Metallacarboranes

Deutsche Ausgabe: DOI: 10.1002/ange.201602440
Internationale Ausgabe: DOI: 10.1002/anie.201602440

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**

Abstract: *Three isomers of* $[(Cp^{*}Ru)_2C_2B_{10}H_{12}]$*, the first examples of 14-vertex heteroboranes containing 14-skeletal electron pairs, have been synthesized by the direct electrophilic insertion of a* $\{Cp^{*}Ru^{+}\}$ *fragment into the anion* $[4\text{-}Cp^{*}\text{-}4,1,6\text{-}RuC_2B_{10}H_{12}]^{-}$*. All three compounds have the same unique polyhedral structure having an approximate* C_s *symmetry and featuring a four-atom trapezoidal face. X-ray diffraction studies could confidently identify only one of the two cage C atoms in each structure. The other C atom position has been established by a combination of i) best fitting of computed and experimental* ^{11}B *and* ^{1}H *NMR chemical shifts, and ii) consideration of the 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.[1] These rules rationalize families of clusters, such as *closo* structures with $n+1$ skeletal electron pairs (SEPs), *nido* structures with $n+2$ SEPs, and *arachno* structures with $n+3$ SEPs (where n is the number of cluster vertices).

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) isomerization.[3] An excellent early example is $[(CpFe)_2C_2B_6H_8]$,[4] a 10-vertex (10-v) 10-SEP species structurally related to the bicapped square antiprismatic 10-v 11-SEP cobalt analogue $[(CpCo)_2C_2B_6H_8]$[5] by a d-s-d rearrangement of the 2-6-10-9 diamond of the latter polyhedron (Figure 1).

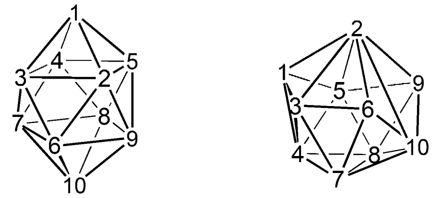

Figure 1. Left: The 10-v 11-SEP bicapped square antiprismatic structure of $2,6\text{-}Cp_2\text{-}2,6,1,10\text{-}Co_2C_2B_6H_8$. Right: The 10-v 10-SEP structure of $2,10\text{-}Cp_2\text{-}2,10,1,9\text{-}Fe_2C_2B_6H_8$, featuring a degree-6 metal atom at vertex 2. The two polyhedra are related by applying a d-s-d sequence to the 2-6-10-9 diamond of the left structure.

A number of these *hypercloso* clusters have been reported by Kennedy et al.[6] who argued that they are actually $n+1$ SEP compounds in which the metal utilizes 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, the authors used the descriptor *isocloso*. Although MO calculations by Mingos and co-workers support the *hypercloso* view[7] and the fact that Spencer et al. have shown that the simple addition of two electrons to [*hypercloso*-$(\eta\text{-}C_6Me_6)RuB_9H_9$] converts it into [*closo*-$(\eta\text{-}C_6Me_6)RuB_9H_9]^{2-}$,[8] the *isocloso* descriptor is still in use in the present day.[6f]

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[9] examples of supraicosahedral *hypercloso* metallacarboranes[10] being the 13-v 13-SEP species $[4,5\text{-}Cp^{*}_2\text{-}4,5,2,3\text{-}Ru_2C_2B_9H_{11}]$ (**I**) and $[4,5\text{-}Cp^{*}_2\text{-}6\text{-}SMe_2\text{-}4,5,2,3\text{-}Ru_2C_2B_9H_{10}]^{+}$ (**II**) isolated by Kudinov and co-workers.[11] In this Communication we describe the synthesis of the first 14-v 14-SEP *hypercloso* metallacarboranes and their characterization by a combination of spectroscopic, crystallographic, and computational studies.

