LUDWIG MOND LECTURE*
Taking Stock: The Astonishing Development of Boron Hydride Cluster Chemistry

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1 Introduction

It is a great privilege to have been invited to give the Ludwig Mond Lectureship during this 150th Anniversary meeting of the Royal Society of Chemistry, and it is a particular personal pleasure to be able to deliver it, for the first time I believe, on a subject in main-group element chemistry: the boron hydrides. In my view this is one of the most exciting and significant areas of modern chemistry and, in choosing my title, I want to pay tribute to the seminal studies of Alfred Stock who started to work on the boranes in 1909, the year that Ludwig Mond died. Stock was born in 1876 when Mond was 37 years old, and he was 33 years old when Mond died. His first publication on the boron hydrides came 3 years later in 1912.

Stock not only pioneered the chemistry of boron and silicon hydrides but he developed, from scratch, the chemical high-vacuum techniques which enabled him to study these extremely reactive, spontaneously flammable materials. He also made important contributions to chemical education and nomenclature, and to the pathology and detection of mercury poisoning from which he himself disastrously suffered. He therefore made major contributions to what we would still regard as the four main concerns of modern chemistry:

(i) Health and safety at work in the laboratory.
(ii) Chemical education at all levels.
(iii) The development of new techniques for handling and measuring compounds.
(iv) The synthesis and characterization of novel chemical combinations.

It is the last of these, Stock's experimental studies on the extraordinary new class of compounds, the boranes, which I want to emphasize in this lecture. Stock's first five papers on the boron hydrides appeared during 1912—1914 and in all he published just 16 papers on the boranes and their derivatives over a period of 20 years. The classic summary of his findings is in his George Fisher Baker Lectures given at Cornell University in 1932.[1] He synthesized and characterized six boranes – B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ – plus a seventh of uncertain composition, possibly B_6H_{12}. Experimentation was made even more difficult by the fact that these compounds rapidly react and interconvert with one another. He also recognized that they formed two rudimentary classes distinguished by their formulae, *viz.* B_nH_{n+4} and B_nH_{n+6}, which we now know as *nido* and *arachno* boranes. No other laboratory anywhere in the world undertook work on these fiendishly difficult compounds during this time but at the very end of the period, in 1931, H. I. Schlesinger and A. B. Burg in Chicago published their first paper on diborane and pentaborane.[2] In fact, no additional boranes beyond Stock's original six or seven were synthesized until 1958 when nonaborane, *n*-B_9H_{15}, was made by W. V. Kotlensky and R. Schaeffer[3] – a hiatus of 30 years – though the very stable anion BH_4^- was made by H. I. Schlesinger and H. C. Brown in 1940.[4] You will notice that BH_4^- is isoelectronic with both methane, CH_4, and the ammonium ion, NH_4^+, but it differs notably from them in being able to form stable complexes as a monohapto, dihapto, or even trihapto ligand.

Starting, then, from this baseline of a mere half-dozen compounds, I want to trace the astonishing developments which have occurred during the past three decades, as a result of which we now know over 50 neutral boron hydride molecules and a similar number of polyhedral borane anions – 100 binary borane species in all, so far![5] In addition there are literally thousands of derivatives incorporating elements from all areas of the periodic table.

From the very beginning the boranes posed serious problems of both structure and bonding. Stock's earliest publications predated the Lewis–Langmuir octet theory of electron-pair bonds by some five years and the boranes proved to be that theory's most troublesome 'exception'. Boron is in Group III (group 13) of the periodic table, so one would expect the simplest hydride to be BH_3. Yet, despite extensive and diligent experimentation, no sign of BH_3 was ever encountered by Stock, and the simplest member of the series was diborane, B_2H_6. The stoicheiometry is clearly similar to that of ethane, C_2H_6, but as the boron atom has one electron less than carbon there are apparently insufficient electrons to form two-centre two-electron bonds between each contiguous pair of atoms. The boranes were said to be 'electron deficient' but, as Robert Rundle correctly observed, it was really chemists who were 'theory deficient'.

The key to the dilemma was found by H. C. Longuet-Higgins in the late nineteen-forties with his seminal concept of the three-centre two-electron bond: if electrons are in short supply then a pair of electrons can bond three atoms in a triangular array, rather than just two atoms.[6] He successfully established and interpreted the bridged dimeric structure of B_2H_6 and then, generalizing from three-centre to multi-centre bonding, made the brilliant prediction of stable polyhedral dianions of unprecedented structure, namely the octahedral cluster $B_6H_6^{2-}$ and the icosahedral cluster $B_{12}H_{12}^{2-}$. This was five years before A. R. Pittochelli and M.F. Hawthorne serendipitously discovered such species in 1960.[6] The structural and bonding systematics

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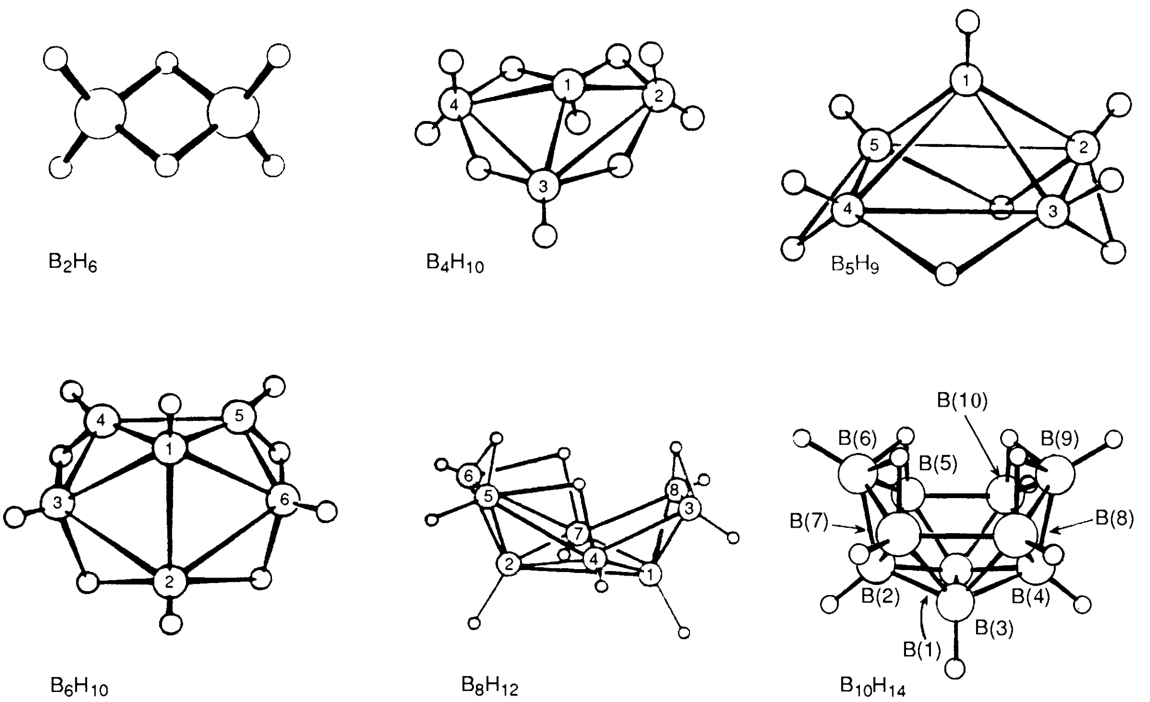

