Metallacarboranes

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A 15-Vertex Heteroborane**

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Following the synthesis[1] and characterization[1,2] of the first supraicosahedral heteroborane, 4-(η-C_5H_5)-4,1,6-*closo*-$CoC_2B_{10}H_{12}$, 35 years ago, experimental work in the area has advanced relatively slowly, with only sporadic reports of new species. Presently, the number of reported 13-vertex compounds, mainly MC_2B_{10}[3] (where M is a metal center) but occasionally $M_2C_2B_9$,[4] is only of the order of 150. Moreover, a mere handful of closed 14-vertex compounds have been reported, all except one being $M_2C_2B_{10}$,[5] and no examples of species with 15 or more vertices in the polyhedron.

The prevalence of metallacarboranes amongst the supraicosahedral heteroboranes reflects that such polyhedra generally contain an increasing number of degree-six vertices. Thus, for example, Brown and Lipscomb,[6] in considering hypothetical triangulated (deltahedral) structures for $[B_nH_n]^{2-}$ for $n = 13$–24, find that the number of degree-six vertices generally increases with increasing n, and the largest single-cage deltahedron currently known, Ge_{18}^{4-} (in $[Pd_2@Ge_{18}]^{4-}$), has recently been shown to contain six degree-six vertices.[7] Metal atoms or fragments, having relatively diffuse frontier orbital compared to {BH} fragments, are able to stabilize such structures, and thus in supraicosahedral metallacarboranes it is the metal atom(s) which tend to occupy the degree-six site(s).[3–5]

However, fuelled by the results of later theoretical calculations[8] suggesting that $[B_nH_n]^{2-}$ ions with $n \geq 16$ might adopt alternative structures which need not be fully triangulated and which are computed[9] to be progressively more favorable than the ubiquitous $[B_{12}H_{12}]^{2-}$ ion, we and others have renewed experimental efforts towards preparing progressively larger supraicosahedral heteroboranes with limited numbers of, or no, metal heteroatoms. As a result, the field of supraicosahedral heteroborane chemistry is currently undergoing an impressive renaissance. In 2003 we reported the first supraicosahedral carborane,[10] having 13 vertices and, interestingly in view of the predictions of

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Schleyer,[8] a non-triangulated (trapezoidal) face. This result was followed by the report by Xie and co-workers of a 14-vertex carborane.[11] In both these species the cage carbon atoms are joined by an exopolyhedral tether, to block the kinetic pathway to decomposition. We now report extensions to these studies—examples of 14-vertex MC_2B_{11} species, and a 15-vertex heteroborane.

The naphthalene-assisted sodium reduction of 1,2-μ-$(CH_2)_3$-1,2-*closo*-$C_2B_{11}H_{11}$[11] in THF and subsequent reaction with an equimolar (in Ru) amount of $[\{(p\text{-cymene})RuCl_2\}_2]$ yielded two bright yellow compounds, **1** and **2**, which were separated by thin layer chromatography. Mass spectrometric data on both were consistent with the anticipated molecular formula (p-cymene)Ru$(CH_2)_3C_2B_{11}H_{11}$ implying that **1** and **2** are isomers. The ^1H and ^{11}B NMR spectra of **1** suggest (time-averaged) C_s molecular symmetry, whereas **2** is clearly asymmetric with unique doublets for each of the four cymene aromatic H atoms, two doublets for the CH_3 protons of the cymene *i*Pr group, and eleven ^{11}B resonances of equal integral.

The structural identities of **1** and **2** were revealed by single-crystal X-ray diffraction.[12] Compound **1** (Figure 1) is a 14-vertex ruthenacarborane with a bicapped hexagonal antiprismatic structure in which the metal atom occupies one degree-six vertex and B14 the other. Both cage carbon atoms are located in the upper hexagonal belt, adjacent to Ru1.

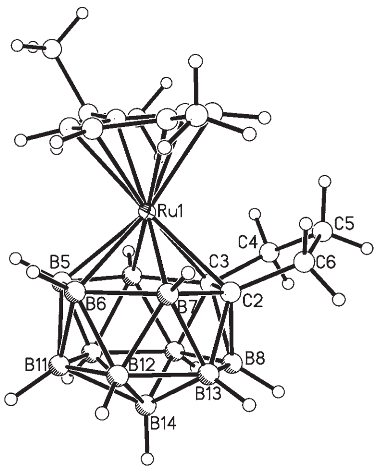

Figure 1. Perspective view of 1-(p-cymene)-2,3-μ-$(CH_2)_3$-1,2,3-*closo*-$RuC_2B_{11}H_{11}$ (**1**).

