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Some thought-provoking polyhedral borane chemistry

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Abstract - Some of the more intriguing results selected from recent work by the Leeds borane group will be presented. The first section considers novel chemical reactions induced by the interaction of various ligands with preformed metallaboranes. This leads naturally to the second section which describes some further examples of unexpected and in some instances unprecedented cluster geometries and their significance. The account concludes with a brief survey of the new and rapidly developing area of aza- and oxa-metallaboranes and related species.

INTRODUCTION

The work of the borane group in Leeds is concerned with two distinct though interrelated aspects of polyhedral borane chemistry. The first concerns the intricate mechanisms by which the boranes themselves react and interconvert under mild thermolytic conditions, often in the gas phase. This aspect was last reviewed at IMEBORON VI in Bechyně (ref. 1) and is also represented by several papers presented elsewhere in this Meeting (refs. 2-4). The second main theme concerns the synthesis, structure, properties, and reaction chemistry of metallaboranes and metallaheteroboranes. Various aspects of this were reviewed at IMEBORON V in Swansea (ref. 5) and IMEBORON VI in Bechyně (ref. 6) and have also been reported in other summary lectures and compilations (refs. 7,8). The present lecture deals with this second main area and concentrates on work completed within the last two or three years, some of it as yet unpublished. The subject matter will be grouped into three sections as indicated in the Abstract.

LIGAND-INDUCED REACTIONS OF METALLABORANES

The advent of high-yield syntheses of several metallaborane types makes the reaction chemistry of these species amenable to further study. One classic reaction of the boranes themselves in the ten-vertex area is the use of ligands to convert *nido*-boranes into *arachno*-bis(ligand) adducts. This reaction was discovered by Riley Schaeffer (ref. 9) and is exemplified by the reaction of methyl cyanide with decaborane:

$$\textit{nido}\text{-}B_{10}H_{14} + 2MeCN \longrightarrow [\textit{arachno}\text{-}6,9\text{-}(MeCN)_2B_{10}H_{12}] + H_2$$

The reaction is quite general for a very large number of neutral and anionic ligands (ref. 10). The adducts as isolated usually have the *exo-exo* configuration though recent work has shown that *exo-endo* adducts can also be made (ref. 11). With a metallaborane the outcome will clearly depend both on the nature of the ligand used and on the particular metallaborane substrate. Several possibilities, some quite unexpected, are described in the following paragraphs.

The most direct and perhaps least interesting mode of interaction involves simple ligand replacement at the metal centre. For example, treatment of the *isocloso*-type compound [1,1-(PPh$_3$)$_2$-2,3-(OEt)$_2$-*closo*-1-RuB$_{10}$H$_8$] (compound 1) with the more basic ligand PMe$_3$ results in the formation of the sixteen-electron ruthenium mixed ligand analogue [1,1-(PMe$_3$)(PPh$_3$)-2,3-(OEt)$_2$-*closo*-1-RuB$_{10}$H$_8$] (compound 2) which was characterized by single-crystal X-ray diffraction analysis as shown in Fig. 1 (ref. 12). A more complex variant of ligand replacement occurs when compound 1 is treated with [RuCl$_2$(PPh$_3$)$_3$] in boiling ethanol: a high yield is obtained of the red-brown binuclear complex [1-(PPh$_3$)-2,3-(OEt)$_2$-*closo*-1-RuB$_{10}$H$_8$-1-Cl$_\mu$-4,5-(H$_\mu$)$_2$-{RuCl(PPh$_3$)$_2$}] (compound 3) in which one of the original PPh$_3$ ligands on the *closo*-ruthenaborane has been replaced by a bridging chlorine atom (Fig. 1). The ruthenium atom Ru(1) is still a sixteen-electron centre but when compound 3 is further treated with the bidentate chelating ligand Ph$_2$PCH$_2$PPh$_2$ (dppm) the remaining PPh$_3$ ligand on Ru(1) is also replaced to give the dark-red, air-stable eighteen-electron product [1-(dppm)-2,3-(OEt)$_2$-*closo*-1-RuB$_{10}$H$_8$-1-Cl$_\mu$-4,5-(H$_\mu$)$_2$-

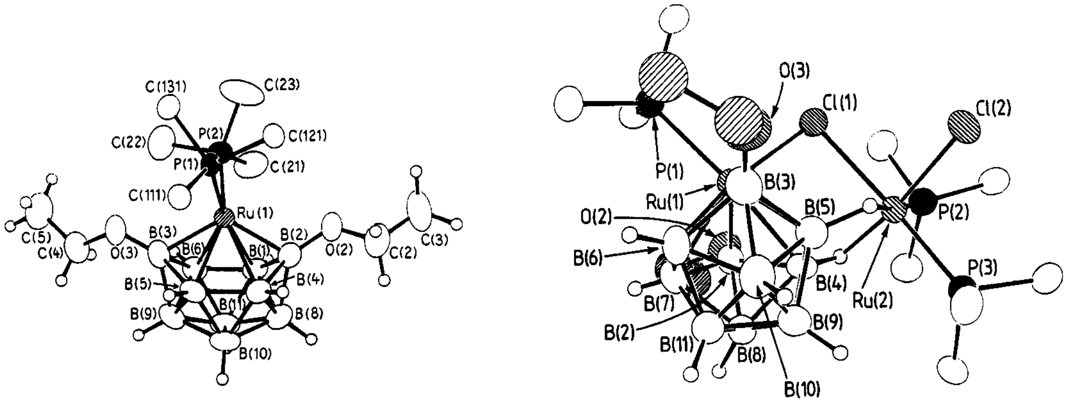


Fig. 1. Molecular structures of the mixed phosphine ligand compound 2, [1,1-(PMe_3)(PPh_3)-2,3-(OEt_2)-closo-1-$RuB_{10}H_8$], and the binuclear compound 3, [1-(PPh_3)-2,3-($OEt)_2$-closo-1-$RuB_{10}H_8$-1-Cl_μ-4,5-$(H_\mu)_2$-{$RuCl(PPh_3)_2$}]

{$RuCl(PPh_3)_2$}] (compound 4) (ref. 13).

