14-Vertex Heteroboranes with 14-Skeletal Electron Pairs: An Experimental and Computational Study

Alasdair P. M. Robertson, Nicholas A. Beattie, Greig Scott, Wing Y. Man, John J. Jones, Stuart A. Macgregor*, Georgina M. Rosair and Alan J. Welch[a]

Abstract: Three isomers of [(Cp*Ru)2C2B9H12], the first examples of 14-vertex 14-Skeletal Electron Pair heteroboranes, have been synthesized by the Direct Electrophilic Insertion of a [Cp*Ru+] fragment into the anion [4-Cp*-4,1,6-RuC2B9H12]. All three compounds have the same unique polyhedral structure having approximate C4 symmetry and featuring a 4-atom trapezoidal face. X-ray diffraction studies could only confidently identify one of the two cage C atoms in each structure. The other C position has been established by a combination of (i) best fitting of computed and experimental 1H NMR chemical shifts and (ii) consideration of lowest computed energy, for series of isomers studied by DFT calculations. In all three isomers one cage C atom occupies a degree-4 vertex on the short parallel edge of the trapezium.

The structures of boranes and heteroboranes are usually interpreted in terms of the electron-counting principles, established by Wade and Mingos more than 40 years ago,[7] which rationalise families of clusters having closo structures and n+1 skeletal electron pairs (SEPs), nido structures and n+2 SEPs and arachno structures and n+3 SEPs, etc.

A small but interesting further family of heteroboranes is that in which the members possess only n SEPs and these species, generally referred to as hypercloso, have been the subject of significant interest in the literature.[2] In general these clusters do not have the structures normally encountered for n+1 SEP species but rather they are related to them by a single diamond-square-diamond (d-s-d) isomerisation.[3] An excellent early example is [(CpFe)2C2B10H10][6],[4] a 10-vertex (10-v) 10-SEP species structurally related to the bicapped square antiprismatic 10-v 11-SEP cobalt analogue [(CpCo)2C2B11H11][3] by a d-s-d rearrangement of the 2-6-10-9 diamond of the latter polyhedron, Figure 1.

A number of these hypercloso clusters have been reported by Kennedy[6] who has argued that they are actually n+1 SEP compounds in which the metal utilises four, as opposed to the usual three, orbitals in cluster bonding. In this approach the compounds are simply regarded as differently-structured closo species and, accordingly, Kennedy has used the descriptor isocloso. Although MO calculations by Mingos support the hypercloso view[7] and the fact that Spencer has shown that the simple addition of 2e to {hypercloso-(η5-C5Me5)RuB3H9} converts it to {closo-(η5-C5Me5)RuB3H9}[8,9] the isocloso descriptor is still in use in the present day.[8]

![Figure 1](image)

Figure 1. (left) The 10-v 11-SEP bicapped square antiprismatic structure of 2,6-Cp*2,6,1,10-C6B10H14. (right) The 10-v 10-SEP structure of 2,10-Cp*:2,10,1,9-FeC2B10H14, featuring a degree-6 metal atom at vertex 2. The two polyhedra are related by applying a d-s-d sequence to the 2-6-10-9 diamond of the left polyhedron.

To date, the small library of hypercloso heteroboranes has almost exclusively been composed of clusters with between 9 and 12 vertices, limiting the possibility of an extensive study of such species. The hypercloso electron count distorts the cluster from a geometry associated with an n+1 SEP species to one in which at least one vertex, usually a transition-metal, becomes highly connected. Accordingly we believe that the supraicosahedral area holds promise with respect to a systematic study of hypercloso compounds since supraicosahedra necessarily contain highly-connected vertices. Currently this field is relatively under-developed, the only confirmed[8] examples of supraicosahedral hypercloso metallacarboranes[8,9] being the 13-v 13-SEP species [4,5-Cp*:4,5,2,3-Ru2C2B9H12] (I) and [4,5-Cp*:6-SMe2:4,5,2,3-Ru2C2B9H12] (II) isolated by Kudinov and co-workers.[5,8,9] In this communication we describe the synthesis of the first 14-v 14-SEP hypercloso metallacarboranes and their characterisation by a combination of spectroscopic, crystallographic and computational studies.