Although the crystallographic study of compound **2** is less precise owing to relatively poor crystal quality, it nevertheless unambiguously identifies **2** as also having a bicapped hexagonal antiprismatic cage (Figure 2). Again, the metal atom occupies one of the degree-six vertices, but this time only one cage carbon atom is adjacent to it; the other resides in the lower hexagonal belt.

Compounds **1** and **2** represent the first examples of 14-vertex MC_2B_{11} metallacarboranes. They are structural isomers, differing in the relative positions of one cage carbon atom, compound **1** having a 1,2,3-RuC_2B_{11} architecture whilst that of compound **2** is 1,2,8-RuC_2B_{11}. The isomeric relationship between **1** and **2** is similar to that between 3,1,2-MC_2B_9 and 4,1,2-MC_2B_9 icosahedral species, and we have recently been investigating the mechanism of the 3,1,2- to 4,1,2-MC_2B_9 isomerization (so-called "1,2→1,2" C atom isomerization) using vertex-substituted species.[13]

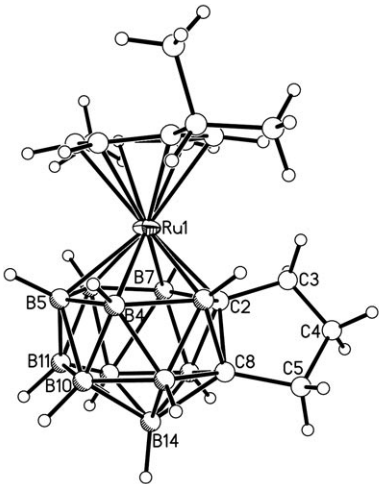

Figure 2. Perspective view of 1-(p-cymene)-2,8-μ-$(CH_2)_3$-1,2,8-*closo*-$RuC_2B_{11}H_{11}$ (**2**).

In an attempt to determine if there is any similar interconversion between **1** and **2**, toluene solutions of each were heated to reflux for 48 h. Compound **1** was recovered unchanged from this process, but compound **2** surprisingly gave way to a new species **3**, the mass spectrum of which suggested incorporation of an additional {BH} vertex. At room temperature, the ^1H NMR spectrum of **3** is consistent with a molecule with C_s symmetry whilst the $^{11}B\text{-}\{^1H\}$ NMR spectrum suggests near-coalescence, with broad, featureless, humps at $\delta \approx 20$, 15, 0, and -30 ppm superimposed upon which are sharper signals at $\delta \approx -11$ and -18 ppm. At 263 K, however, the $^{11}B\text{-}\{^1H\}$ spectrum consists of eight sharp integral-1 resonances and one (presumably co-incident) integral-4 resonance, consistent with a molecule lacking symmetry.

The molecular structure of **3** was revealed by crystallographic analysis[14] (Figure 3). It comprises a 15-vertex polyhedron with a degree-six Ru atom bound to an upper hexagonal B_6 belt (B2–B7), below which is an antiprismatic CB_5 belt (C8–B13). Below this, in turn, sits the C14B15 unit. Thus the gross polyhedral structure of **3** is related to the D_{3h}-symmetric hexacosahedron (26 faces) predicted[6,8] for the parent borane ion $[B_{15}H_{15}]^{2-}$. However, whilst the hexacosahedron, which contains three degree-six vertices, is fully triangulated (Figure 4), in **3** the B12–C14 connectivity, 2.383(5) Å, is formally missing, generating a quadrilateral B12-B13-C14-B15 face. Thus the polyhedron in **3** is formally a pentacosahedron (25 faces). The degree-six vertices are Ru1 and B9. If the B12–C14 connectivity were present then B12 would also be a degree-six vertex, and the cage would have effective mirror symmetry.