If secondary phosphines rather than tertiary phosphines are used, more extensive reaction can occur which induces not only loss of a boron cluster vertex but also B-H_t substitution and phosphine bridging between the metal vertex and a non-adjacent boron atom in the cluster. Thus, treatment of the nido-rhodadecaborane cluster compound [6-(η^5-C_5Me_5)-nido-6-RhB_9H_{13}] (structure I) with $PHPh_2$ affords the yellow, air-stable, phosphine-bridged compound [2,5-(μ-PPh_2)-1-($PHPh_2$)-2-(η^5-C_5Me_5)-arachno-2-RhB_8H_9] (compound 5, structure II) in 22% yield (ref. 14).

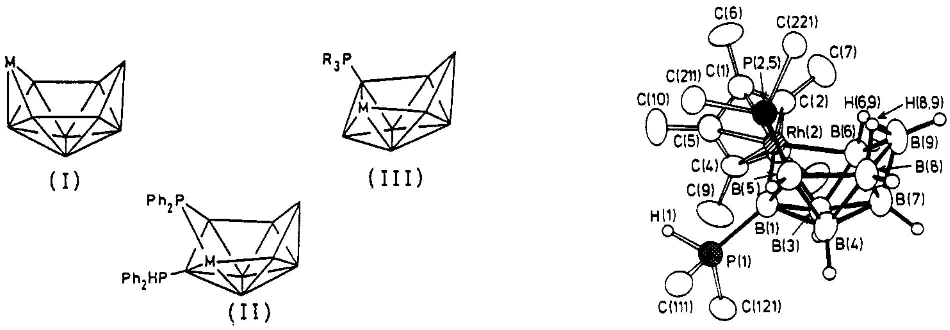


Fig. 2. Skeletal structures I, II, and II, and the molecular structure of compound 5, [2,5-(μ-PPh_2)-1-($PHPh_2$)-2-(η^5-C_5Me_5)-arachno-2-RhB_8H_9]

The structure (Fig. 2) was established by X-ray diffraction analysis and is a nine-vertex arachno-system of the iso-B_9H_{15} skeletal type in which the rhodium atom is on one of the projecting positions on the open face, and in which the PPh_2 group bridges the metal atom and a (non-adjacent) projecting boron position also on the open face. There is, in addition, a $PHPh_2$ ligand bound exo to the cluster at B(1) and two bridging hydrogen atoms at positions (6,9) and (8,9) on the open face. In spite of the arachno formulation the cluster retains much nido nine-vertex character, as judged by geometrical and n.m.r. data. The reaction contrasts sharply with that between the same nido-rhodadecaborane starter and the tertiary phosphine PMe_2Ph; this gives, inter alia, the nine-vertex nido-rhodaborane [2-(η^5-C_5Me_5)-5-(PMe_2Ph)-nido-2-RhB_8H_{10}] (structure III) (ref. 15).

Use of a potentially reactive ligand such as an isonitrile opens up several further possibilities. In the simplest case, we have found that direct bis(ligand) adducts can be formed with the loss of dihydrogen and concomitant cluster modification from nido to arachno but, instead of the exo-exo configuration as found in the original Schaeffer adducts, $L_2B_{10}H_{12}$, an endo-exo configuration may result. For example, reaction between MeNC and the nido ten-vertex rhodaborane cluster [6-(η^5-C_5Me_5)-nido-6-RhB_9H_{13}] in toluene results in the formation of the stable, yellow, arachno ten-vertex cluster [6-(η^5-C_5Me_5)-6,9-$(MeNC)_2$-arachno-6-RhB_9H_{11}] (compound 6) in 64% yield; the endo-exo configuration was established by the detailed n.m.r. similarity between this compound and its p-tolyl analogue, compound 1, (Fig.3) which was formed similarly, though in much lower yield, and for which a crystal structure was obtained (ref. 16).

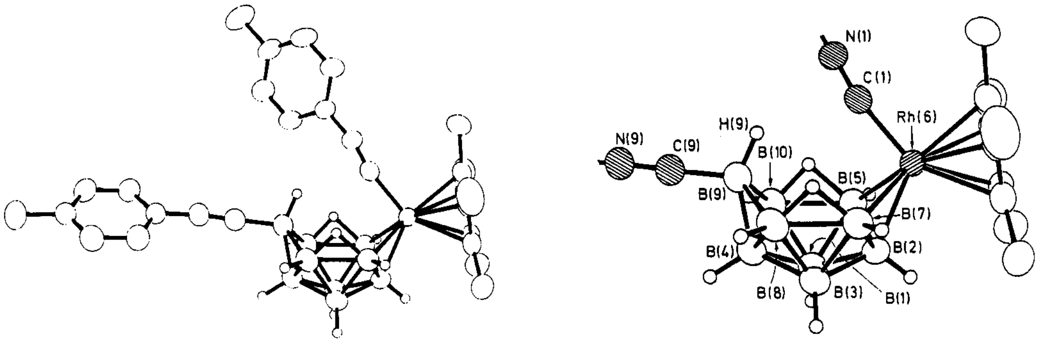


Fig. 3. Molecular structure of $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}endo,exo\text{-}(p\text{-}MeC_6H_4NC)_2\text{-}6\text{-}RhB_9H_{11})]$, compound 7, showing (left) an overall ORTEP drawing of the structure and (right) a more detailed plot of the cluster indicating the numbering system used (ref. 16)

The parallel reaction of MeNC with the ten-vertex nido-iridaborane analogue $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6\text{-}IrB_9H_{13}]$ also afforded the pale-yellow arachno endo-exo bis(ligand) adduct $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}endo,exo\text{-}(MeNC)_2\text{-}arachno\text{-}IrB_9H_{11}]$ (compound 8, Fig. 4) in 62% yield, together with a smaller amount (18% yield) of the related nine-vertex homologue $[4\text{-}(\eta^5\text{-}C_5Me_5)\text{-}4\text{-}(endo\text{-}MeNC)\text{-}arachno\text{-}4\text{-}IrB_8H_{12}]$, compound 9, Fig. 4 (ref. 17).

