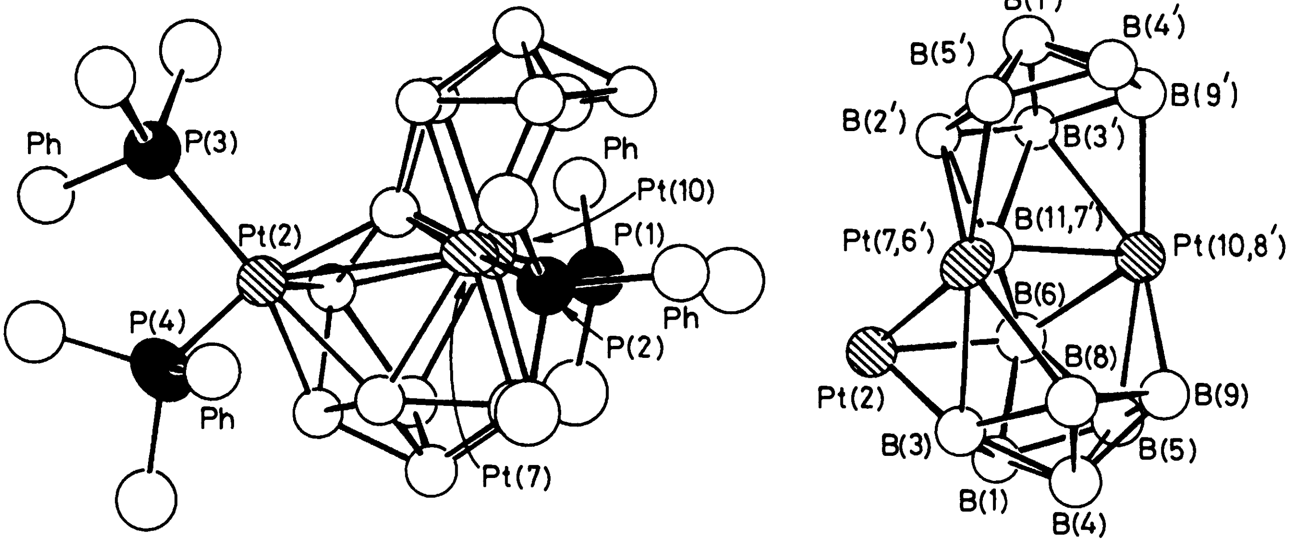


Figure 18 (a) *The structure of the 17-vertex macropolyhedral platinaborane* [(PMe$_2$Ph){PtB$_{16}$H$_{18}$(PMe$_2$Ph)}] *showing the* η^6*-bonding of the* B$_{16}$ *cluster to the* Pt *atom* via B(6)B(2)B(8′)B(2′)B(6′)B(11′) *and with* Pt–B *distances in the range* 223—229 pm. (b) *A stick diagram illustrating the* B$_6$ *and* B$_{10}$ *subclusters fused at* commo-B(8′) *and a simplified version of the bonding envisaged to the* Pt *atom*



(a)

(b)

Figure 19 (a) *The structure of the 17-vertex macropolyhedral triplatinaborane* [$(PMe_2Ph)_4Pt_3B_{14}H_{16}$]. (b) *A slightly different orientation of the cluster showing two* nido-*hexaboranyl subclusters conjoined by a* Pt_3B_2 *belt*

$[(PMe_2Ph)_2Pt_2B_8H_{14}]$ [Figure 16(a)].

An even more complex series of 17-vertex macropolyhedral metallaboranes has been obtained by mild thermolysis of the nine-vertex *arachno*-platina-nonaborane $[(PMe_2Ph)_2PtB_8H_{12}]$ in refluxing toluene (*ca.* 110 °C).[43–45] The first such compound to be characterized was the air-stable, flame-red macropolyhedral cluster $[(PMe_2Ph)\{PtB_{16}H_{18}(PMe_2Ph)\}]$ [Figure 18(a)].[43] The structure can be viewed as a complex between a tetradentate η^6-B_{16} ligand and the platinum centre. The B_{16} *conjuncto*-borane (which is at present unknown as a neutral binary borane) features a B_6 and a B_{10} subcluster fused at a *commo*-B(8′) atom [Figure 18(b)] and is clearly related to the $\{B_6 + B_9\}$ structure of *conjuncto*-$B_{15}H_{23}$ shown in Figure 6. As such the complex affords a further example of a hypothetical borane cluster stabilized by co-ordination to the metal centre. An alternative description of the macropolyhedral cluster is as a *nido*-$\{PtB_7\}$ subcluster edge fused along the Pt–B(8′) vector to a *nido*-$\{PtB_{10}\}$ subcluster.

A second 17-vertex macropolyhedral cluster isolated from the same thermolysis reaction is the unprecedented dark-green trimetallaborane $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$ shown in Figure 19(a).[44] The cluster geometry is shown in a slightly different orientation in Figure 19(b); it comprises two *nido*-type B_6 subclusters conjoined *via* a complex five-atom belt, $PtPtB_2Pt$. The two B_6 subclusters are oriented with their bases parallel and facing. When the three Pt atoms are removed, the remaining hypothetical B_{14} ligand is seen to have a quite different structural motif than that in the known $B_{14}H_{20}$ or the 14-atom skeleton in Figure 15.

It is possible to devise a simple set of localized bonding orbitals to describe the bonding in both the 17-vertex clusters discussed in the preceding two paragraphs but this enterprise is unnecessarily detailed for our present purpose. Suffice it to say that the introduction of metal centres having vacant bonding orbitals or readily removable ligands often facilitates the synthesis or geometric rearrangement of clusters or the construction of macropolyhedral metallaboranes.

6 Summary

Some 40 different elements can be incorporated as cluster vertices in polyhedral heteroboranes.[19] Over 75 different cluster geometries have been identified so far amongst the products of cluster syntheses [19,22] and well over half of these have no counterpart among the familiar structures of the binary boranes and borane anions. This diversity arises in part from the fact that metal centres can contribute varying numbers of orbitals and valence electrons to the cluster bonding. In fact, a selection of metal vertices is available which can be thought to contribute 1, 2, 3, or 4 orbitals and 0, 1, 2, 3, or 4 bonding electrons to the cluster. This extends considerably the Williams–Wade formalism[6–9] which has proved so helpful for

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[43] M. A. Beckett, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 552.

[44] M. A. Beckett, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 1228.

[45] M. A. Beckett, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, submitted.

clusters constructed from vertices which are formal conical three-orbital contributors.

A series of tectonic principles and corollaries has been formulated which incorporate these earlier perceptions and which extend them systematically to a wide variety of other circumstances. In particular, examples are presented in which:

(*a*) *iso-nido* and *iso-arachno* clusters are obtained from *closo* deltahedra by notional removal of vertices with differing connectivities;

(*b*) *iso-closo* deltahedra are obtained by the capping of *arachno* rather than *nido* clusters with a single vertex which can be thought to contribute four orbitals rather than three to the cluster bonding;

(*c*) macropolyhedral *conjuncto*-boranes are generated by incorporation of metals which contribute a T-shaped or related suite of frontier orbitals.

This tectonic approach not only helps to systematize the known types of polyhedral cluster but also places on a firm and more systematic basis the design and construction of novel polyhedral clusters, thereby assisting the planned synthesis of potentially useful or interesting target molecules.