In compound **3**, the formal breaking of a connectivity between an otherwise degree-six boron atom and an otherwise degree-five carbon atom is highly reminiscent of the

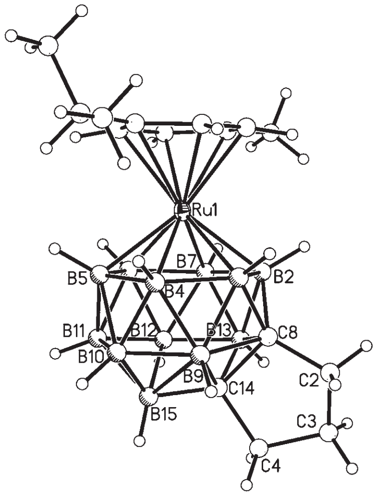

Figure 3. Perspective view of the 15-vertex ruthenacarborane 1-(*p*-cymene)-8,14-μ-$(CH_2)_3$-1,8,14-*closo*-$RuC_2B_{12}H_{12}$ (**3**).

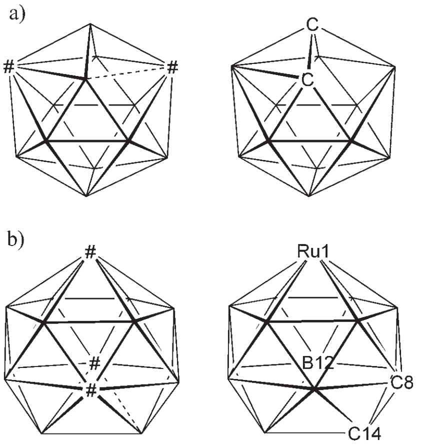

Figure 4. Topological relationships between; a) left: the docosahedron and right: the henicosahedron found in the 13-vertex carborane; b) left: the hexacosahedron and right: the pentacosahedron found in the 15-vertex ruthenacarborane. In each case the dashed bond in the left structure between a degree-six B atom and degree-five C atom (degree-six vertices shown as #) is formally absent in the right structure.

formal breaking of a similar B–C connectivity in the 13-vertex carborane,[10] transforming a docosahedron into a henicosahedron. Figure 4 shows the topological relationships between a) the docosahedron and henicosahedron, and b) the hexacosahedron and the pentacosahedron. As already noted, {BH} vertices are not particularly well-suited to degree-six vertices because their valence orbitals are not diffuse. A (relatively electronegative) cage C atom will cause further contraction of the valence orbitals of all adjacent B atoms, and this presumably results in the formal breaking of the former $B_{degree\text{-}six}$–C connectivity. In solution at elevated temperatures we assume a rapid (on the NMR timescale) fluctional process in which B12–C14 connection of **3** is made, and the B9–C14 connection broken, rendering the molecule C_s symmetric. This "square–diamond–square" rearrangement is exactly analogous to that which we have proposed to account for the final stereochemistry of B-substituted 13-vertex carborane,[10] and which we have subsequently shown is responsible for the fluctionality of unsubstituted 13-vertex carborane.[15]

The isolation of compound **3** from thermolysis of **2** was unexpected, and clearly involves adventitious capture of a {BH} fragment. To date we have not been able to prepare analogues of **3** by the more logical route of reduction of **2** followed by addition of BRX_2, but studies in this direction continue.

Compound **3** is to our knowledge the first 15-vertex heteroborane.[18] Its molecular structure, like that of the 13-vertex carborane, has responded to the presence of an unfavorable degree-six boron vertex by the formal breaking of a B–C connectivity. We are currently investigating ways of stabilizing degree-six boron vertices in supraicosahedral heteroboranes which may remove the need for such structural deformations. On the other hand, we are now only one vertex away from the size of polyhedron that Schleyer has suggested[8] (at least for $[B_nH_n]^{2-}$ ions) could form stable structures without degree-six vertices. We look forward to the next developments in this area with great anticipation.[18]

Experimental Section

1 and **2**: Reduction (Na/naphthalene) of 1,2-μ-$(CH_2)_3$-1,2-*closo*-$C_2B_{11}H_{11}$ (150 mg) in THF (20 mL), transfer to an equimolar THF suspension of $[\{(p\text{-cymene})RuCl_2\}_2]$ (234 mg) at −197 °C, warming to room temperature and overnight stirring afforded **1** and **2** in 22 % and 15 % yields (not optimized), respectively, subsequent work-up involving extraction into CH_2Cl_2, thin layer chromatography on SiO_2, and crystallization from CH_2Cl_2/petroleum ether.