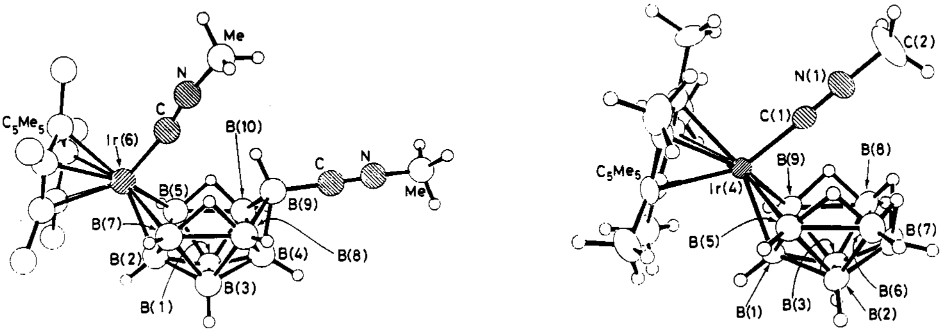


Fig. 4. Proposed molecular structure of $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}endo,exo\text{-}(MeNC)_2\text{-}arachno\text{-}6\text{-}IrB_9H_{11}]$ (compound 8) based on the extreme similarity of its ^1H and ^{11}B n.m.r. data to those of the X-ray crystallographically defined compound 7 (Fig. 3), and the crystallographically determined molecular structure of $[4\text{-}(\eta^5\text{-}C_5Me_5)\text{-}4\text{-}(endo\text{-}MeNC)\text{-}arachno\text{-}4\text{-}IrB_8H_{12}]$, compound 9 (ref. 17)

By contrast, the reaction of MeNC in toluene at room temperature with the ostensibly very similar nido-ruthenaborane substrate $[6\text{-}(\eta^6\text{-}C_6Me_6)\text{-}nido\text{-}6\text{-}RuB_9H_{13}]$ proceeds quite differently by effecting the facile stepwise reduction of MeNC to Me_2NH:

$$MeNC + [(C_6Me_6)RuB_9H_{13}] \longrightarrow MeNHCH_3 + [(C_6Me_6)RuB_9H_9] \text{ (compound 10)}$$

The reaction proceeds via the rapid (<10 min) and essentially quantitative formation of an unstable yellow adduct $[(C_6Me_6)RuB_9H_{11}(CH_2NMe)]$ (compound 11), which features a cluster-bound, partially-reduced, bridging unit $\text{-}NMeCH_2\text{-}$ resulting from the reductive capture of a MeNC molecule. This intermediate (11) reacts further over a period of several hours at room temperature to complete the reduction of MeNC with consequent extrusion of Me_2NH from the cluster and the high-yield formation of the ten-vertex isocloso product $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}isocloso\text{-}1\text{-}RuB_9H_9]$ (compound 10) (ref. 18). In an attempt further to elucidate the structure of the intermediate bridged compound 11, the reaction mixture containing 11 was quenched with the stronger ligand PMe_2Ph; this resulted in the unexpected formation of the air-stable, rearranged, orange adduct $[\mu\text{-}6,9\text{-}(NMe_2)\text{-}10\text{-}(PMe_2Ph)\text{-}5\text{-}(\eta^6\text{-}C_6Me_6)\text{-}arachno\text{-}5\text{-}RuB_9H_{10}]$ (compound 12), which was characterized by n.m.r. spectroscopy and by a single-crystal X-ray analysis (Fig. 5). Compound 12 exhibits several interesting features including (a) a $\{\mu\text{-}6,9\text{-}NMe_2\}$ bridging moiety that is reasonably presumed to represent another of the two-electron transfer steps in the overall four-electron reduction of MeNC to $MeNHCH_3$, and (b) an arachno ten-vertex 5-metallaborane structure for which there is little precedent (ref. 19). The structure, shown in Fig. 5, clearly also implies a cluster rearrangement from the initial 6-ruthena- to the final 5-ruthena-decaborane species.

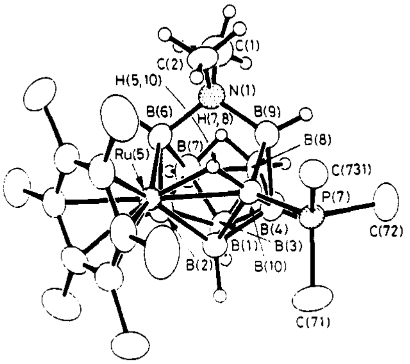


Fig. 5. Molecular structure of compound 12, [μ-6,9-(NMe_2)-10-(PMe_2Ph)-5-(η^6-C_6Me_6)-arachno-5-RuB_9H_{10}] (ref. 18)

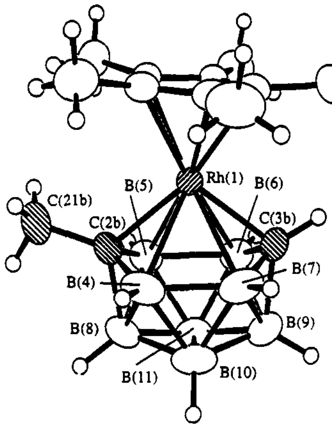


Fig. 6. Molecular structure of compound 13, [1-(η^5-C_5Me_5)-2-Me-closo-1,2,3-$RhC_2B_8H_9$] (ref. 20)

Even more extensive cluster changes can be induced if the reaction with alkyl isocyanides is carried out in boiling toluene (∼110 °C) rather than at room temperature. Under these more forcing conditions the reaction of MeNC with [6-(η^5-C_5Me_5)-nido-6-RhB_9H_{13}] does not give significant amounts of compound 6 but rather the C-methyl-substituted eleven-vertex closo-rhodadicarbaborane cluster [1-(η^5-C_5Me_5)-2-Me-closo-1,2,3-$RhC_2B_8H_9$, compound 13, whose structure (Fig. 6) was confirmed by X-ray diffraction analysis (ref. 20). Compound 13 can, of course, be synthesized independently (in 64% yield) by the more direct reaction between [{(η^5-C_5Me_5)$RhCl_2$}$_2$] and the dicarbaborane anion [6-Me-nido-6,9-$C_2B_8H_9$]$^{2-}$. The route via MeNC represents an unprecedented synthesis of a metalladicarbaborane which involves not only the elimination of a boron vertex from the cluster but also the intriguing incorporation of C(2)-Me and C(3)-H with complete elimination of the nitrogen atoms from two isonitrile molecules.

Reaction of the same nido-rhodadecaborane starter with EtNC (rather than MeNC) under similar conditions (boiling toluene) results in the incorporation of a single carbon atom into the cluster without loss of boron to give, as the predominant product, the red amine-substituted eleven-vertex closo-metallacarbaundecaborane derivative [1-(η^5-C_5Me_5)-2-(NHEt)-5-(CNEt)-closo-1,2-$RhCB_9H_8$] (compound 14, Fig. 7) (ref. 20).