The two-electron reduction of $[1,2\text{-}C_2B_{10}H_{12}]$ with Na in THF followed by treatment with $[Cp^{*}Ru(MeCN)_3]Cl$ and cation metathesis afforded the 13-v 14-SEP ruthenacarborane $[BTMA][4\text{-}Cp^{*}\text{-}4,1,6\text{-}RuC_2B_{10}H_{12}]$ (**1**) in 76% yield ($BTMA = PhCH_2NMe_3$). Salt **1** was fully characterized spectroscopically and crystallographically (see the Supporting Information).[21] As is common for $4,1,6\text{-}MC_2B_{10}$ species, the anion in **1** is fluxional in solution at room temperature

---

[*] 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: s.a.macgregor@hw.ac.uk
a.j.welch@hw.ac.uk

Supporting information (containing the experimental, spectroscopic, crystallographic, and computational details of all new compounds reported herein) and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201602440.

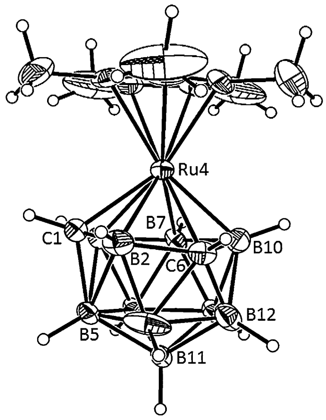

Figure 2. Solid-state structure of the anion of **1**.[21] The structure is partially disordered and only the major component is shown. Selected bond lengths [Å]: Ru4–C1 2.213(4), Ru4–B2 2.301(4), Ru4–C6 2.259(4), Ru4–B10 2.242(3), Ru4–B7 2.267(3), Ru4–B3 2.256(2), Ru4–C(Cp*) 2.192(5)–2.242(5).

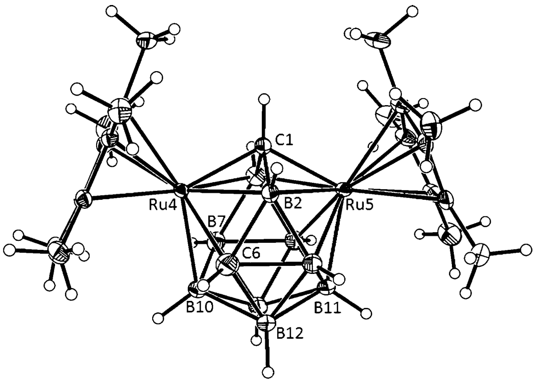

Figure 3. Solid-state structure of compound **2**.[21] Selected bond lengths [Å]: Ru4–C1 2.0254(16), Ru4–B2 2.2788(19), Ru4–C6 2.204(2), Ru4–B10 2.2167(19), Ru4–B7 2.2117(19), Ru4–B3 2.2801(19), Ru5–C1 2.0342(16), Ru5–B2 2.2786(19), Ru5–B9 2.2029(19), Ru5–B11 2.2119(19), Ru5–B8 2.2229(19), Ru5–B3 2.299(2), Ru4–C(Cp*) 2.2308(16)–2.2510(15), Ru5–C(Cp*) 2.2294(16)–2.2469(17).

through a double d-s-d process,[12] with NMR spectra revealing time-averaged C_s symmetry. A perspective view of the anion is shown in Figure 2.

