

Metallaboranes of the earlier transition metals. An *arachno* nine-vertex, nine-skeletal electron pair rhenaborane of novel shape: importance of total vertex connectivities in such systems

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The synthesis and characterization of Cp^{*}₂Re₂B₇H₁₁ provides the first example of an open hypoelectronic metallaborane which is shown to possess an *arachno* geometry based on a total vertex connectivity identical with that of a canonical *arachno* nine-vertex, twelve-skeletal electron pair cluster.

Extensive catenation is a characteristic shared by the adjacent elements boron and carbon albeit expressed differently in structure, *e.g.* cages *vs.* rings and chains. The origin of the differences is well understood and the established relationship between geometry and the number of skeletal electron pairs (*sep*) for borane cages serves to provide interconnections between borane, heteroborane, carbocation, transition metal cluster and Zintl phase cluster chemistries.^{1–6} The metal sites in a heteroborane, *e.g.* a metallaborane, perturb the borane bonding network and the structural response can be measured.^{7,8} In an expression of the isolobal analogy, metallaboranes containing late transition metals frequently mimic simple main group fragments generating geometries that conform to the canonical structures associated with equivalent *sep* (the term canonical refers to the set of shapes and associated *sep*'s exhibited by the known boranes).^{9,10}

The observations of Kennedy and coworkers of 'disobedient' metallaboranes¹¹ with *closo* geometries deviating from most spherical deltahedra (most homogeneous vertex connectivities)¹² have been interpreted in terms of a metal providing more orbitals to meet the *p* + 1 *sep* rule ('*isocloso*'—missing electrons localized on the metal)¹³ or fewer electrons (*p sep*) demanding a skeletal shape with no borane analog ('*hypercloso*'—missing electrons delocalized over the skeleton).¹⁴ Despite these contrasting analyses, what is clear is that the observed geometric structures are related by diamond–square–diamond (*dsd*) rearrangements.¹⁵ Recently, we have described a homologous series of *closo*-metallaboranes, Cp^{*}₂Re₂B_{*n*}H_{*n*} (*n* = 7–10, Cp^{*} = η⁵-C₅Me₅), with *p* – 2 *sep*.¹⁶ In addition, we completed a 10-atom, closed metallaborane series for *sep* running from *p* + 1 to *p* – 2.^{17,18} These results demonstrate that the formal *sep* can vary widely from the canonical number and, as it decreases, the cluster shape deviates from that of a most spherical deltahedron. Taking the canonical shapes and *sep*'s as the standard, we follow Corbett and designate these compounds as hypoelectronic.¹⁹ Note that because hypoelectronic and canonical structures are related by *dsd* rearrangements, the total connectivity of the deltahedral framework is the same for a given value of *p*.

Kennedy and coworkers have also described examples of '*isonido*' metallaboranes (*p* + 1 *sep*) related to canonical *nido* geometries (*p* + 2 *sep*) in the same manner as '*isocloso*' are to *closo*.¹¹ For this reason we have sought examples of open clusters of the earlier metals in which the formal *sep* is even lower. Herein we describe an open rhenaborane with *p sep* and show how it can be classified as an *arachno* shape which normally requires *p* + 3 *sep*.

As previously reported, the reaction of BH₃·thf with Cp^{*}₂Re₂H₄B₄H₄ leads to the formation of Cp^{*}₂Re₂B₇H₇ and subsequent conversion to the higher analogs.^{16,20,21} A minor product with an *R_f* higher than Cp^{*}₂Re₂B₇H₇ was greatly enhanced by using a lower borane to metallaborane ratio and reduced temperature and reaction time.† This new compound, **1**, has been isolated in modest yield and characterized spectroscopically and by a single crystal X-ray diffraction study.‡ The molecular mass corresponds to Cp^{*}₂Re₂B₇H₁₁ **1**, and the ¹H (temperature independent to –90 °C) and ¹¹B NMR spectra suggest two planes of symmetry. Besides the BH_{terminal} protons (1 : 2 : 4) two equivalent BHB and two equivalent BHRh protons are also observed. A ¹H/¹¹B HETCOR experiment shows the latter four protons to be coupled exclusively to the four boron atoms equivalent in the NMR spectrum.