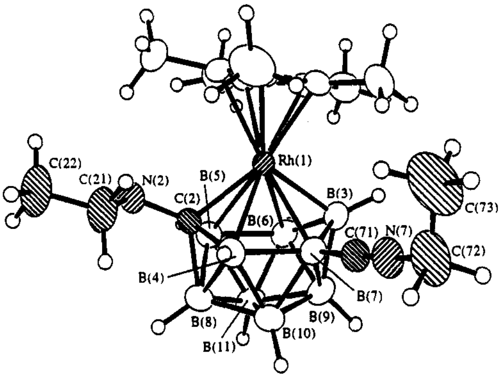


Fig. 7. Molecular structure of compound 14, [1-(η^5-C_5Me_5)-2-(NHEt)-5-(CNEt)-closo-1,2-$RhCB_9H_8$] (ref. 20)

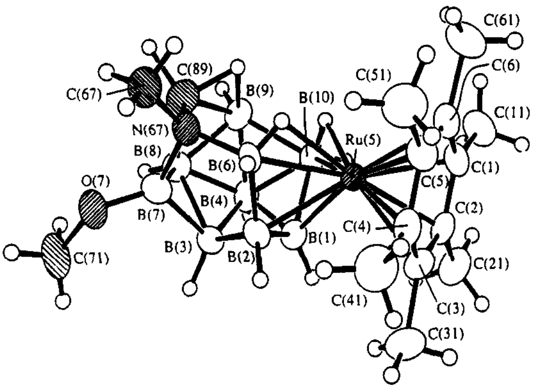
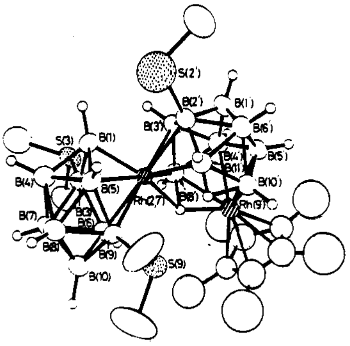


Fig. 8. Molecular structure of compound 15, [5-(η^6-C_6Me_6)-7-(OMe)-arachno-RuN(Me)C(H)B_9H_{11}] (ref. 20)

A further thought-provoking variation of the reaction of an isonitrile with a nido-metalladecaborane is illustrated by the reaction of MeNC with [6-(η^6-C_6Me_6)-nido-6-RuB_9H_{13}] in the presence of ethanol. Instead of the isocloso compound 10 being formed (as when the reaction is carried out in toluene) a fascinating and unprecedented arachno-type twelve-vertex {$RuNCB_9$} cluster emerges whose formulation as [5-(η^6-C_6Me_6)-7-(OMe)-arachno-5-RuN(Me)C(H)B_9H_{11}] (compound 15, Fig. 8) was established by X-ray diffraction analysis (ref. 20). Unique features of this structure include the presence of a four-membered (BBCN), a five-membered (BBBCN), and a six-membered (RuBBBCN) open face. The four- and five-membered open faces carry no bridging hydrogen atoms but the six-membered face has two BHRu bridges and a BHC bridge, this last feature being, as far as we are aware, previously unobserved in any known carbaborane cluster. It is notable that the elements of MeNC are clearly discernible in the cluster, the 'isonitrile' group itself being intimately involved as a bridging unit in all three open-faces. Further details and extensions of these extraordinary reactions are at present being explored.

The final example of ligand-induced reactions of metallaboranes concerns the reaction of Me_2S with nido-6-metalladecaboranes in refluxing toluene (ref. 21). With [6-(η^6-C_6Me_6)-nido-6-RuB_9H_{13}] a clean reaction ensues which affords an 80% yield of [1-(η^6-C_6Me_6)-isocloso-1-RuB_9H_9], identical with compound 10 above. However, use of the analogous [6-(η^5-C_5Me_5)-nido-6-RhB_9H_{13}] gives a variety of products, one of which (20% yield) is the novel, brown, air-stable dirhodium conjuncto species [9'-(η^5-C_5Me_5)-2',3,9-$(SMe_2)_3$-nido-7',9'-dirhodaundecaborano-(7':2)-closo-2-rhodadecaborane] (compound 16). The structure, as shown in Fig. 9, is based on a unique isonido-type eleven-vertex cluster {7',9'-Rh_2B_9} conjoined by a common rhodium atom, commo-(7':2)-Rh, to a closo ten-vertex {2-RhB_9} cluster. This latter is a straightforward ten-vertex '22-electron' bicapped square antiprism but the open-faced eleven-vertex {Rh_2B_9} subcluster is novel: it is formally a '24-electron' eleven-vertex system for which a closo structure might have been anticipated, but it has an open face with two bridging hydrogen atoms. Moreover, the five-membered open face {Rh(7')B(8')Rh(9')B(10')B(11')} has a bent configuration with an unusual triply-bridging hydrogen atom associated with Rh(7')B(8')Rh(9').



9. Molecular structure of compound 16, [9'-(η^5-C_5Me_5)-2',3,9-$(SMe_2)_3$-nido-7',9'-$Rh_2B_9H_{10}$-closo-commo(7':2)-RhB_9H_7] (ref. 21)

The conditions for the formation of this conjuncto compound 16 are quite critical. When the reaction is carried out at room temperature, the main products are [5-(η^5-C_5Me_5)-8- or 10-(SMe_2)-nido-5-RhB_9H_{11}] (65%) and [5-(η^5-C_5Me_5)-7-(SMe_2)-nido-5-RhB_9H_{11}] (ca. 25%), and subsequent mild thermolysis of these in boiling toluene, either as isolated species or admixed with their coproducts, does not yield significant quantities of the conjuncto species (ref. 21). Several other variants have been tried and lead to further interesting species which time (space) does not permit us to describe in detail.