Figure 1 Molecular structures of some simple boranes: large circles represent boron atoms and small circles represent hydrogen atoms. Note the prevalence of triangles of boron atoms and the occurrence of 2-coordinate bridging hydrogen atoms.

were developed into a topological theory by W. N. Lipscomb[7] and the apotheosis of these ideas found expression in the elegant yet powerful simplicity of K. Wade's rules (in 1971) relating electron counting to cluster geometry.[8]

The structures of some of the simpler boranes are shown in Figure 1 from which it can be seen that the predominant structure motifs are fragments of triangulated polyhedral clusters. However, in viewing these and similar structures it is crucial always to remember that straight lines joining pairs of atoms no longer necessarily represent pairs of electrons, they merely indicate geometrical connectivities: three-centre and multicentre bonding is the rule.

As first shown by R. E. Williams in 1971 and elaborated by him in a later review,[9] the observed clusters fall into three geometrically distinct stoicheiometric series which he called *closo*-$B_nH_n^{2-}$, *nido*-B_nH_{n+4} and *arachno*-B_nH_{n+6}. The last two stoicheiometries clearly correspond with Stock's two rudimentary series mentioned earlier. The structural relations between the three series are shown in Figure 2; with *nido*-boranes being formed by removing one highly connected vertex from the corresponding *closo* polyhedron, and *arachno*-boranes by removal of two normally adjacent vertices. The electron-counting systematics of Wade's rules then indicate that clusters with $(2n + 2)$ skeletal electrons adopt a *closo* structure, those with $(2n + 4)$ skeletal electrons adopt a *nido* structure, and those with $(2n + 6)$ an *arachno*.

So much by way of general introduction. For the rest of the lecture I want to concentrate on what I believe are the two major intellectual puzzles and challenges of polyhedral borane chemistry: first, what are the mechanisms and reaction pathways by which these cluster molecules interconvert so facilely and build up into still larger clusters; and second, is this cluster behaviour unique to boron or can other elements be incorporated into the cluster framework? As a result of work in our own laboratory and elsewhere important advances have been secured in both these areas and I shall attempt to summarize some of the more significant results obtained so far.

2 Gas-Phase Thermolysis Reactions

Stock observed in his earliest experiments that the simple boranes rapidly interconvert with each other at very moderate temperatures. However, without large-scale supplies of the purified boranes, and in the absence of rapid and reliable methods for product analysis, detailed kinetic and mechanistic studies were impossible. And yet the intriguing question remains: how does diborane manage to build up into larger clusters – what are the mechanisms of these facile interconversion and aufbau reactions which occur so readily at what are really very low temperatures, in the range 50—150 °C? The problem is clearly one of some complexity and the answers are only now becoming clear. In fact, the reactions occurring in gaseous mixtures of boron hydrides probably comprise one of the most complex sequences of interconnected reactions ever to be studied in any detail in the whole of chemistry. Kinetic studies began in the USA in 1951. Where have we got to 40 years on?

2.1 Thermolysis of Diborane(6)

Early work established that the gas phase thermolysis of diborane at moderate temperatures and pressures was homogeneous with an order of reaction of 3/2, at least in the initial stages. The activation energy appeared to be in the range 92—135 kJ mol^{-1}, the most recent value being 93 ± 5 kJ mol^{-1}. The generally accepted mechanism (until two years ago) was a three-step process:

$$B_2H_6 \overset{\text{equil.}}{\rightleftharpoons} 2\{BH_3\} \qquad (1)$$

$$\{BH_3\} + B_2H_6 \overset{\text{fast}}{\rightleftharpoons} \{B_3H_9\} \qquad (2)$$

$$\{B_3H_9\} \overset{\text{slow}}{\rightleftharpoons} \{B_3H_7\} + H_2 \qquad (3)$$

In these and subsequent reactions, species in curly brackets are non-isolable reaction intermediates. The scheme clearly explained the 3/2 order in diborane since the rate-determining reaction 3 involved a triboron species. It was also consistent with the observation that the rate of thermolysis was repressed by the presence of an excess of dihydrogen, and with several other features of the reaction. However, recent very high level computations were able to locate the transition state and led to the