Treatment of **1** in THF with 0.25 equiv $[Cp^*RuCl]_4$ followed by heating to reflux over 16 h produced a complex mixture of products with eight well-defined species clearly visible by thin-layer chromatography (see Plate S1 in the Supporting Information). Four of these species have been successfully characterized 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 $[(Cp^*Ru)_2C_2B_9H_{11}]$ by mass spectrometry and NMR spectroscopy. Notably, however, NMR spectroscopy indicated this was clearly not the 4,5,2,3-$Ru_2C_2B_9$ species **I** isolated by Kudinov et al. since both the ^1H and ^{11}B NMR spectra reveal no molecular symmetry. Moreover there is no very high-frequency ^{11}B NMR resonance signal in the spectrum of **2** ($\delta_{max} = 31$ ppm in **2**; $\delta_{max} = 97$ ppm in the 4,5,2,3 compound). Instead, there is a high frequency resonance signal in the ^1H NMR spectrum ($\delta = 16.6$ ppm) attributable to the $C_{cage}H$ proton. A crystallographic study (Figure 3) established that **2** is $[4,5\text{-}Cp^*_2\text{-}4,5,1,6\text{-}Ru_2C_2B_9H_{11}]$, a 13-v 13-SEP *hypercloso* species and a positional isomer of **I**.[21] We assume that **2** is formed by loss of the {B5H} fragment from the anion of **1** or (possibly more likely) its 4,1,8-RuC_2B_{10} isomer,[13] 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 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 C_{2v}-symmetric docosahedron necessarily has nondegenerate molecular orbitals.[14] We have shown that the HOMO of the parent borate $[B_{13}H_{13}]^{2-}$ 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.[15] This allows us to rationalize the facts that the 1-2 and 1-3 distances in **2** are about 0.09–0.10 Å longer, and the 6-9 and 7-8 distances in **2** are about 0.02–0.04 Å longer, than the equivalent distances in crystallographically characterized 13-v 14-SEP 4,5,1,6-$M_2C_2B_9$ species (see the Supporting Information).[15,16]

The fastest moving band (identified as purple compound **3**), the third fastest band (dark green compound **4**), and the sixth fastest moving band (purple compound **5**) were also studied, with elemental analysis and/or mass spectrometry suggesting the formula $[(Cp^*Ru)_2C_2B_{10}H_{12}]$ for all three. The ^1H NMR spectra of **3**–**5** contain one relatively high frequency $C_{cage}H$ resonance signal ($\delta = 8.6$ to 10.5 ppm) and two resonance signals corresponding to the Cp* H atoms. The asymmetry of all three compounds is confirmed by their ^{11}B NMR spectra which exhibit ten equal-integral resonance signals for **4** and **5** and nine resonance signals for **3** (one less signal as a result of the overlapping of two signals). In all three compounds, the range of ^{11}B chemical shifts is relatively large, $\delta = 76.0$ 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)[11,16b,17] of a $\{Cp^*Ru^+\}$ fragment into the anion of **1**, and it was clearly of importance to characterize 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**, isomers of each other differing only in the positions of the cage C atoms, share the same basic skeleton, which is shown together with an arbitrary numbering scheme in Figure 4. As in **2**, the carborane central cores in **3**–**5** are flanked by two large {Cp*Ru} fragments whose Cp* rings are inclined at about 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 (i.e., 6-connected with respect to the polyhedron, vertices 2 and 7) occupied by the Ru atoms, ten degree-5 vertices, and two degree-4 vertices (1 and 4)

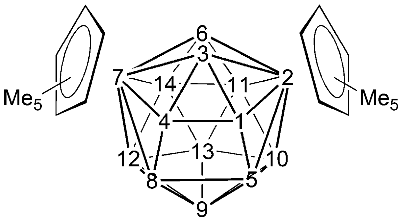

Figure 4. Generalized representation of compounds **3**–**5** and atomic numbering scheme.

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 2.196(6), 2.024(9), and 2.049(5) Å for compounds **3**, **4** and **5**, respectively. The whole molecule has approximate C_s 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 structure 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 $[(Cp^*Ru)_2C_2B_{10}H_{12}]$ isomer is which for each of compounds **3**–**5** 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 (that is, 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 localized in the two peripheral {Cp*Ru} fragments which are effectively symmetry-related, resulting in a degree of pseudo-symmetry overall and comparatively poor definition of the asymmetric $\{C_2B_{10}\}$ 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 analyze 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, whereas 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** (C_s 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 Supporting Information.