SOME UNEXPECTED CLUSTER GEOMETRIES

The geometry of nido-$B_{10}H_{14}$ is such that four distinct nido-metalladecaboranes are anticipated as a result of isolobal subrogation of a BH vertex at positions 6, 5, 2, or 1, as indicated in Fig. 10 structures I, II, III, and IV. Examples of the first two structure types are well-documented (ref. 8) and occasional examples of III have been reported e.g. [2-(η^5-C_5Me_5)-nido-2-CoB_9H_{13}] (ref. 22) and [2-(η^6-C_6Me_6)-nido-2-RuB_9H_{13}] (compound 17, ref. 23). However, when the first example of the ostensibly analogous nido-1-subrogated derivative (Fig. 10, structure IV) was recently thought potentially to have been prepared it turned out unexpectedly to have the previously unknown isoarachno-type structure V (ref. 23). Thus, treatment of [arachno-B_6H_{11}]$^-$ with [{(η^6-C_6Me_6)$RuCl_2$}$_2$] in thf-CH_2Cl_2 at -25 °C afforded [1-(η^6-C_6Me_6)-'isoarachno'-1-RuB_9H_{13}] (compound 18) as a yellow, air-stable solid in 5% yield, together with the nido-2-metalla derivative (compound 17) in 9% yield. The structure of 18, shown in Fig. 10, features the expected four BHB bridges but, surprisingly, the B(5)···B(10) distance has increased to a non-bonding value of 249.7 pm [compared with 183.5 pm for B(7)-B(8)], thereby generating a novel 7-membered RuB_6 open face. Consistent with the isoarachno-type geometry of compound 18, its ^{11}B n.m.r shielding behaviour deviates widely from that of nido-$B_{10}H_{14}$ and its straightforward 6-, 5-, and 2-metalla derivatives. It is tempting to speculate that the rupture of the B(5)-B(10) linkage in compound 18 reflects an increased electron contribution from the ruthenium to the cluster electron count, though at present there is

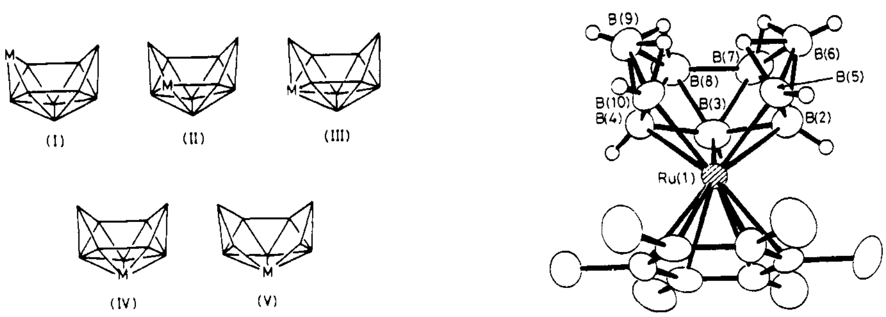


Fig. 10. Skeletal structures for metalla-nido-decaboranes (I-IV) and for the isoarachno-1-subrogated cluster (V), together with the crystallographically determined structure of $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}isoarachno\text{-}RuB_9H_{13}]$, compound 15

no experimental evidence as to whether the compound is more accurately described as a Ru^{II} or Ru^{IV} derivative. It is noteworthy that the isoarachno geometry (Fig. 10) can notionally be derived by removal of two adjacent vertices from the known isocloso twelve-vertex cluster geometry observed for $\{WC_2B_9\}$ in $[Pt(PEt_3)_2(CO)_2WC_2B_9H_8Me_2(CH_2C_6H_4Me)]$ (ref. 24).

A second recent example of an unexpected cluster geometry is provided by the orange-yellow, air-stable metalladicarbaborane cluster $[2,4\text{-}Me_2\text{-}1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)\text{-}1,2,4\text{-}RuC_2B_8H_8]$, compound 19. In the absence of direct experimental evidence, such eleven-vertex, '24-electron' species had previously been assumed to have a symmetrical closo deltahedral cluster structure (refs. 25-27) but, in fact, as shown in Fig. 11a, compound 19 has a quadrilateral open face Ru(1)C(2)C(4)B(5) with an essentially non-bonding Ru(1)···C(4) distance of 268.3(7) pm (ref. 28); this compares with a distance of 212.4(6) pm for Ru(1)-C(2). Compound 19 was obtained in 30% yield by reaction of $[\{(\eta^6\text{-}MeC_6H_4Pr^i)RuCl_2\}_2]$ and $[5,6\text{-}Me_2\text{-}nido\text{-}5,6\text{-}C_2B_8H_{10}]$ in the presence of 'proton sponge' (N,N,N',N'-tetramethylnaphthalene-1,8-diamine) in dichloromethane solution for 2 hours, and use of $[\{(\eta^6\text{-}C_6Me_6)RuCl_2\}_2]$ gave the corresponding open-faced hexamethylbenzene derivative (ref. 29.). Thermolysis of compound 19 at 400 °C gave a quantitative yield of the yellow symmetrical isomer, $[2,3\text{-}Me_2\text{-}1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)\text{-}closo\text{-}1,2,3\text{-}RuC_2B_8H_8]$, (compound 20, Fig. 11b, ref. 29); here the 'distortion' is manifest as a substantial lengthening of Ru(1) to each of the four directly bonded boron atoms in the η^6-dicarbaborane ligand. Overall formal polar C_{2v} symmetry is thereby maintained and the cluster distortion can be characterized as a 'symmetrical elongation' rather than a 'slippage'. Further insight into structure/electron-count relationships in the eleven-vertex system is provided by the non-carbon-containing cluster $[1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)\text{-}closo\text{-}1\text{-}RuB_{10}H_{10}]$, compound 21, which was made in 87% yield by direct insertion of $\{(\eta^6\text{-}pcym)Ru\}$ into $closo\text{-}B_{10}H_{10}{}^{2-}$ using $[\{(\eta^6\text{-}pcym)RuCl_2\}_2]$. Here there is a formal 22-electron count (rather than a 24-electron count as in the dicarba derivatives 19 and 20) and, as seen in Fig. 11c, there is a compact symmetrical structure of C_{2v} cluster symmetry, the distance of Ru(1) from the mean B(4)B(5)B(6)B(7) plane being some 11 pm less than for the dicarba analogue, compound 20. The significance of these and other dimensional differences are fully discussed in ref. 29.