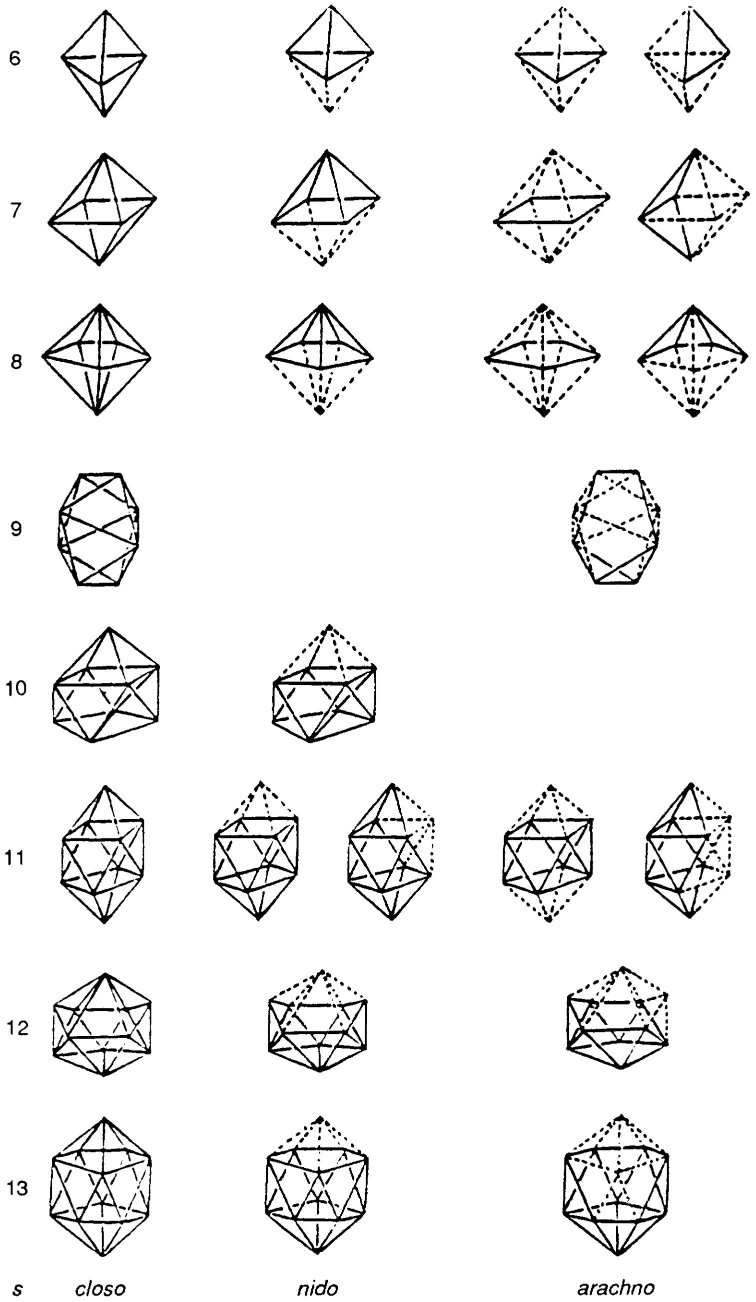

Figure 2 The polyhedral shapes of *closo*, *nido*, and *arachno* boranes and related clusters; *s* = number of skeletal electron pairs. The one *exo* hydrogen atom attached to each skeletal atom in these species, and the *endo* hydrogen atoms of the *nido* and *arachno* species have been omitted for clarity.

(Reproduced by permission from M. E. O'Neill and K. Wade, 'Comprehensive Organometallic Chemistry', Vol. 1, ed. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford 1982, Chapter 1).

conclusion that it was reaction 2 that was rate-determining.[10] The calculations were also at variance with the literature value of about 5:1 for the relative rates of thermolysis of B_2H_6 and B_2D_6, giving a value of only about 1.7 for this ratio if reaction 2 were rate-determining. To resolve these difficulties we undertook a careful experimental reinvestigation of the relative rates using a sophisticated mass spectrometric technique to monitor the initial stages of the reaction.[11] As a result of many runs at 147 °C and an initial pressure of about 3.5 mm Hg we found the ratio to be 2.57 ± 0.65. We had previously found[12] that, under similar conditions, the initial rate of decomposition of B_2H_6 was decreased by a factor of about 3.4 in the presence of a 14-fold excess of H_2 and subsequent work showed that D_2 depressed the rate of thermolysis of B_2D_6 by a similar amount.[13] We can therefore now say that, taken as a whole, the experimental and computational results indicate that the rate-determining step following the symmetric dissociative equilibrium 1 is neither the *formation* of $\{B_3H_9\}$ by reaction 2 nor its subsequent *decomposition* by reaction 3 but rather the *concerted* formation and decomposition of $\{B_3H_9\}$ in a single step:

$$\{BH_3\} + B_2H_6 \overset{\text{slow}}{\rightleftharpoons} \{B_3H_7\} + H_2 \qquad (4)$$

This is an important result, but it is salutary to recall that it has taken so long to get an explanation of this reaction which Alfred Stock first observed and exploited 75 years ago. Moreover, this only takes us as far as $\{B_3H_7\}$ which is itself an unstable, non-isolable reaction intermediate. There is no time to tell the rest of the story in any great detail but a few other highlights can be briefly mentioned. The first isolable intermediate was established as B_4H_{10} by the elegant work of Riley Schaeffer.[14] It is probably formed mainly by the reaction:

$$\{B_3H_7\} + B_2H_6 \rightarrow B_4H_{10} + \{BH_3\} \qquad (5)$$

However, B_4H_{10} is itself unstable above about 45 °C so we decided to study its decomposition and co-thermolysis with other small boranes.

2.2 Thermolysis of Tetraborane(10)[15,16]

When we started, there was uncertainty about all aspects of B_4H_{10} thermolysis. By developing a novel, versatile, and rapid mass spectrometric method of product analysis we were able to establish that the initial gas-phase reaction was homogeneous and first order, with an activiation energy of 99.4 ± 3.4 kJ mol^{-1}. A typical reaction profile is shown in Figure 3 from which it can be seen that, during the first 30 min at 78 °C, more than half of the B_4H_{10} is consumed, and there is a rapid formation of H_2 and B_5H_{11} with lesser amounts of B_6H_{12}, B_2H_6, and $B_{10}H_{14}$. Further work showed that added H_2 substantially retarded the rate of reaction but left the activation energy unchanged; there was likewise no change in the relative rate of B_5H_{11} production but a marked increase in the rate of B_2H_6 production, almost complete inhibition of solid 'polymer' formation, and a complete absence of B_6H_{12} and $B_{10}H_{14}$.

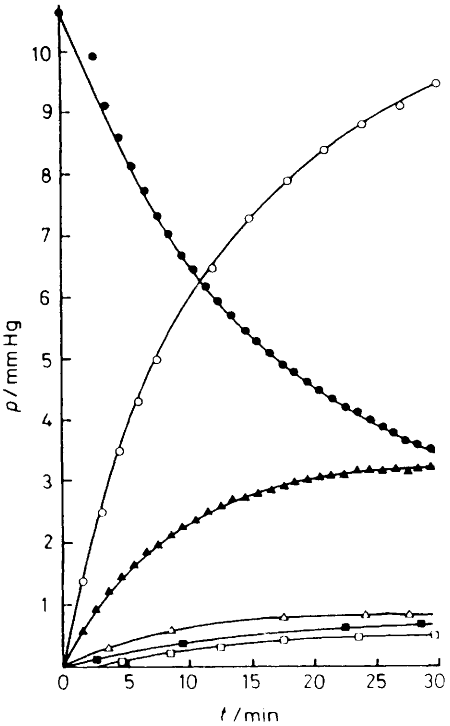

Figure 3 Reaction profile for the thermolysis of B_4H_{10} (see text): (○)H_2, (●)B_4H_{10}, (▲)B_5H_{11}. For clarity, only selected data points have been plotted for the minor species (■)B_2H_6, (△)B_6H_{12} and (□)$B_{10}H_{14}$.

Furthermore, in the presence of D_2, B_4H_{10} rapidly underwent H/D exchange. These results can all be interpreted in terms of an initial rate-determining loss of H_2 from B_4H_{10} to form $\{B_4H_8\}$ followed by rapid reaction with a second molecule of B_4H_{10}:

$$B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2 \qquad (6)$$

$$\{B_4H_8\} + B_4H_{10} \rightarrow B_5H_{11} + \{B_3H_7\} \qquad (7)$$

Thus, reaction 6 explains the ready exchange with D_2 and also the effect of an excess of H_2 in repressing the rate of decomposition without a change in activation energy, whilst reaction 7 ensures that the relative rate of B_5H_{11} production to B_4H_{10} consumption remains unaltered in the presence of H_2. The $\{B_3H_7\}$ formed in reaction 7 would then react with an excess H_2 by the reverse of reactions 4 and 1, thus ensuring the enhanced formation of B_2H_6 and absence of other products.