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 (0.73(4) Å). However, although 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. Using DFT, the crystallographically determined skeleton was used to build ten isomers $[2,7\text{-}Cp^*\text{-}2,7,12,a\text{-}Ru_2C_2B_{10}H_{12}]$ (with $a = 1, 3, 4, 5, 6, 8, 9, 11, 13$, and 14; $a = 10$ can be disregarded since that would be mirror-symmetric) and each isomer was optimized using the BP86 functional. Following optimization, the ^{1}H and ^{11}B NMR chemical shifts of each isomer were calculated at the B3LYP level and compared with those measured experimentally.[20] In summary, the isomer $[2,7\text{-}Cp^*\text{-}2,7,1,12\text{-}Ru_2C_2B_{10}H_{12}]$ very clearly gave the best agreement between theory and experiment. Thus linear regression of the computed and experimental ^{11}B NMR shifts yields an R^2 value for the 2,7,1,12 isomer of 0.9954, compared with $R^2 = 0.8676$ for the next-best isomer (2,7,3,12). In terms of ^{1}H NMR shifts, the difference in the sum ($\Delta\Sigma\delta$) of the calculated and actual chemical shifts for the two $C_{cage}H$ resonance signals is only 1.21 ppm for the 2,7,1,12 isomer, compared with 5.01 ppm for the next-best isomer (2,7,4,12). Finally, of all of 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, which had a value 3.5 kcal mol^{-1} below that of the next most stable isomer (2,7,4,12). Thus compound **4** is identified as $[2,7\text{-}Cp^*\text{-}2,7,1,12\text{-}Ru_2C_2B_{10}H_{12}]$. 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 the B6−H6 distance is only 0.50(3) Å (the next shortest B−H distance is at vertex 1 and measures 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**, $[2,7\text{-}Cp^*\text{-}2,7,6,b\text{-}Ru_2C_2B_{10}H_{12}]$ (with $b = 1, 5, 11$, and 12). DFT calculations strongly suggest that $b = 1$. R^2 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 signal

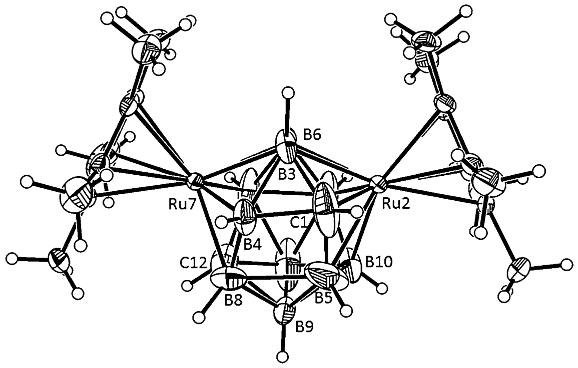

Figure 5. Solid-state structure of compound **4**.[21] Selected bond lengths [Å]: Ru2−C1 2.049(4), Ru2−B5 2.315(7), Ru2−B10 2.127(5), Ru2−B11 2.187(4), Ru2−B6 2.264(4), Ru2−B3 2.258(4), Ru7−B3 2.253(4), Ru7−B4 2.132(4), Ru7−B8 2.197(5), Ru7−C12 2.147(4), Ru7−B14 2.158(4), Ru7−B6 2.265(4), Ru2−C(Cp*) 2.236(3)–2.271(3), Ru7−C(Cp*) 2.243(3)–2.261(3), B4···B5 2.220(11).

attributed to $C_{cage}H$ protons was evident in the ^{1}H NMR spectrum of **5** (see the Supporting Information) but it fits best ($\Delta\delta = 0.61$ ppm) with one of the computed shifts for the 2,7,1,6 isomer (next smallest $\Delta\delta = 4.90$ ppm). Finally, the 2,7,1,6 isomer has the lowest computed free energy of all four isomers considered, being 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-$Ru_2C_2B_{10}H_{12}$]. There is partial disorder between the C1 and B4 centers 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 apparently short B−H distances, measuring 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 over two positions (see the Supporting Information). Nevertheless, for this compound DFT calculations were performed on two sets of isomers, [2,7-Cp*-2,7,5,*c*-$Ru_2C_2B_{10}H_{12}$] (with $c = 1$, 3, 4, 6, 9, 10, 11, 12, 13, and 14), and [2,7-Cp*-2,7,1,*d*-$Ru_2C_2B_{10}H_{12}$] (with $d = 3$, 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 being located at vertex 13. Location of this atom at vertex 13 afforded the best fit between calculated and actual ^{11}B NMR chemical shifts ($R^2 = 0.9939$), the lowest free energy, and the third best fit between calculated and actual ^{1}H NMR chemical shifts ($\Delta\Sigma\delta = 0.93$ ppm). In the former case (that is, with one cage C atom at vertex 5), the situation was anomalous, with the 2,7,3,5 isomer being best in terms of ^{11}B NMR shifts, the 2,7,4,5 isomer best in terms of ^{1}H NMR shifts, and the 2,7,5,13 isomer having the lowest free energy. None of these, however, was either better or lower in value 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-$Ru_2C_2B_{10}H_{12}$] 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 shown in Figure 4) on the short parallel edge of a trapezoidal polyhedral face. The formation of multiple isomers by a DEI reaction has precedent[17] 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–metalation synthesis of metallacarboranes 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 A.P.M.R. and J.J.J. (project RPG-2014-286) and the Engineering and Physical Sciences Research Council both for support of W.Y.M. (project EP/I031545/1) and for DTP studentships supporting N.A.B. and G.S.