The 2e reduction of [1,2-C2B3H12] with Na in THF followed by treatment with [Cp*Ru(MeCN)3]Cl and cation metathesis afforded the 13-v 14-SEP ruthenacarborane [BTMA][4-Cp*:4,1,6-Ru2C2B9H12] (1) in 76% yield (BTMA = PhCH2NMe2). Salt 1 was fully characterized spectroscopically and crystallographically [see the Supporting Information (SI) for experimental, spectroscopic, crystallographic and computational details of all new compounds reported in this paper]. As is common for 4,1,6-MC2B10 species, the anion in 1 is fluxional in solution at room temperature via a double d-s-d process[12] with NMR spectra revealing time-averaged C4 symmetry. A perspective view of the anion is shown in Figure 2.

[a] Dr A. P. M. Robertson, N. A. Beattie, Dr G. Scott, Dr W. Y. Man, J. J. Jones, Prof. S. A. Macgregor, Dr G. M. Rosair, Prof. A. J. Welch
Institute of Chemical Sciences
Heriot-Watt University
Edinburgh EH14 4AS (UK)
E-mail: a.j.welch@hw.ac.uk; s.a.macgregor@hw.ac.uk

Supporting information for this article is given via a link at the end of the document.
Treatment of 1 in THF with 0.25[Cp*RuCl]₂ followed by heating under reflux for 16 h produced a complex mixture of products with eight well-defined species clearly visible by thin layer chromatography (see SI, Plate S1). Four of these have been successfully characterised by a combination of mass spectrometry, multinuclear NMR spectroscopy, X-ray diffraction and DFT calculations.

The seventh fastest moving band is an orange compound (2) which was assigned as [(Cp*Ru)₂C₂B₇H₁₀] by mass spectrometry and NMR spectroscopy. Notably, however, the latter indicated that this was clearly not the 4,5,2,3-Ru₂C₂B₅ species isolated by Kudinov since both the ¹H and ¹¹B NMR spectra reveal no molecular symmetry. Moreover there is no very high-frequency ¹¹B resonance in the spectrum of 2 (δ max = 31 ppm in 2; δ max = 97 ppm in the 4,5,2,3 compound), rather there is a high frequency resonance in the ¹H spectrum (δ = 16.6 ppm) assigned to C₅MeH. A crystallographic study (Figure 3) established that 2 is [4,5-Cp*Ru₂₃₋₄₋₅₋₆₋₇₋₈₋₉₋₁₀₋₁₁₋₁₂₋₁₃₋₁₄₋₁₅₋₁₆₋₁₇₋₁₈₋₁₉₋₂₀₋₂₁₋₂₂₋₂₃₋] a 13-v 13-SEP hypercloso species and a positional isomer of I. We assume that 2 is formed by loss of the [BSH] fragment from the anion of 1 or (possibly more likely) its 4,1,8-Ru₂C₁₀ isomer,¹⁹ and capping of the open face thus produced by a [Cp*Ru⁺] fragment.

The diruthenacarborane cage in 2 has a docosahedral structure, essentially the same gross structure as found in 13-v 14-SEP species, and the origin of this superficially unusual result has been traced to the fact that the C₅Me symmetric docosahedron necessarily has non-degenerate molecular orbitals.¹⁹ We have shown that the HOMO of the parent borate [B₃H₁₂]²⁻ is strongly bonding with respect to the 1−2 and 1−3 edges, and moderately strongly bonding with respect to the 6−9 and 7−8 edges.¹⁹ This allows us to rationalise the facts that the 1−2 and 1−3 distances in 2 are ca. 0.09−0.10 Å longer, and the 6−9 and 7−8 distances in 2 are ca. 0.02−0.04 Å longer than the equivalent distances in crystallographically characterised 13-v 14-SEP 4,5,1,6-Me₂C₂B₅ species (see Supporting Information).¹⁵¹⁶