2.3 Structure and Thermolysis of B_5H_{11}

arachno-Pentaborane is a mobile colourless liquid that boils at 65 °C. Its molecular structure is based on a B_5 skeleton formed by removing one apical and one equatorial vertex from a pentagonal bipyramidal *closo*-B_7 cluster. However, an *X*-ray diffraction study led to a structure which lacked the expected mirror-plane symmetry (C_s). To see whether this was a crystal packing distortion or whether the asymmetry persisted in the gas-phase molecule the structure was redetermined by gas electron-diffraction analysis;[17] there is indeed a definite distortion to C_1 symmetry which places the apical *endo*-hydrogen atom above the open face significantly closer to B(2) than to B(5) (see Figure 4). Subsequent *ab initio* calculations confirmed this distortion and gave values for B(2)$-H_{endo}$ and B(5)$-H_{endo}$ of 143.7 and 204.3 pm respectively, a difference of 60.6 pm; there were other smaller distortions in the molecule also.[18]

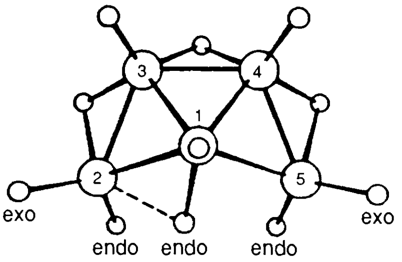

Figure 4 Structure of *arachno*-B_5H_{11} as determined by gas-phase electron diffraction. Note the C_1 symmetry resulting from the fact that the semi-bridging $H(1)_{endo}$ atom is closer to B(2) than to B(5).

Thermolysis studies of B_5H_{11} in the temperature range 40—150 °C established first order kinetics with a rather low activation energy of 72.6 ± 2.4 kJ mol^{-1} and the astonishingly small Arrhenius pre-exponential factor $A = 1.3 \times 10^7\ s^{-1}$ (see later).[19] The main volatile products were H_2 and B_2H_6, the latter appearing at the rate of about 0.5 mol per mol of B_5H_{11} consumed. B_5H_9 is also produced, plus smaller amounts of the hexaboranes and $B_{10}H_{14}$, and traces of B_4H_{10}. Neither the activation energy nor the absolute rate of disappearance of B_5H_{11} was affected by a 14-fold excess of H_2 but there was a dramatic change in product distribution, with B_4H_{10} being the main product, its rate of formation in the initial stages being almost equal to the rate of consumption of B_5H_{11}; B_2H_6 also appears but the formation of all other boranes is almost entirely suppressed.[16]

These results find ready interpretation if the initial rate-determining step is

$$B_5H_{11} \rightleftharpoons \{B_4H_8\} + \{BH_3\} \qquad (8)$$

followed by the reverse of reaction 1 to give $\frac{1}{2}B_2H_6$. Alternatively, the $\{BH_3\}$ could react with a second molecule of B_5H_{11} to generate a further molecule of $\{B_4H_8\}$ plus B_2H_6 in the correct mole ratio:

$$\{BH_3\} + B_5H_{11} \rightleftharpoons \{B_4H_8\} + B_2H_6 \qquad (9)$$

The precise fate of the $\{B_4H_8\}$ moiety was not rigorously established in the thermolysis of B_5H_{11} alone, though several plausible reactions release appropriate amounts of H_2 (see reference 19 for details). In the presence of an added excess of H_2 this rapidly reacts with the $\{B_4H_8\}$ *via* the reverse of reaction 6.

Note that the absence of any effect of added H_2 on the rate and activation energy of the thermolysis of B_5H_{11} stems from the fact that reaction 8 is the rate-determining initial step, and these observations also eliminate the possibility of the alternative initial reaction path to give $B_5H_9 + H_2$ directly. The results also establish for the first time that the well-known (1933) Burg–Schlesinger equilibrium (reaction 10)[20]

$$B_5H_{11} + H_2 \rightleftharpoons B_4H_{10} + \tfrac{1}{2}B_2H_6 \qquad (10)$$

does not occur as a bimolecular reaction but rather as the monomolecular dissociation (reaction 8) followed by the reverse of reactions 6 and 1.

2.4 The Structure and Thermolysis of B_6H_{12}

It has already been mentioned (see Figure 3) that the second most abundant borane product in the initial thermolysis of B_4H_{10} at moderate temperatures is the elusive B_6H_{12}, Stock's possible seventh borane. Very little was known about this borane though viable preparative routes had been devised in the 1970s and its NMR spectrum had been studied in the preceding decade. It is the one simple borane whose structure has not yet been determined by *X*-ray diffraction analysis since it tends to form a non-crystalline glassy solid when cooled. However, its structure has now been determined by gas-phase electron diffraction.[20] It turns out to be a chiral molecule of C_2 symmetry as shown in Figure 5 (see also reference 18*b*). Note the incipient BH_3 units in the structure; it is like a B_4H_{10} butterfly with two extra BH_2 groups replacing bridging H_μ atoms on opposite sides of the butterfly. This turned out to be crucial to its chemistry.

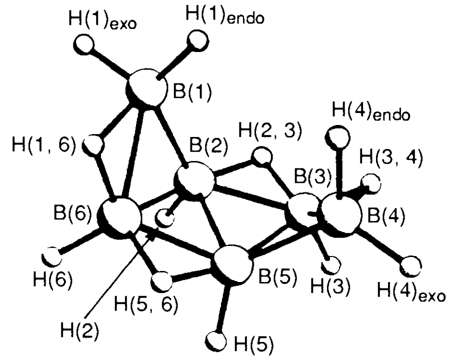

Figure 5 The chiral C_2 structure of *arachno*-B_6H_{12}.

There is a more subtle structural point. The C_2 molecule has been described as an 'icosahedral belt' (*i.e.* $B_6 = \tfrac{1}{2}B_{12}$) but such a description implies that the dihedral angles between successive B_3 triangular planes should be close to the internal dihedral angle of an icosahedron, 138.2° (*i.e.* $\pi - \sin^{-1} 2/3$). However the observed dihedral angles in B_6H_{12} are 167 ± 22° between the inner faces joined by B(2)–B(5), and 128 ± 12° between the outer pairs of faces joined by B(2)–B(6) and B(3)–B(5). This is just what one would expect on the basis of Wade's rules since *arachno*-B_6H_{12} should be geometrically related to the dodecahedral cluster of *closo*-$B_8H_2^-$ by removal of two adjacent five-connected vertices (see Figure 2). The characteristic internal dihedral angles of a regular triangular dodecahedron are 157° and two of 120°, close to the observed angles. This suggests that the structure of *arachno*-B_6H_{12} retains some information of its putative parent, *closo*-$B_8H_8^{2-}$, and that the magnitude of dihedral angles is a useful supplementary criterion for distinguishing between alternative geometrical descriptions of open clusters.