Three other examples of distortions from expected closo geometry in eleven-vertex, '24-electron' clusters have recently come to light. Thus, the molecular structure of $[1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}isonido\text{-}1,2,4\text{-}IrC_2B_8H_{10}]$, compound 22, which had previously been assumed to have a regular closo structure, (ref. 30) has been found by single-crystal X-ray diffraction analysis to have a clearly defined quadrilateral open face Ir(1)C(2)C(4)B(7) as shown in Fig. 12a (ref. 31): the distance Ir(1)···C(4) is 277.9(8), as compared to 219.2(7) for Ir(1)-C(2). A related distortion has been found in the putative '24-electron', eleven-vertex dimetalla cluster $[1,4\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}\mu\text{-}1,4\text{-}H\text{-}isonido\text{-}1,4\text{-}RhIrB_9H_{10}]$, compound 23, (ref. 32). This stable yellow compound was obtained in 6% yield from the reaction in CH_2Cl_2 of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ with $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6\text{-}IrB_9H_{13}]$ in the presence of 'proton sponge'. The structure, as determined by X-ray diffraction analysis, is shown in Fig. 12b and features a Rh(1)Ir(4)B(7)B(3) quadrilateral face despite the presumed closo electron count. In fact, the X-ray evidence reveals three types of disorder in the crystals of this compound: one with respect to interchange of the two metal types across the B(2)B(9)B(11) plane, a second with respect to interchange of C_5Me_5 rotamers across the plane, and a third with regard to exchange in the pseudo mirror plane of the BH(2) group between the position shown in Fig. 12b and the 'vacant' site above the quadrilateral open face. As a result, the hydrogen atoms were not located in the X-ray analysis but were apparent from n.m.r. spectroscopy which revealed the expected nine BH_{exo} groups, the Rh(1)-H-Ir(4) bridge, and the B(3)-H-B(7) bridge.

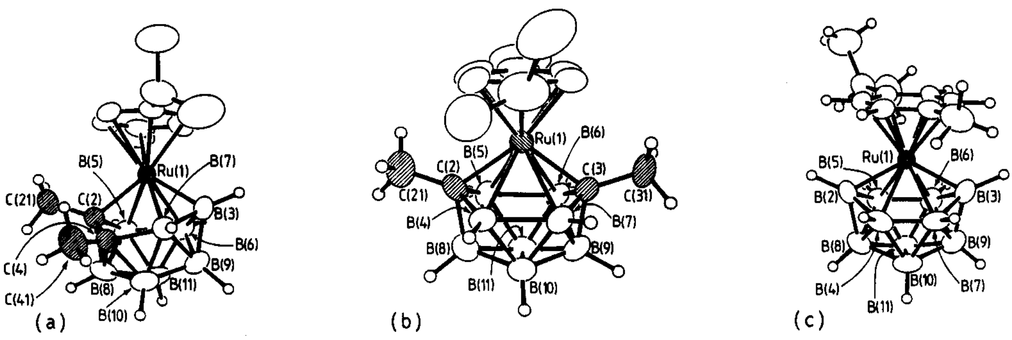


Fig. 11. (a) Molecular structure of compound 19, $[2,4\text{-}Me_2\text{-}1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)\text{-}1,2,4\text{-}RuC_2B_8H_8]$, showing the quadrilateral open face Ru(1)C(2)C(4)B(5) (refs. 28,29); (b) molecular structure of compound 20, $[2,3\text{-}Me_2\text{-}1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)\text{-}$*closo*$\text{-}1,2,3\text{-}RuC_2B_8H_8]$, showing the slightly stretched C_{2v} cluster geometry (ref. 29); (c) molecular structure of compound 21, $[1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)\text{-}$*closo*$\text{-}1\text{-}RuB_{10}H_{10}]$, showing the compact symmetrical C_{2v} cluster geometry (ref. 29)

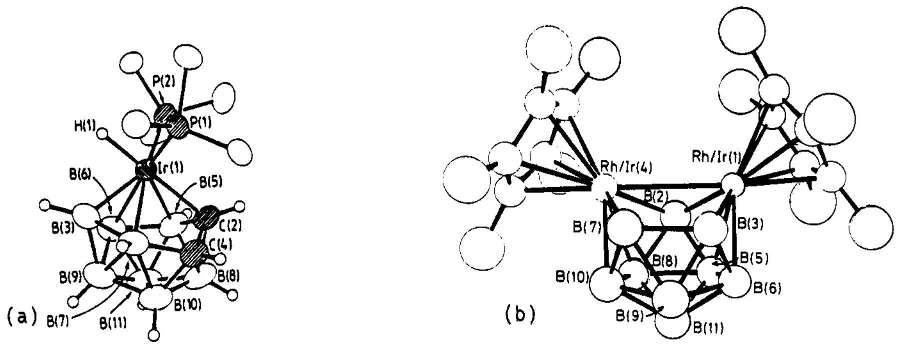


Fig. 12. (a) Molecular structure of compound 22 $[1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}$*isonido*$\text{-}IrC_2B_8H_{10}]$, showing the quadrilateral open face Ir(1)C(2)C(4)B(7) (ref. 31); (b) molecular structure of compound 23, $[1,4\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}\mu\text{-}1,4\text{-}H\text{-}$*isonido*$\text{-}1,4\text{-}RhIrB_9H_{10}]$, showing the position of non-hydrogen atoms only (see text) (ref. 32)

The final example concerns the unexpected structure of the orange, air-stable species $[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}8,10\text{-}Me_2\text{-}$*nido*$\text{-}2,8,10\text{-}OsC_2B_8H_8]$, compound 24, which is obtained quantitatively by thermal rearrangement (14 min at 400 °C) of its isomer, the presumed *closo* species $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}OsC_2B_8H_8]$ (ref. 33). As seen in Fig. 13a, compound 24 exhibits a five-membered BCBCB open face and is thus fundamentally different from the *closo* configuration previously assumed and generally accepted for a '24-electron' eleven-vertex cluster. The structure clearly resembles that of the '26-electron' species [*nido*-$B_{11}H_{14}]^-$, Fig. 13b (ref. 34), despite having two less cluster electrons (as supplied by the unique H_{endo} and the single negative charge in $[B_{11}H_{14}]^-$. It is also noteworthy that the Os(2) ~~atom~~ is not in the open-face of the cluster, so that a rationale analogous to that invoked (ref. 35) to account for the 'slipped' structures of certain platinadicarbaboranes does not apply in this case. Such structural behaviour is without precedent, and since there is no obvious *a priori* reason for expecting anything other than a straightforward closed structure, it re-emphasizes the importance of backing theoretical deliberations in this area with definitive experimental evidence (ref. 36).