The fastest (purple compound 3), third fastest (dark green compound 4) and sixth fastest (purple compound 5) moving bands were also studied, with elemental analysis and/or mass spectrometry suggesting the formula [(Cp*Ru)₂C₂B₇H₁₂] for all three. The ¹H NMR spectra of 3−5 contain one relatively high-frequency C₅MeH resonance (δ 8.6 to 10.5 ppm) and two resonances corresponding to the Cp⁺ H atoms. The asymmetry of all three compounds is confirmed by their ¹¹B NMR spectra which exhibit ten equal-integral resonances for 4 and 5 and nine resonances for 3 (one 1+1 co-incidence). In all three compounds the range of ¹¹B chemical shifts is relatively large, δ 76.0 to −13.6 ppm for 3, 54.8 to −22.9 ppm for 4 and 72.1 to −12.1 ppm for 5.

Thus compounds 3−5 appear to be the first examples of 14-v 14-SEP hypercloso species, presumably formed by Direct Electrophilic Insertion (DEI)¹⁴¹¹¹⁶ of a [Cp*Ru⁺] fragment into the anion of 1, and it was clearly of importance to characterise each of them crystallographically. To our initial surprise compounds 3, 4 and 5 are all isomorphous with 2 but the origin of this became clear when the structures were solved. Compounds 3−5, isothers of each other differing only in the positions of the cage C atoms, share the basic skeleton, which is shown together with an arbitrary numbering scheme in Figure 4. As in 2 the carbaborane central cores in 3−5 are flanked by two large {Cp*Ru} fragments whose Cp⁺ rings are inclined at ca. 47°. The isomorphism presumably results from the packing of molecules in the crystal being determined by the same overall shape of the molecules and not the relatively minor differences in dipole moment that arise from different C atom positions or the presence (in 3−5) of one additional BH unit. The 14-vertex cluster has two degree-6 vertices (2 and 7) occupied by the Ru atoms, ten degree-5 vertices and two degree-4 vertices (1 and 4) occupying the short parallel edge of an approximate trapezium (1−4−8−5). The 1−4 distances are 1.642(4), 1.618(6) and 1.612(4) Å and the 5−8 distances are 2.196(6), 2.024(9) and 2.049(5) Å for compounds 3, 4 and 5 respectively. The whole molecule has approximate C₅ symmetry about the plane containing vertices 3, 6, 9 and 13. To the best of our knowledge this is the first time such a cluster structure has been reported. It is clearly distinct from the bicapped hexagonal antiprism (bha) typical of 14-v 15-SEP
species,[17][18] again reflecting the unique structures of hypercloso clusters. Formally, a bha could be formed from this unique polyhedron by making the 4–5 connection and applying a d-s-d process to the 1-2-10-5-diamond.

It is clearly important to identify which isomer of [(Cp*Ru)2C3B12H12] each of compounds 3-5 is by establishing the positions of the cage C atoms. Analysis of the various NMR spectra confirms that in none of the compounds do both cage C atoms occupy vertices on the approximate mirror plane of symmetry, i.e. vertices 3, 6, 9 and 13, nor are they related by that plane of symmetry. Distinguishing between BH and CH vertices in (hetero)carborane structures studied crystallographically is well-known to be challenging, and it is particularly so in the case of compounds 3-5. This arises because 76% of the X-ray scattering power of the molecules is localised in the two peripheral [Cp*Ru] fragments which are effectively symmetry-related, resulting in a degree of pseudo-symmetry and comparatively poor definition of the asymmetric [C3B12H12] fragments.

We have recently described two new approaches, the vertex-centroid distance (VCD) [19] and boron-hydrogen distance (BHD) [17] methods, that are useful in distinguishing cage B and cage C atoms in carboranes and heterocarboranes. Both methods analyse the Prostructure, the result of refinement in which all B or C vertices are treated as B. The VCD method works by comparing distances from topologically-equivalent vertices to the polyhedral centroid, whilst in the BHD method each B–H distance is compared against all others. Although both methods were successfully used to identify the cage C atoms in 1 and 2 the relatively low symmetry of the polyhedra in compounds 3-5 (C3 at best) means that for these compounds the more useful approach is the BHD method. B–H distances in the Prostructures of 3-5 are given in the SI.