We also found that, when highly purified, B_6H_{12} was rather more stable than earlier workers had found but it does thermolyse at a convenient rate in the range 90—100 °C.[21] Typical data are shown in Figure 6 from which is can be seen that the predominant products are B_5H_9 and B_2H_6 (formed in a 2:1 molar ratio) with a rather smaller amount of B_6H_{10} and H_2 (formed in equimolar amounts). There were virtually no other volatile products or solid 'polymer' formation, thus making the thermolysis of B_6H_{12} the cleanest and simplest of all boranes yet studied. Further analysis showed that the thermolysis was first order with an activation energy of 81.3 ± 2.6 kJ mol^{-1} and an unusually low Arrhenius pre-exponential factor of 3.1×10^8 s^{-1} similar to those found for B_5H_{11} (preceding section). These facts find ready interpretation in terms of an initial unimolecular rate-determining loss of $\{BH_3\}$ to give B_5H_9, as in reaction 11 followed by dimerization of $\{BH_3\}$ by the reverse of reaction 1.

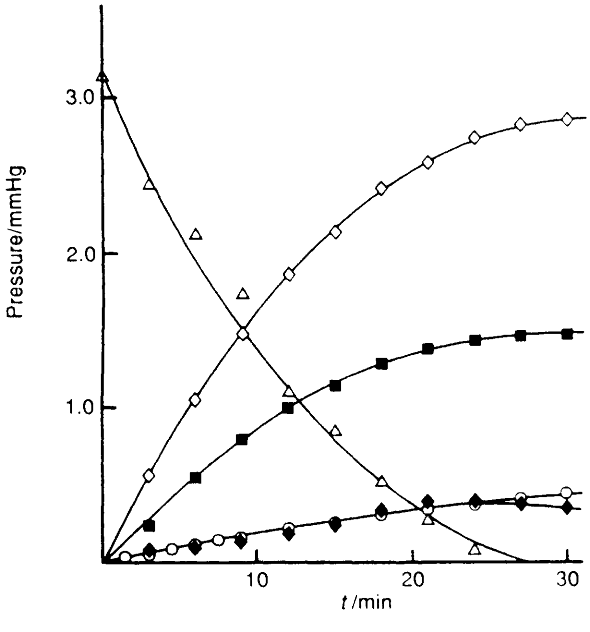

Figure 6 Concentration–time profile for the thermolysis of *arachno*-B_6H_{12} at 100 °C. Only every fifth datum point on each curve has been plotted, for clarity: (○)H_2, (■)B_2H_6, (◇)B_5H_9, (◆)B_6H_{10}, and (△)B_6H_{12}.

$$B_6H_{12} \rightleftharpoons B_5H_9 + \{BH_3\} \qquad (11)$$

$$\{BH_3\} \rightleftharpoons \tfrac{1}{2}B_2H_6 \qquad (-1)$$

The alternative possibility that $\{BH_3\}$ reacted with a second molecule of B_6H_{12} was eliminated by co-thermolysis of B_6H_{13} with $\{BH_3\}$-radical generators such as $BH_3.CO$, and with CO.[22]

$$B_6H_{12} + \{BH_3\} \not\longrightarrow B_5H_9 + B_2H_6 \qquad (12)$$

Reactions 11 and − 1 explain the major reaction-product stoicheiometry and the minor products appear to result from the alternative reaction path 13:

$$B_6H_{12} \rightleftharpoons B_6H_{10} + H_2 \qquad (13)$$

Reactions 11 and 13 could well proceed *via* the same reaction intermediate (see Figure 7) since the breaking of the three-centre bond between B(3)B(4)B(5) leads to a pendant BH_3 group, $H_\mu BH_2$, which could then either eliminate with cluster closure at B(1)–B(3) to form B_5H_9 and $\{BH_3\}$, or swing round to insert at this position, thereby forming B_6H_{10} with elimination of H_2.

The close structural relationship between the three *arachno*-boranes B_4H_{10}, B_5H_{11}, and B_6H_{12} is emphasized in Figure 8, which also shows the close similarities between the Arrhenius parameters of the latter two: the very similar activation energies and extremely low pre-exponential factors are particularly notable features of both B_5H_{11} and B_6H_{12} thermolyses, both these boranes having structural features which are absent in B_4H_{10}.

There are many other systems that have been studied, including numerous co-thermolysis reactions and also the thermolysis

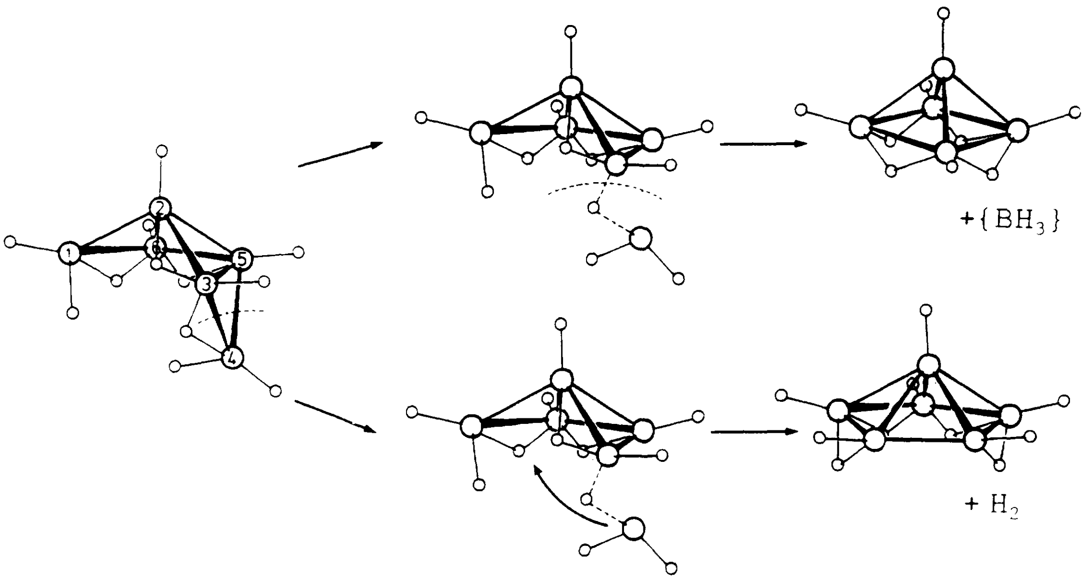

Figure 7 Suggested mechanisms for the elimination of either {BH_3} or H_2 from B_6H_{12} *via* a common intermediate to form B_5H_9 or B_6H_{10} respectively.