1: IR (CH_2Cl_2): $\tilde{\nu}_{max}$ at 2584 cm^{-1} (BH); ^{1}H NMR (C_2D_6CO, 200 MHz, 298 K): $\delta = 5.78$ (d, $^3J \approx 8$ Hz, 2 H, $CH_3C_6\mathit{H}_4CHMe_2$), 5.69 (d, $^3J \approx 8$ Hz, 2 H, $CH_3C_6\mathit{H}_4CHMe_2$) 2.81–2.99 (m, 4 H, $C\mathit{H}_2$ {3H} and $CH_3C_6H_4C\mathit{H}Me_2$ {1H}), 2.53 (m, 3 H, $C\mathit{H}_2$), 2.19 (s, 3 H, $C\mathit{H}_3C_6H_4CHMe_2$), 1.23 ppm (d, $^3J \approx 8$ Hz, 6 H, $CH_3C_6H_4CH\mathit{Me}_2$); ^{11}B-{^{1}H} NMR ($C_2D_6CO$, 128 MHz, 298 K): $\delta = -5.86$ (3 B), −13.58 (2 B), −14.73 (1 B), −17.39 (3 B), −20.69 ppm (2 B); MS (EI): m/z 430 [M^+]. Satisfactory microanalytical data were obtained.

2: IR (CH_2Cl_2): $\tilde{\nu}_{max}$ at 2591 cm^{-1} (B-H); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): $\delta = 5.83$ (d, $^3J \approx 5$ Hz, 1 H, $CH_3C_6\mathit{H}_4CHMe_2$), 5.77 (d, $^3J \approx 5$ Hz, 1 H, $CH_3C_6\mathit{H}_4CHMe_2$), 5.45 (d, $^3J \approx 5$ Hz, 1 H, $CH_3C_6\mathit{H}_4CHMe_2$), 5.39 (d, $^3J \approx 5$ Hz, 1 H, $CH_3C_6\mathit{H}_4CHMe_2$), 3.22 (m, 1 H, $C\mathit{H}_2$), 2.98 (m, 1 H, $CH_3C_6H_4C\mathit{H}Me_2$), 2.56 (m, 1 H, $C\mathit{H}_2$), 2.27 (s, 3 H, $C\mathit{H}_3C_6H_4CHMe_2$), 2.24 (m, 2 H, $C\mathit{H}_2$), 2.01 (m, 2 H, $C\mathit{H}_2$), 1.27 (d, $^3J \approx 8$ Hz, 3 H, $CH_3C_6H_4CH\mathit{Me}_2$), 1.21 ppm (d, $^3J \approx 8$ Hz, 3 H, $CH_3C_6H_4CH\mathit{Me}_2$); ^{11}B-{^{1}H} NMR ($CDCl_3$, 128 MHz, 298 K): $\delta =$ 14.73 (1 B), 3.38 (1 B), 2.62 (1 B), −0.70 (1 B), −6.30 (1 B), −10.11 (1 B), −13.19 (1 B), −18.03 (1 B), −20.00 (1 B), −27.03 (1 B), −31.38 ppm (1 B); MS (EI): m/z 430 [M^+]. Satisfactory microanalytical data were obtained.

3: Heating to reflux a toluene solution (20 mL) of **2** (35 mg) for 48 h afforded **3** in 67 % yield after work-up involving thin layer chromatography on SiO_2 (no other mobile bands were isolated) and crystallization from CH_2Cl_2/petroleum ether. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ at 2529 cm^{-1} (B-H); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): $\delta = 5.77$ (d, $^3J \approx 8$ Hz, 2 H, $CH_3C_6\mathit{H}_4CHMe_2$), 5.66 (d, $^3J \approx 8$ Hz, 2 H, $CH_3C_6\mathit{H}_4CHMe_2$), 2.64–2.90 (m, 3 H, $C\mathit{H}_2$ {2H} and $CH_3C_6H_4C\mathit{H}Me_2$ {1H}), 2.39 (m, 2 H, $C\mathit{H}_2$), 2.07 (s, 3 H, $C\mathit{H}_3C_6H_4CHMe_2$), 1.92 (m, 2 H, $C\mathit{H}_2$), 1.18 ppm (d, $^3J \approx 8$ Hz, 6 H, $CH_3C_6H_4CH\mathit{Me}_2$); ^{11}B-{^{1}H} NMR ($CD_2Cl_2$, 128 MHz, 263 K): $\delta = 19.44$ (1 B), 14.89 (1 B), −0.98 (1 B),

−3.20 (1B), −11.92 (1B), −15.10 (1B), −18.49 (4B), −28.48 (1B), −31.34 ppm (1B); MS (EI): m/z 443 [M^+].