The compound in which the clearest indication is given of the position of one of the cage C atoms is compound 4, which has B12–H12 0.33(6) Å in the Prostructure. The next shortest B–H distance is at vertex 1, 0.78(4) Å. However, whilst we are fully confident that in 4 one cage C atom is at vertex 12 we have sought further evidence for the position of the second C atom through DFT calculations. In these the crystallographically-determined skeleton was used to build ten isomers [2,7-Cp*-2,7,12,1-Ru2C3B12H12] for a = 1, 3, 4, 5, 6, 8, 9, 11, 13 and 14 (a = 10 can be disregarded since that would be mirror-symmetric) and each isomer was optimised using the BP86 functional. Following optimisation the 1H and 10B NMR chemical shifts of each isomer were calculated at the B3LYP level and compared with those measured experimentally.[20] In summary, the isomer [2,7-Cp*-2,7,1,12-Ru2C3B12H12] very clearly gave the best agreement between theory and experiment. Thus linear regression of the computed and experimental 10B NMR shifts yields an R2 value for the 2,7,1,12 isomer of 0.9954 c.f. 0.8676 for the next-best isomer (2,7,3,12).

In terms of 1H NMR shifts the difference in the sum (∑) of the calculated and actual chemical shifts for the two C3B12H12 resonances is only 1.21 ppm for the 2,7,1,12 isomer cf. 5.01 ppm for the next best isomer (2,7,4,12). Finally, of all the ten isomers the lowest free energy computed (BP86-D3 with a correction for the THF solvent) was for the 2,7,1,12 isomer, 3.5 kcal mol−1 below that of the next most stable isomer (2,7,4,12). Thus compound 4 is identified as [2,7-Cp*-2,7,1,12-Ru2C3B12H12]. The position of the second cage C atom at vertex 1 is, moreover, chemically sensible in that vertex 1 is the degree-4 vertex in the trapezoidal face which subtends an acute angle, B4–C1–B5 = 86.7(4)°, consistent with B4...B5 being an incipient connectivity, 2.220(11) Å. A perspective view of 4 is given in Figure 5.

In the Prostructure of compound 5 there is also one strong indication of a cage carbon atom since B6–H6 is only 0.50(3) Å [the next shortest B–H is at vertex 1, 0.96(3) Å]. Since vertex 6 lies on the effective mirror plane of the molecule there are only four possible isomers for compound 5, [2,7-Cp*-2,7,6-b-Ru2C3B12H12] for b = 1, 5, 11 and 12. DFT calculations strongly suggest that b = 1. R2 is 0.9899 for the 2,7,1,6 isomer compared to 0.8611 for the next best fit (2,7,6,11). Only one resonance attributed to C3B12H12 was evident in the 1H NMR spectrum of 5 (see Supporting Information) but it fits best (Δ = 0.61 ppm) with one of the computed shifts for the 2,7,1,6 isomer (next smallest Δ = 4.99 ppm). Finally, the 2,7,1,6 isomer has the lowest computed free energy of all four isomers considered, 4.9 kcal mol−1 more stable than the next most stable isomer (2,7,5,6). We therefore conclude that compound 5 is [2,7-Cp*-2,7,1,6-Ru2C3B12H12]. There is partial disorder between C1 and B4 in the crystallographically-determined structure of 5 but this does not change the isomer since 2,7,1,6 and 2,7,4,6 are enantiomeric.

For compound 3 the BHD analysis is complicated by three apparent short B–H distances, 0.58(4), 0.74(3) and 0.87(4) Å at vertices 5, 1 and 13 respectively, although the significance of the short B5–H5 distance may be questioned since B5 is disordered.

Figure 4. Generalised representation of compound 3-5 and atomic numbering scheme.