Keywords: cage compounds · carboranes · density functional calculations · ruthenium · structure elucidation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 8706–8710
Angew. Chem. **2016**, *128*, 8848–8852

---

[1] a) K. Wade, *J. Chem. Soc. D* **1971**, 792 – 793; b) D. M. P. Mingos, *Nat. (London) Phys. Sci.* **1972**, *236*, 99 – 102.

[2] See, for example: a) R. T. Baker, *Inorg. Chem.* **1986**, *25*, 109 – 111; b) J. D. Kennedy, *Inorg. Chem.* **1986**, *25*, 111 – 112.

[3] a) A. Kaczmarczyk, R. D. Dobrott, W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA* **1962**, *48*, 729 – 733; b) W. N. Lipscomb, *Science* **1966**, *153*, 373 – 378.

[4] K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, M. F. Hawthorne, *J. Am. Chem. Soc.* **1975**, *97*, 296 – 302.

[5] E. L. Hoel, C. E. Strouse, M. F. Hawthorne, *Inorg. Chem.* **1974**, *13*, 1388 – 1392.

[6] See, for example: a) J. Bould, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc. Chem. Commun.* **1982**, 465 – 467; b) J. E. Crook, M. Elrington, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1985**, 2407 – 2415; c) E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc. Chem. Commun.* **1988**, 1262 – 1264; d) J. Bould, N. N. Greenwood, J. D. Kennedy, *J. Chem. Soc. Dalton Trans.* **1990**, 1451 – 1458; e) J. Bould, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.* **1992**, 563 – 576; f) J. Bould, R. W. Harrington, W. Clegg, J. D. Kennedy, *J. Organomet. Chem.* **2012**, *721 – 722*, 155 – 163; and references therein.

[7] a) R. L. Johnston, D. M. P. Mingos, *Inorg. Chem.* **1986**, *25*, 3321 – 3323; b) R. L. Johnston, D. M. P. Mingos, P. Sherwood, *New J. Chem.* **1991**, *15*, 831 – 841.

[8] R. Littger, U. Englich, K. Ruhlandt-Senge, J. T. Spencer, *Angew. Chem. Int. Ed.* **2000**, *39*, 1472 – 1474; *Angew. Chem.* **2000**, *112*, 1532 – 1534.

[9] The compound [$(CpFe)_2C_2B_9H_{11}$] (13-v 13-SEP) is proposed to have a 4,5,2,3-$Fe_2C_2B_9$ structure based on spectroscopic data, but no crystallographic study has been reported. C. G. Salentine, M. F. Hawthorne, *Inorg. Chem.* **1978**, *17*, 1498 – 1501.

[10] 15-v 15-SEP and 16-v 16-SEP metallaboranes have been reported. See: a) D. K. Roy, B. Mondal, P. Shankhari, R. S. Anju, K. Geetharani, S. M. Mobin, S. Ghosh, *Inorg. Chem.* **2013**, *52*, 6705 – 6712; b) D. K. Roy, S. K. Bose, R. S. Anju, B. Mondal, V. Ramkumar, S. Ghosh, *Angew. Chem. Int. Ed.* **2013**, *52*, 3222 – 3226; *Angew. Chem.* **2013**, *125*, 3304 – 3308.