AZA- AND OXA-METALLABORANES AND RELATED SPECIES

Main-group-element atoms can be incorporated onto or into metallaborane clusters with varying degrees of intimacy. Substitution of one or more terminal hydrogen atoms on the cluster affords amine, amino, alkoxy etc. derivatives in which the heteroatom can be *exo* to the cluster, *endo* to the cluster, or in a bridging position between two (often non-adjacent) cluster vertices, and several examples of such species and their phosphine and sulphide analogues have already been mentioned in preceding sections. Direct involvement of the heteroatom as a cluster vertex is also well documented for both light and heavy heteroatoms, the classic examples of the former being the multitudinous metalla derivatives

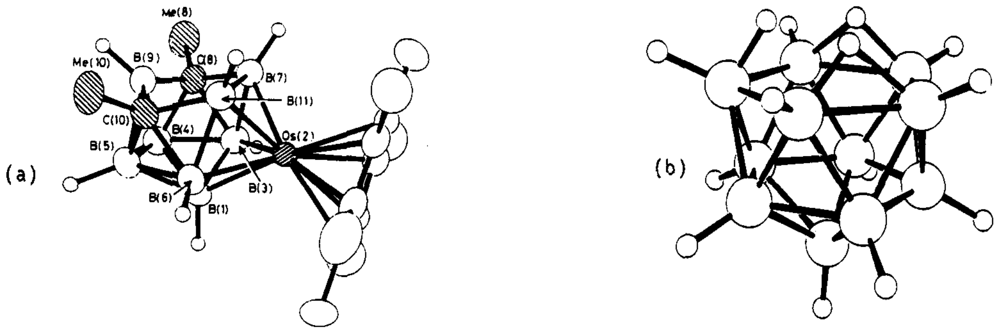


Fig. 13. (a) Molecular structure of compound 24, $[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}8,10\text{-}Me_2$-nido-$2,8,10\text{-}OsC_2B_8H_8]$, showing the 5-membered BCBCB open face which does not involve the osmium atom (ref. 33); (b) the closely related structure of the nido anion $B_{11}H_{14}^-$ (ref. 34)

of the dicarbaboranes. Incorporation of the appreciably more electronegative first row heteroatoms N and O as cluster vertices in metallaboranes has been much less extensively studied, though a small number of such species is now beginning to emerge. These, and some related metallaborane compounds having B-N or B-O linkages, form the subject of this concluding section.

An example, which is so-far unique, of a multiply-bonded nitrogen-substituted metallaborane involving N$\rightleftarrows$B π donation into a polyhedral cluster is afforded by $[1\text{-}(\eta^5\text{-}C_5Me_5)\text{-}4\text{-}(NEt_2)$-isocloso-$1\text{-}RhB_{10}H_9]$, compound 25; this is obtained in 66% yield as purple air-stable crystals by the reaction of Et_2NH with the orange-yellow isocloso eleven-vertex metallaborane $[1\text{-}(\eta^5\text{-}C_5Me_5)\text{-}1\text{-}RhB_{10}H_{10}]$ in CH_2Cl_2 solution at room temperature (ref. 37). The detailed molecular structure (Fig. 14a) reveals a planar nitrogen atom and a short N(4)-B(4) distance [142.7(8) pm, compared with the usual 'single-bond' N-B distance of about 158 pm]. These are both indicative of partial double bonding, N$\rightleftarrows$B, and this is confirmed by variable-temperature proton n.m.r. spectroscopy which shows that the barrier to rotation about the N$\rightleftarrows$B linkage is 53.8 ± 0.5 kJ mol^{-1} at 272 K. So far as we are aware, these three observations are the first direct evidence for exo-element-to-boron π-donation in a borane cluster compound of any type. Further indirect manifestations of the N$\rightleftarrows$B bonding are (a) the lengthening, towards an isonido structure, of the Rh(1)-B(4) distance [to 246.1(7) pm compared to 227.6(8) and 227.7(8) for the Rh(1)-B(5) and Rh(1)-B(6) distances, respectively], and (b) the slight tilting of the η^5-C_5 plane away from B(4), the dihedral angle between η^5-C_5 and B(4)B(5)B(6)B(7) being 5° (ref. 37). Proton n.m.r. also reveals a barrier to rotation for the 6-NEt_2 group in the disubstituted ten-vertex isocloso analogue $[1\text{-}(\eta^5\text{-}C_5Me_5)\text{-}2,6\text{-}(NEt_2)_2\text{-}1\text{-}RhB_9H_7]$ with $\Delta G^{\ddagger}_{278}$ ca. 56 kJ mol^{-1}, but we have yet to confirm by X-ray diffraction analysis whether this is also accompanied by N-atom planarity and/or partial cluster opening.

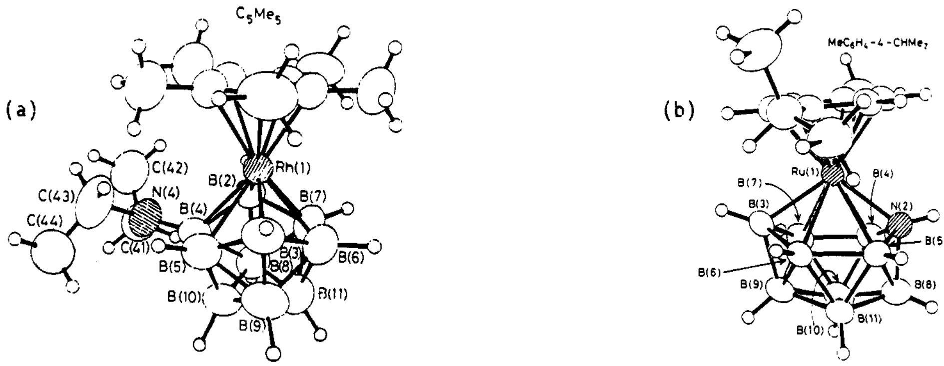


Fig. 14. (a) Molecular structure of compound 25, $[1\text{-}(\eta^5\text{-}C_5Me_5)\text{-}4\text{-}(NEt_2)$-isocloso-$1\text{-}RhB_{10}H_9]$ (ref. 37); (b) molecular structure of the azametallaborane compound 26, $[1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)$-closo-$1,2\text{-}RuNB_9H_{10})$(ref. 38).