The framework structure of **1** only became clear when the solid state structure was determined (Fig. 1). Yet again an unanticipated shape is observed for a rhenaborane. **1** displays an open structure such that the edges defining the opening describe a boat shaped cyclohexane-like ring. Although the B–B and Re–B distances are comparable to those found in Cp^{*}₂Re₂B₇H₇^{22,23} and higher homologues,¹⁶ the ReRe distance is *ca.* 0.15 Å longer. On the other hand it is nearly the same as the W–W distance in Cp^{*}₂W₂H₂B₇H₇^{20,21} and, thus, we suggest the presence of cross-cage metal–metal bonding in **1**. Based on the NMR results, the extra hydrogens can be placed on this skeleton in two ways as shown in Fig. 2(a) and (b). In (a) the ReH hydrogens lie in the plane of symmetry containing the two Re atoms and the unique B atom. In (b) they bridge two of the four

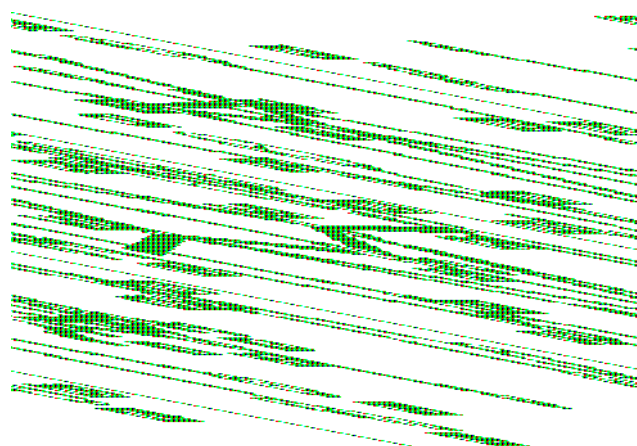


Fig. 1 Molecular structure and labelling diagram for (Cp^{*}Re)₂B₇H₁₁. Selected bond distances (Å) for one of two independent but chemically equivalent molecules: Re(1)–Re(2) 2.9744(5), Re(1)–B(1) 2.216(13), Re(1)–B(3) 2.221(13), Re(1)–B(5) 2.241(12), Re(1)–B(6) 2.271(11), Re(2)–B(2) 2.227(12), Re(2)–B(4) 2.211(12), Re(2)–B(5) 2.236(12), Re(2)–B(6) 2.258(13), Re(2)–B(7) 2.091(12), B(1)–B(2) 1.753(17), B(1)–B(5) 1.728(17), B(2)–B(5) 1.736(19), B(3)–B(4) 1.747(16), B(4)–B(6) 1.734(18), B(5)–B(7) 2.012(18), B(6)–B(7) 2.044(17).

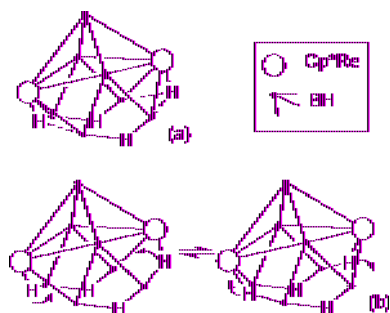


Fig. 2 Two possible placements of the four endo hydrogen atoms on **1**.

Re–B edges on the hexagonal opening thereby demanding a low barrier process for the exchange shown. We favor (b) as it is difficult to explain the observed coupling to boron with model (a).

As the Cp*Re fragment is a zero-electron fragment, the formal number of sep in **1** is 9; however, we find no way of connecting the geometry of **1** to either the canonical deltahedra or the observed deltahedra of Cp*₂Re₂B_nH_n ($n = 7–10$) by simple vertex removal. Therefore, we suggest an alternative approach which promises some generality. As already mentioned, the geometries adopted by Cp*₂Re₂B_nH_n ($n = 7–10$), have total vertex connectivities (tvc) equal to those of the canonical deltahedra, e.g. Cp*₂Re₂B₇H₇ possesses two six-coordinate, two five-coordinate, five four-coordinate vertices (tvc = 42) whereas the canonical tricapped trigonal prism has six five-coordinate, three four-coordinate vertices (tvc = 42). An examination of the canonical *closo* series for $p = 6–12$ shows that the tvc increases monotonically in units of 6, i.e. tvc runs from 24 to 60.¹⁶ This holds true for Cp*₂Re₂B_nH_n ($n = 7–10$) as well.¹⁵ Likewise, if one uses Williams' preferred *nido* and *arachno* geometries,²⁴ one finds, that for *nido* cages, $p = 6–11$, tvc runs from 20 to 50 in units of 6 and for *arachno* cages, $p = 6–10$, tvc runs from 18 to 42 in units of 6. The assumption that tvc is conserved for *nido* and *arachno* structures, as already demonstrated for *closo* structures, yields a shape independent method for classifying non-canonical geometries.