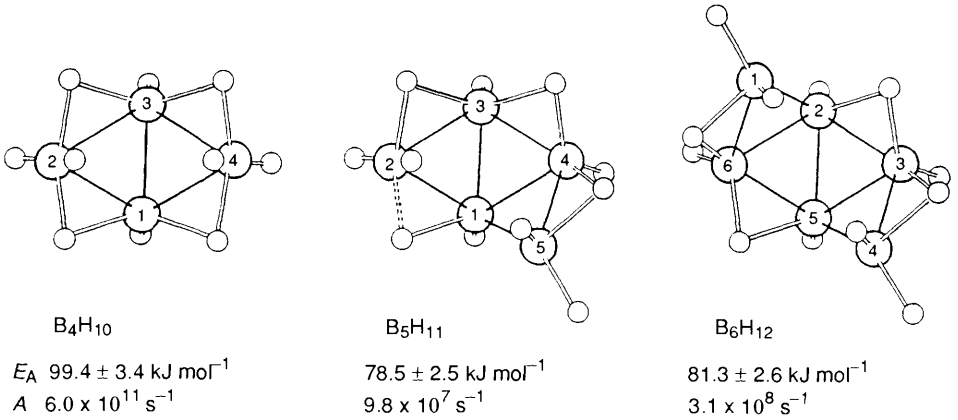

Figure 8 Structural relationship between the three *arachno* boranes B_4H_{10}, B_5H_{11}, and B_6H_{12}, together with a comparison of their Arrhenius parameters, showing the great similarity of the last two.

of *nido*-B_6H_{10} which turns out to be second order.[23,24] Unfortunately there is not the space to discuss these in detail here. However, one final point should be made: the ease with which these various thermolysis reactions occur does not derive from the weakness of BBB or BHB three-centre bonds but from the availability of unfilled orbitals and alternative structures at thermally accessible energies. Indeed, the cluster bonds in the borane molecules are amongst the strongest two-electron covalent bonds known, as indicated by the data in Table 1. Thus the average bond dissociation energy of boron is greater than that of either dihydrogen or carbon (diamond) as determined by the heats of atomization of the elements (column 1); likewise intercomparison of the values in columns 2 and 3 shows that the bond enthalpy of B–B is almost identical to that of C–C, whilst the three-centre bond enthalpies of BBB and BHB probably exceed these of the two-centre B–C and H–H bonds respectively.[24]

To summarize this first half of the lecture we can say that, as a result of our work in Leeds and that of several other laboratories particularly in the USA and Czechoslovakia, Stock's original six or seven boranes have now expanded to over 50 neutral boranes and a further 50 or more anions, making about 100 binary borane species in all. Perhaps even more significantly we are now finally solving the mysterious details of the complex but extremely facile thermal interconversions and aufbau reactions by which diborane and its homologues can grow into larger clusters.

Table 1 Enthalpies of atomization ($\Delta_f H°_{298}$) and bond enthalpy contributions, $\bar{E}$(X–Y)

$\Delta_f H°_{298}$/kJ mol^{-1}		$\bar{E}$(X–Y)/kJ mol^{-1}		$\bar{E}$(X–Y)/kJ mol^{-1}	
H(g)	$\frac{1}{2}$ × 436	B–B(2c,2e)	332	C–C	331
B(g)	566	BBB(3c,2e)	380	B–C	372
C(g)	356	B–H(2c,2e)	381	C–H	416
		BHB(3c,2e)	441	H–H	436

3 Metallaboranes and Other Heteroatom Boranes

Let me now introduce the second major theme of the lecture by asking the question: is boron unique in this ability to form molecular clusters? Are there any other elements that have, like boron, fewer electrons than orbitals available for bonding? The answer is, of course, yes; there are many such elements: we call them metals. And so we asked ourselves the question (over 25 years ago now): is it possible to incorporate one, two, or even more metal centres within polyhedral borane clusters? It turned out to be an amazingly fruitful idea and the field of boron cluster chemistry has expanded enormously as a result. So far, over 45 elements have been included as cluster vertices, some 40 of them being metals or metalloids. Metals could therefore be regarded as 'honorary boron atoms' in these polyhedral clusters. Moreover, because many metals can contribute differing numbers of electrons and orbitals to the cluster bonding, instead of the invariable two electrons and three orbitals of a BH vertex, such elements can be regarded as 'flexi-boron atoms'. Examples are now known of elements which can contribute 0, 1, 2, 3, or 4 cluster-bonding electrons and 1, 2, 3, or 4 frontier orbitals. In this way novel cluster geometries can be constructed which are unknown among the binary boranes themselves.

Much of this work has been reviewed already in my Liversidge Lecture[25] and elsewhere[26–30] and I want to recall here only the salient overall themes before mentioning some exciting new developments which have occurred during the last two or three years.

3.1 Metallaboranes

We found that, far from being 'electron deficient', many boranes and particularly their anions are very effective polyhapto ligands to appropriate metal centres. The resulting metallaboranes are often much more stable than the parent borane ligands, and this concept of 'boranes as ligands' can be used to systematize a huge body of new information by means of isolobal sequences and the general rules of coordination chemistry. But there were surprises too, as indicated at the end of the preceding paragraph, and novel *iso-closo*, *iso-nido*, and *iso-arachno* cluster geometries emerged,[25–30] different from those illustrated in Figure 2. Clusters of clusters are also possible in which boranes or metallaboranes are conjoined in various ways, for example (a) *via* a direct B–B or B–H–B bond, (b) *via* a *commo* B or M atom, (c) by sharing a common edge of two atoms, (d) by sharing a common triangular face, or (e) by more complex conjunctions. Thus two *nido*-decaboranyl units, $-B_{10}H_{13}$, can be joined *via* a B–B bond to give 11 distinct geometrical isomers of *conjuncto*-$B_{20}H_{26}$, four of which exist as enantiomeric pairs making 15 isomers in all, most of which have been isolated and characterized.[31]

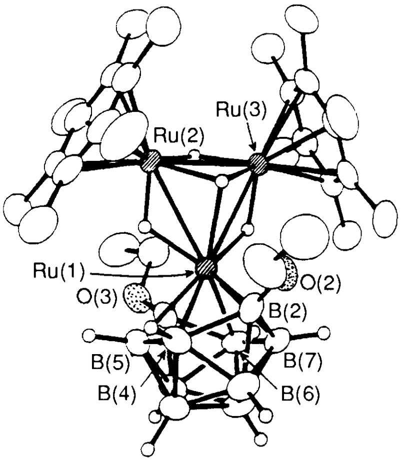

Figure 9 Crystallographically determined molecular structure of the double cluster compound $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$.