Actual incorporation of a nitrogen atom as a fully contiguous cluster vertex in a metallaborane was first achieved in work we have done in collaboration with the group at Rež. The reaction of $[\{(\eta^6\text{-}MeC_6H_4Pr^i)RuCl_2\}_2]$ with nido-$6\text{-}NB_9H_{12}$ in the presence of proton sponge in thf gave, as one of the products (isolated in 15% yield), the orange-red, air-stable crystalline compound 26, $[1\text{-}(\eta^6\text{-}MeC_6H_4Pr^i)$-closo-$1,2\text{-}RuNB_9H_{10}]$, of which the structure is shown in Fig. 14b (ref. 38). The only other azametallaborane previously reported is the ten-vertex platinum species $[6,6\text{-}(PPh_3)_3$-arachno-$6,9\text{-}PtNB_8H_{11}[$ (compound 27) in which the nitrogen vertex is an NH group, formally equivalent to a BH_2^- unit in an open-face arachno position (ref. 39). A subsequent example of a metallaheteroborane containing a nitrogen atom as a contiguous cluster vertex has already been mentioned as compound 15 (Fig. 8) in the preceding section. A closo structure is to be anticipated for the new compound 26 as it is 'isoelectronic' with closo-$B_{11}H_{11}^{2-}$, but it should be noted that the Ru(1)-N(2) distance of 208.8(6) pm is rather long and suggests some 'slippage' from true closo geometry, reminiscent of the more prominent slippage already discussed in the related compound 19 in Fig. 11a.

Oxametallaboranes are also rare commodities at present. Perhaps the first example was the nido ten-vertex compound 28, $[2\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}2,6\text{-}FeOB_8H_{10}]$, which was reported in 1984 and has the cluster structure I shown in Fig. 15 (ref. 40). A second example, from our own laboratory in the following year, was the red crystalline compound 29, $[7\text{-}(\eta^5\text{-}C_5Me_5)\text{-}8\text{-}Cl\text{-}11\text{-}(PMe_2Ph)\text{-}nido\text{-}7,12\text{-}RhOB_{10}H_9]$ (ref. 41). Compound 29, which has the skeletal structure II (Fig. 15) 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 reported that does not also contain carbon atoms as cluster vertices.

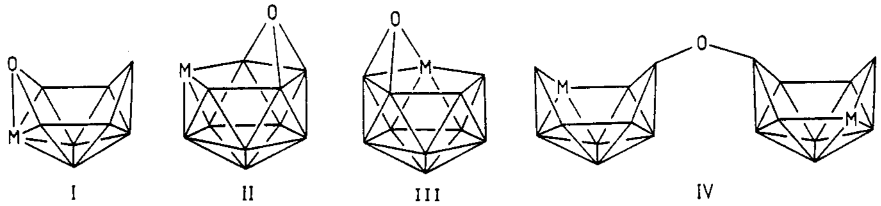
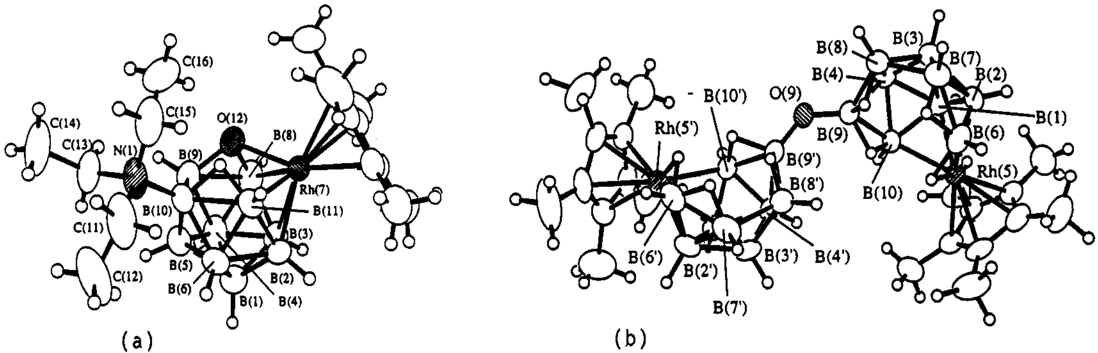


Fig. 15. Skeletal structure types of various oxametallaboranes (see text)

Other examples of oxametallaboranes are now beginning to emerge as a result of mild air oxidation of rhodaboranes. Thus, treatment of the quadruply hydrogen-bridged nido eleven-vertex species $[7\text{-}(\eta^5\text{-}C_5Me_5)\text{-}9\text{-}Cl\text{-}nido\text{-}7\text{-}RhB_{10}H_{13}]$, compound 30, with NEt_3 followed by chromatography on silica in air yields viable amounts of a new orange compound 31 of skeletal type III (Fig. 15) (ref. 42). Detailed X-ray diffraction analysis and other evidence leads to the formulation of compound 31 as $[7\text{-}(\eta^5\text{-}C_5Me_5)\text{-}10\text{-}(NEt_3)\text{-}nido\text{-}7,12\text{-}RhOB_{10}H_{10}]$ having the single hydrogen-bridged open twelve-vertex structure shown in Fig. 16a. It should be noted that, in the absence of NEt_3, compound 30 oxidizes to a mixture of oxo- and hydroxo-substituted rhodaboranes amongst which the 9,9'-oxo-bridged compound 32, $[\{5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}5\text{-}RhB_9H_{12}\}_2O]$ of skeletal type IV (Fig. 15), has been identified by single-crystal X-ray diffraction analysis (Fig. 16b)(ref. 42).



(a) (b)

Fig. 16. (a) Molecular structure of compound 31, $[7\text{-}(\eta^5\text{-}C_5Me_5)\text{-}10\text{-}(NEt_3)\text{-}nido\text{-}7,12\text{-}RhOB_{10}H_{10}]$; and (b) molecular structure of compound 32, $[\{5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}5\text{-}RhB_9H_{12}\}_2O]$ (ref. 42)

The aza- and oxa-metallaborane compounds 15, 26-29, 31, and 32 can be regarded as the harbingers of a much more extensive metallaheteroborane chemistry where the main-group heteroatom is a polyvalent electronegative first-row element other than carbon, and we are at present seeking to explore further this potentially rich area of cluster chemistry.

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