[11] a) A. R. Kudinov, D. S. Perekalin, S. S. Rynin, K. A. Lyssenko, G. V. Grintselev-Knyazev, P. V. Petrovskii, *Angew. Chem. Int. Ed.* **2002**, *41*, 4112 – 4114; *Angew. Chem.* **2002**, *114*, 4286 – 4288; b) A. R. Kudinov, M. I. Rybinskaya, D. S. Perekalin, V. I. Meshcheryakov, Yu. A. Zhuravlev, P. V. Petrovskii, A. A. Korlyukov, D. G. Golovanov, K. A. Lyssenko, *Russ. Chem. Bull.* **2004**, *53*, 1958 – 1962.

[12] a) D. F. Dustin, G. B. Dunks, M. F. Hawthorne, *J. Am. Chem. Soc.* **1973**, *95*, 1109 – 1115; b) A. Burke, D. Ellis, D. Ferrer, D. L. Ormsby, G. M. Rosair, A. J. Welch, *Dalton Trans.* **2005**, 1716 – 1721.

[13] D. F. Dustin, M. F. Hawthorne, *J. Am. Chem. Soc.* **1974**, *96*, 3462 – 3467; See also Ref. [16].

[14] M. E. O'Neill, K. Wade, *Polyhedron* **1984**, *3*, 199 – 212.

[15] M. E. Lopez, M. J. Edie, D. Ellis, A. Horneber, S. A. Macgregor, G. M. Rosair, A. J. Welch, *Chem. Commun.* **2007**, 2243 – 2245.

[16] a) W. Y. Man, S. Zlatogorsky, H. Tricas, D. Ellis, G. M. Rosair, A. J. Welch, *Angew. Chem. Int. Ed.* **2014**, *53*, 12222 – 12225; *Angew. Chem.* **2014**, *126*, 12418 – 12421; b) W. Y. Man, D. Ellis, G. M. Rosair, A. J. Welch, *Angew. Chem. Int. Ed.* **2016**, *55*, 4596 – 4599; *Angew. Chem.* **2016**, *128*, 4672 – 4675.

[17] A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair, A. J. Welch, *Dalton Trans.* **2014**, *43*, 5095 – 5105.

[18] a) W. J. Evans, M. F. Hawthorne, *J. Chem. Soc. Chem. Commun.* **1974**, 38 – 39; b) W. M. Maxwell, R. Weiss, E. Sinn, R. N. Grimes, *J. Am. Chem. Soc.* **1977**, *99*, 4016 – 4029; c) J. R. Pipal, R. N. Grimes, *Inorg. Chem.* **1978**, *17*, 6 – 10; d) D. Ellis, M. E. Lopez, R. McIntosh, G. M. Rosair, A. J. Welch, *Chem. Commun.* **2005**, 1917 – 1919; e) L. Deng, H.-S. Chan, Z. Xie, *Angew. Chem. Int. Ed.* **2005**, *44*, 2128 – 2131; *Angew. Chem.* **2005**, *117*, 2166 – 2169; f) R. D. McIntosh, D. Ellis, G. M. Rosair, A. J. Welch, *Angew. Chem. Int. Ed.* **2006**, *45*, 4313 – 4316; *Angew. Chem.* **2006**, *118*, 4419 – 4422; g) J. Zhang, L. Deng, H. S. Chan, Z. Xie, *J. Am. Chem. Soc.* **2007**, *129*, 18 – 19; h) A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair, A. J. Welch, *Dalton Trans.* **2013**, *42*, 671 – 679.

[19] A. McAnaw, G. Scott, L. Elrick, G. M. Rosair, A. J. Welch, *Dalton Trans.* **2013**, *42*, 645 – 664.

[20] Full computational details including the calculated chemical shifts and test calculations based on the B3LYP-optimized structures are given in the Supporting Information.

[21] CCDC 1458452 – 1458456 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: March 9, 2016
Revised: April 19, 2016