An intriguing example of a *commo* structure is provided by $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$ which comprises an Ru_3 cluster and an RuB_{10} cluster conjoined at a common ruthenium atom Ru(1) as shown in Figure 9.[32] This dark red triruthenium-decaboron double cluster compound was obtained in 32% yield by reacting the yellow *arachno* four-vertex species $[Ru(\eta^2\text{-}B_3H_8)(\eta^6\text{-}C_6Me_6)Cl]$ with *closo*-$[B_{10}H_{10}]^{2-}$ in refluxing ethanol. It is the first (and so far only) example of a ruthenium cluster compound that does not contain carbonyl ligands, and has several other interesting features such as a triply bridging H atom and three doubly bridging H atoms. Note also that, as each $\{Ru(\eta^6\text{-}C_6Me_6)\}$ vertex is isolobal with a $\{BH\}$ unit, the $\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}$ moiety is equivalent to a polyhapto B_2H_6 group. Many examples of the other concatenating modes (c)—(e) are now also known in the numerous *conjuncto* and macropolyhedral metallaboranes previously reviewed.[25–30]

Heterobimetallic clusters can also readily be constructed starting with a given metallaborane substrate and adding a second, different metal vertex. This procedure sometimes generates novel cluster geometries as, for example, when the *nido*-decaborane analogue $[6\text{-}(\eta^5\text{-}C_5Me_5)IrB_9H_{13}]$ reacts with the rhodium dimer $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ in the presence of 'proton sponge' (*i.e.* *N,N,N′,N′*-tetramethylnapthalene-1,8-diamine) in dichloromethane solution at room temperature:[33] the dimetalla product has the structure shown in Figure 10.

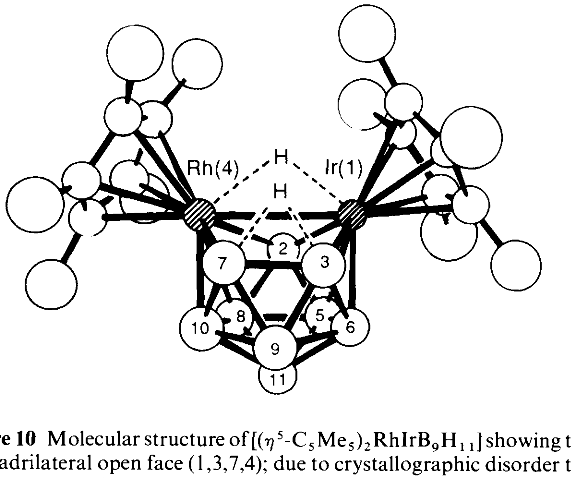

Figure 10 Molecular structure of $[(\eta^5\text{-}C_5Me_5)_2RhIrB_9H_{11}]$ showing the quadrilateral open face (1,3,7,4); due to crystallographic disorder the two metal positions are not assignable between Rh and Ir and there is a 50:50 occupancy factor between B(2) and its equivalent position above the (1,3,7,4) face. For clarity the methyl H atoms and the nine terminal borane H atoms are omitted; the two bridging H_μ atoms between Ir(1)Rh(4) and B(3)B(7) respectively were located by NMR spectroscopy.

The Rh–H–Ir and B–H–B hydrogen bridges in the quadrilateral open face were detected by NMR spectroscopy. It will be noted that, since both $\{Rh(\eta^5\text{-}C_5Me_5)\}$ and $\{Ir(\eta^5\text{-}C_5Me_5)\}$ are isolobal with $\{BH\}$ and all are expected to provide two electrons to the cluster bonding, the dimetalla product is a 24-electron $(2n + 2)$ 11-vertex species. One might therefore have expected a *closo* configuration. However, the product has neither a *closo* nor a regular *nido* structure (with a 5-vertex open face) but adopts an *isonido* configuration with a quadrilateral open face. Several other 11-vertex $(2n + 2)$ heteroborane clusters which in the past have reasonably been assumed to have a *closo* octadecahedral structure similar to that long postulated for *closo*-$[B_{11}H_{11}]^{2-}$ (see Figure 2) have recently been shown to have the quadrilateral open-faced *isonido* structure,[28] and this has important implications for cluster-bonding theories.

3.2 Incorporation of Very Electronegative Atoms as Cluster Vertices

Most transition metals and post-transition metals have an electronegativity that is very similar to that of boron (2.0 on the Pauling scale). Their incorporation into polyhedral borane clusters therefore poses no great electrovalent distortion on the predominantly covalent cluster bonding. Carbaboranes, thiaboranes, and their metalla derivatives are also well known (electronegativity of C and of S is 2.5). However, with the even more electronegative elements nitrogen (3.0) and oxygen (3.5) it is more difficult to devise successful synthetic strategies and few azaboranes, oxaboranes, and the corresponding metallaboranes were known until very recently. Related constraints are the ease with which Lewis-base adducts can be formed, and the great affinity of boron for oxygen which makes it difficult to prevent hydrolysis or complete oxidation of the poly(metalla)borane cluster to $B(OH)_3$, $B(OR)_3$, B_2O_3, or similar species.

The first fully contiguous azametallaborane to be reported was the air-stable, orange-red eleven-vertex *closo*-type ruthenium compound $[(\eta^6\text{-MeC}_6H_4\text{-4Pr}^i)RuNB_9H_{10}]$ shown in Figure 11.[34]

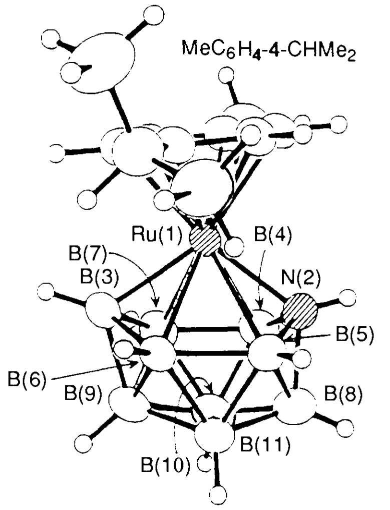

Figure 11 Crystallographically determined molecular structure of the 11-vertex *closo*-azaruthenaborane $[(\eta^6\text{-MeC}_6H_4\text{-4-Pr}^i)RuNB_9H_{10}]$.