Consider the new rhenaborane. **1** has an open structure with a tvc = 36. The canonical nine fragment *closo*, *nido* and *arachno* shapes have tvc's of 42, 38 and 36, respectively (Fig. 3). Thus, **1** is classified as a 9 sep *arachno* analog of a 12 sep canonical *arachno* borane. This parallels the relationship of 7 sep *closo* Cp*₂Re₂B₇H₇ to a 10 sep *closo* canonical cage. The beauty of the approach is that it avoids the question of how many electrons a metal fragment actually contributes to cluster bonding ('*isocloso*' vs. '*hypercloso*') and suggests that,

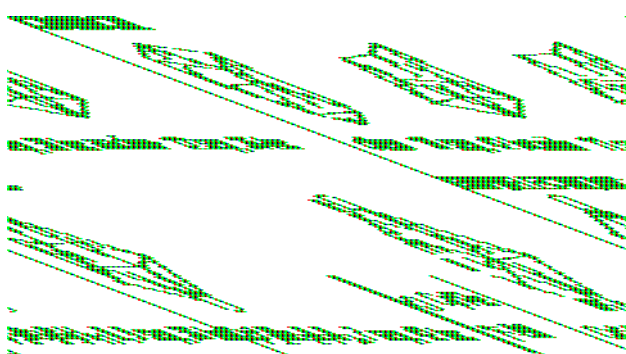


Fig. 3 Comparison of the canonical nine-atom *closo*, *nido* and *arachno* geometries with observed examples of *closo* and *arachno* hypoelectronic rhenaboranes with formal sep's three lower than the canonical values.

vided tvc is conserved, the shape adopted can be tailored to the electronic demands of the metal. The drawback is that, although this approach limits the number of shapes possible, it is not predictive. However, with the characterization of an increasing number of metallaboranes containing earlier metals, the role of the metal may eventually become sufficiently well defined to permit predictions as well as rationalizations.

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Notes and references

† *Synthetic procedure for 1*: to a 100 mL Schlenk tube, containing 0.15 g (0.21 mmol) of (Cp*ReH₂)₂B₄H₄ in 15 mL of toluene was slowly added a three-fold excess of BH₃·thf. The reaction mixture was thermolysed for 15 h at 75 °C after which volatiles were removed *in vacuo*, the residue was extracted in hexane, and the extract filtered through Celite. After removal of solvent from the filtrate, the residue was chromatographed on silica gel TLC plates. Elution with hexane yielded four very closely spaced bands. The first yellow band to elute was Cp*₂Re₂B₇H₁₁ **1** (0.026 g, 17%) and the subsequent bands were (Cp*Re)₂B_nH_n ($n = 7–10$).

Selected data for 1: ν (hexane)/cm⁻¹ 2498w, 2444w (B–H_{term}); δ_{H} (C₆D₆, 22 °C) 10.61 (pcq, 1BH₃), 7.51 (pcq, 4BH₃), 0.72 (pcq, 2BH₃), 0.04 (br, 2B–H–B), 1.76 (s, 30H, 2Cp*), –10.77 (s, 2Re–H–B); δ_{B} (C₆D₆, 22 °C, J/Hz) 98.1 (d, J_{BH} 162, 2B), 28.3 (d, J_{BH} 130, 4B), –7.2 (d, J_{BH} 141, 2B); HR-EIMS, m/z : ¹²C₂₀¹H₄₁¹¹B₇¹⁸⁷Re₂, calc. 732.2982, obs. 732.2948; isotope distribution corresponding to 7B, 2Re.

‡ *Crystal data for (Cp*Re)₂B₇H₁₁*: $M = 759.5$, triclinic, $P\bar{1}$, yellow, $a = 8.7967(2)$, $b = 17.7865(3)$, $c = 18.0509(4)$ Å, $\alpha = 111.5640(10)$, $\beta = 102.924(2)$, $\gamma = 99.4110(10)^\circ$, $V = 2464.21$ Å³, $Z = 4$, $D_c = 2.046$ g cm⁻³, μ (Mo–K α) = 98.2 cm⁻¹, $R(F) = 0.0485$, $R(wF2) = 0.1372$. Of 20 160 reflections collected, 8614 were independent. All non-hydrogen atoms were refined anisotropically. All Cp* hydrogen atoms were placed in idealized locations; the seven terminal B–H hydrogen atoms were located and refined. The four bridging hydrogen atoms were not located. CCDC 155582. See <http://www.rsc.org/suppdata/cc/b1/b101918j/> for crystallographic data in .cif or other electronic format.

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