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[9] As defined by ΔH values computed for the reactions: $[B_{12}H_{12}]^{2-} + 4B_6H_{10} \rightarrow [B_{16}H_{16}]^{2-} + 4B_5H_9$ and $[B_{12}H_{12}]^{2-} + 5B_6H_{10} \rightarrow [B_{17}H_{17}]^{2-} + 5B_5H_9$. See equations (5) and (6) of ref. [8].

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[12] General crystallographic procedure: crystals were mounted in inert oil on a glass fiber and cooled to 100(2) K on a Bruker X8 APEX2 diffractometer equipped with $Mo_{K\alpha}$ X-ray radiation. Intensity data were corrected for absorption semi-empirically and structures solved by direct and difference-Fourier methods. Refinement[16] was by full-matrix least-squares analysis on F^2. Crystal data for **1**: $C_{15}H_{31}B_{11}Ru{\cdot}CH_2Cl_2$, $M_r = 516.3$, triclinic, $P\bar{1}$, $a = 8.5881(11)$, $b = 9.0273(13)$, $c = 16.032(2)$ Å, $\alpha = 86.703(7)$, $\beta = 79.245(7)$, $\gamma = 72.148(6)°$, $V = 1162.3(3)$ Å^3, $Z = 2$, $\rho = 1.475$ Mg m^{-3}, $\mu = 0.907$ mm^{-1}, $F(000) = 524$. 49377 data collected to θ_{max} 33.23°, 8880 independent reflections ($R_{int} = 0.0429$), $R_1 = 0.0293$, $wR_2 = 0.0705$ for data with $I > 2\sigma(I)$, $S = 1.019$, largest peak 1.05 and deepest hole −1.20 e Å^{-3}. Crystal data for **2**: $C_{15}H_{31}B_{11}Ru$, $M_r = 431.4$, monoclinic, $P2_1/c$, $a = 14.3739(19)$, $b = 8.4638(15)$, $c = 17.601(3)$ Å, $\beta = 104.756(6)°$, $V = 2070.7(6)$ Å^3, $Z = 4$, $\rho = 1.384$ Mg m^{-3}, $\mu = 0.754$ mm^{-1}, $F(000) = 880$. 80519 data collected to θ_{max} 25.38°, 3809 independent reflections ($R_{int} = 0.0728$), $R_1 = 0.0643$, $wR_2 = 0.1760$ for data with $I > 2\sigma(I)$, $S = 1.056$, largest peak 0.89 and deepest hole −1.05 e Å^{-3}. CCDC-603297 (**1**), CCDC-603298 (**2**), and CCDC-603299 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] Crystal data for **3**: $C_{15}H_{32}B_{12}Ru$, $M_r = 443.2$, monoclinic, $P2_1/n$, $a = 11.2945(14)$, $b = 12.4801(12)$, $c = 15.5893(18)$ Å, $\beta = 109.112(5)°$, $V = 2076.3(4)$ Å^3, $Z = 4$, $\rho = 1.418$ Mg m^{-3}, $\mu = 0.754$ mm^{-1}, $F(000) = 904$. 36900 data collected to θ_{max} 33.20°, 7905 independent reflections ($R_{int} = 0.0252$), $R_1 = 0.0337$, $wR_2 = 0.0747$ for data with $I > 2\sigma(I)$, $S = 1.020$, largest peak 1.50 and deepest hole −1.43 e Å^{-3}.[17]

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[17] There is partial disorder in the crystallographic model, with atoms C3, C4, and B15 equally distributed over pairs of adjacent positions. We have associated C4 with B15 (as opposed to B15A) on the basis that C4 and C15 lie on opposite sides of the effective mirror plane through the cage.

[18] Note added in proof: While this manuscript was in press we have learnt of the synthesis of another 15-vertex metallacarborane by a different group: L. Deng, J. Zhang, H.-S. Chan, Z. Xie, *Angew. Chem.* **2006**, *118*, 4415–4419; *Angew. Chem. Int. Ed.* **2006**, *45*, 4309–4313, preceding Communication in this issue.