Figure 5. Solid-state structure of compound 4. Ru2–C1 2.049(4), Ru2–B5 2.315(7), Ru2–B10 2.127(5), Ru2–B11 2.187(4), Ru2–B6 2.264(4), Ru2–B3 2.258(4), Ru7–B3 2.253(4), Ru7–B4 2.132(4), Ru7–B12 2.187(4), Ru7–B6 2.264(4), Ru7–B2 2.289(4), Ru7–B3 2.253(4), Ru7–B4 2.132(4), Ru7–B5 2.197(5), Ru7–C12 2.147(4), Ru7–B14 2.158(4), Ru7–B6 2.265(4), Ru7–C(Cp*) 2.236(3)-2.271(3), Ru7–C(Cp*) 2.243(3)-2.261(3), B4...B5 2.220(11) Å.
over two positions (see SI). Nevertheless, for this compound DFT calculations were performed on two sets of isomers, [2,7-Cp*-2,7,5,c-Ru2C8B14H12] for c = 1, 3, 4, 6, 9, 10, 11, 12, 13 and 14, and [2,7-Cp*-2,7,1,d-Ru2C8B14H12] for d = 3, 5, 6, 8, 9, 10, 11, 12, 13 and 14. In the latter case these calculations gave strong support for the second cage C atom at vertex 13, this affording the best fit between calculated and actual 1H NMR chemical shifts ($R^2 = 0.9939$), the lowest free energy and the third best fit between calculated and actual 1H NMR chemical shifts ($\Delta \Sigma = 0.93$ ppm). In the former case (one cage C at vertex 5) the situation was anomalous, with the 2,7,3,5 isomer being best in terms of 11B shifts, the 2,7,4,5 isomer best in terms of 1H shifts and the 2,7,5,13 isomer having the lowest free energy. None of these, however, was either better or lower than the corresponding measure for the 2,7,1,13 isomer and therefore we tentatively suggest that compound 3 is [2,7-Cp*-2,7,1,13-Ru2C8B14H12] based on the available data.

In conclusion we have prepared the first examples of 14-v 14-SEP (hypercloso) heteroboranes and established that they have unique cluster structures. By a combination of spectroscopic, crystallographic and computational studies we have determined the isomeric nature of three examples, establishing that in all cases one cage C atom occupies a degree-4 vertex (vertex 1 in our arbitrary numbering scheme, Figure 4) on the short parallel edge of a trapezoidal polyhedral face. The formation of multiple isomers by a DEI reaction has precedent \(^{[1]}\) and is to be expected since there are likely to be multiple sites on the surface of the closo anionic cage where the electrophile can attack, unlike the conventional reduction-metallation synthesis of metallacarbornes in which an open face is presented to the incoming electrophile. Future contributions will develop this theme and expand further the unique chemistry of supraicosahedral hypercloso metallacarboranes.

Acknowledgements

We thank The Leverhulme Trust for support of APMR and JJ (project RPG-2014-286) and the Engineering & Physical Sciences Research Council both for support of WYM (project EP/I031545/1) and for DTP studentships supporting NAB and GS.

Keywords: metallacarborane • ruthenium • synthesis • structure • DFT calculations

Supporting information for this article is available on the WWW under http://????????? CCDC 1458452-1458456 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[9] The compound [[CpFel]2C8B14H12] (13-v-13-SEP) is proposed to have a conventional reduction-metallation synthesis of metallacarbornes in which an open face is presented to the incoming electrophile. Future contributions will develop this theme and expand further the unique chemistry of supraicosahedral hypercloso metallacarboranes.
The first three examples of 14-v 14-SEP heteroboranes have been prepared and characterised by a combination of spectroscopic, crystallographic and computational techniques. The compounds \([\text{Cp}^*\text{Ru}]_2\text{C}_2\text{B}_{10}\text{H}_{12}\) all share a unique cluster structure featuring a trapezoidal face.

Alasdair P. M. Robertson, Nicholas A. Beattie, Greig Scott, Wing Y. Man, John J. Jones, Stuart A. Macgregor*, Georgina M. Rosair, and Alan J. Welch*

Page No. – Page No.
14-Vertex 14-Skeletal Electron Pair Heteroboranes: an Experimental and Computational Study