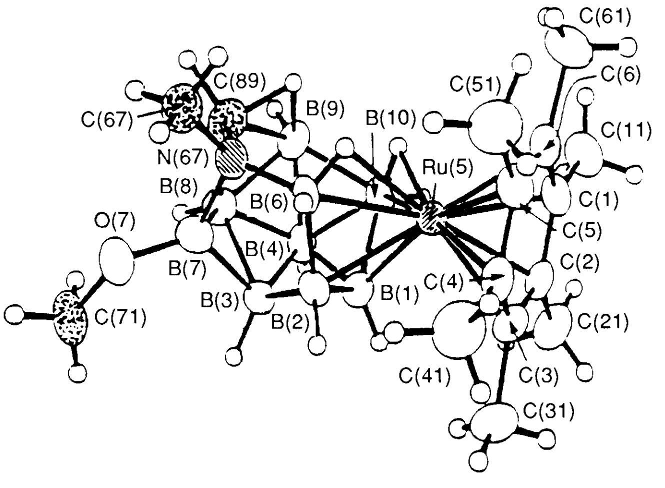

Figure 12 Molecular structure of the 12-vertex *arachno*-azacarbaruthenaborane $[(\eta^6\text{-C}_6Me_6)RuN(Me)C(H)B_9H_{11}(OMe)]$; the six-membered open face Ru(5)B(10)B(9)C(89)N(67)B(6) carries the three bridging H atoms. The four-membered open face B(7)B(8)C(89)N(67) and the five-membered open face B(6)B(2)B(3)B(7)N(67) can also be seen.

The *arachno* ten-vertex azaplatinaborane $[6,9\text{-}\{(PPh_3)_2Pt\}NB_8H_{11}]$ is also known.[35] A subsequent example of a contiguous metallaheteroborane, containing both nitrogen and carbon cluster vertices, is the extraordinary *arachno*-type twelve vertex {RuNCB$_9$} cluster compound $[\{(\eta^6\text{-C}_6Me_6)Ru\}N(Me)C(H)B_9H_{11}(OMe)]$ which was made by reacting the *nido* ten-vertex ruthenaborane $[\{(\eta^6\text{-C}_6Me_6)Ru\}B_9H_{13}]$ with MeNC in the presence of methanol.[36] The unprecedented structure is in Figure 12, which clearly shows the presence of four-membered (BBCN), five-membered (BBBBN), and six-membered (RuBBCNB) open faces. The elements of MeNC are also clearly discernible, the isonitrile group itself being intimately involved as a bridging unit in all three open-faces.

A differing structural motif is displayed in the Me_2N-bridged *arachno* cluster $[\mu\text{-6,9-(NMe}_2)\text{-5-}\{(\eta^6\text{-C}_6Me_6)Ru\}B_9H_{10}\text{-10-}(PMe_2Ph)]$ which is formed during the stepwise reduction of MeNC to Me_2NH by $[\{(\eta^6\text{-C}_6Me_6)Ru\}B_9H_{13}]$ in the presence of PMe_2Ph.[37] An even more remarkable dialkylamino derivative of a metallaborane is the purple air-stable compound *isocloso*-$[1\text{-}\{(\eta^5\text{-C}_5Me_5)Ru\}B_{10}H_9\text{-4-(NEt}_2)]$ which is readily obtained in 66% yield by the reaction of Et_2NH with the orange-yellow *isocloso* eleven-vertex parent metallaborane $[\{(\eta^5\text{-C}_5Me_5)Rh\}B_{10}H_{10}]$.[38] The compound is so far unique in being the only known example of a multiply-bonded N-substituted metallaborane involving $N \rightleftharpoons B$ π bonding into the cluster; the multiple bonding is manifest by (a) the unusually short N–B distance of 142.7(8) pm (compared with the usual 'single-bond' N–B distance of about 158 pm), (b) the planar arrangement of bonds about the N atom, and (c) the pronounced barrier to 180° rotation about the B–N linkage of 53.8(5) kJ mol^{-1} at 272 K. A recent review of various routes to non-metal-containing azaborane clusters should also be mentioned.[39]

Oxametallaborane clusters are even less numerous, and fewer than half a dozen species have so far been synthesized and characterized. The first to be reported[40] was the oxaferra *nido* ten-vertex compound $[\{(\eta^5\text{-C}_5Me_5)Fe\}OB_8H_{10}]$ which has the skeletal structure I shown in Figure 13.

A second example, from our own laboratory the following year,[41] was the red crystalline *nido* cluster compound $[\{(\eta^5\text{-C}_5Me_5)Rh\}OB_{10}H_9Cl(PMe_2Ph)]$ which has the skeletal structure II in Figure 13; it is of particular interest in being the first example of a cluster that incorporates a contiguous oxygen atom vertex bound solely to boron atoms, and the first open-faced twelve-vertex metallaborane cluster that does not also contain carbon atoms as cluster vertices. Other examples of oxametalla boranes are now beginning to emerge as a result of mild air-oxidation of rhodaboranes, for example the *nido* twelve-vertex cluster compound $[\{(\eta^5\text{-C}_5Me_5)Rh\}OB_{10}H_{10}(NEt_3)]$ and the oxo-bridged bis-*nido* compound $[\{(\eta^5\text{-C}_5Me_5)RhB_9H_{12}\}_2O]$ which have been shown by detailed *X*-ray diffraction analysis to have the skeletal structures III and IV in Figure 13.[42]

Clearly the range of structural possibilities for metallaheteroatomborane clusters is far from exhausted, and exciting possibilities for the synthesis and characterization of such aesthetically pleasing and potentially useful compounds abound. Stock's elegant and perceptive studies on the six original boron hydrides have certainly stimulated some astonishing and deeply significant developments.

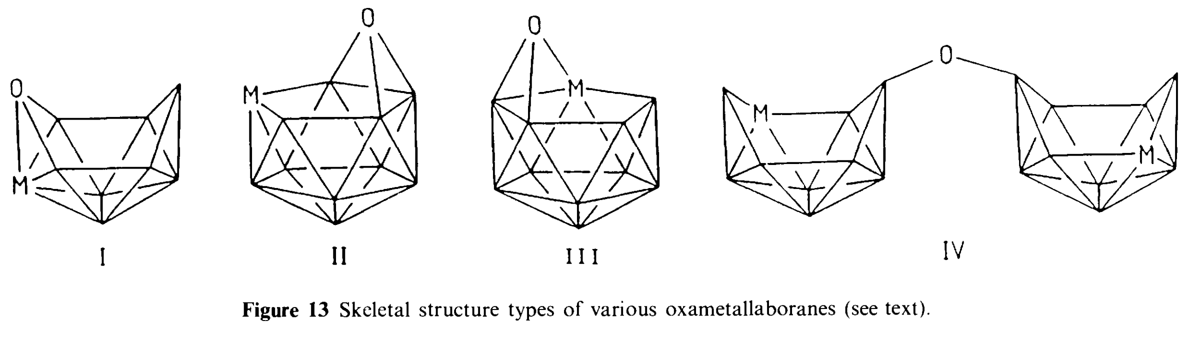

Figure 13 Skeletal structure types of various oxametallaboranes (see text).

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