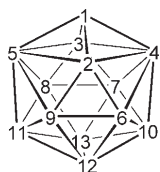


The Mechanism of Reduction and Metalation of *para* Carboranes: The Missing 13-Vertex MC_2B_{10} Isomer**

Sergey Zlatogorsky, Michael J. Edie, David Ellis, Stefan Erhardt, Maria Elena Lopez, Stuart A. Macgregor,* Georgina M. Rosair, and Alan J. Welch*

Thirteen-vertex heteroboranes generally adopt the docosahedral architecture predicted for the (as yet) unknown species $[\text{B}_{13}\text{H}_{13}]^{2-}$,^[1] although the first 13-vertex carborane^[2] and some MC_2B_{10} metallacarboranes^[3] adopt an alternative henicosahedral structure. In the docosahedron (Scheme 1),



Scheme 1. Numbering scheme for the docosahedron.

vertex 1 is of degree four, vertices 4 and 5 are of degree six, and all other vertices are of degree five. Several isomers of docosahedral MC_2B_{10} species are known, but in all of them vertex 1 is occupied by a carbon atom and vertex 4 (equivalent to vertex 5) by the metal atom, in accord with the well-known preferences of such heteroatoms for low- and high-connected polyhedral sites, respectively.^[4] Thus, reduction and metalation of either 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ or its derivatives affords 4,1,6- MC_2B_{10} species,^[5] which can be progressively isomerized to 4,1,8- and

4,1,12-isomers by thermolysis. 4,1,2- MC_2B_{10} compounds are afforded upon reduction and metalation of C,C-tethered carboranes.^[3] Two years ago we extended this list by describing the new isomer 4,1,10- MC_2B_{10} , formed by reduction and metalation of 1,12-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ or its C,C-dimethyl analogue.^[6]

The only remaining members of the docosahedral 4,1,x- MC_2B_{10} family are the 4,1,5- and 4,1,11-isomers. The former is very unlikely ever to be isolated as it has the second C atom in the unfavorable degree-six vertex 5. We describe herein the first report of the missing 4,1,11-isomer with the isolation and characterization of the ruthenacarborane 1,11- Ph_2 -4-(*p*-cymene)-4,1,11-*closo*- $\text{RuC}_2\text{B}_{10}\text{H}_{10}$. We also describe a computational study of the reduction of 1,12-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ and rationalize the formation of five isomeric metallacarboranes from its subsequent metalation.

Very recently^[7] we reported that room-temperature reduction (Na in THF) and metalation ($[\{\text{Ru}(\text{p-cyme-}$

ne) $\text{Cl}_2\}_2]$) of 1,12- Ph_2 -1,12-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ affords 1,6- Ph_2 -4-(*p*-cymene)-4,1,6-*closo*- $\text{RuC}_2\text{B}_{10}\text{H}_{10}$ (**1**)^[8] as the major product instead of the expected 4,1,10- $\text{RuC}_2\text{B}_{10}$ isomer.^[6] We have now isolated and analyzed the two minor coproducts of this reaction. Both are formed in trace amount (less than 1%). One of them, identified by ^1H and ^{11}B NMR spectroscopies, is 1,8- Ph_2 -4-(*p*-cymene)-4,1,8-*closo*- $\text{RuC}_2\text{B}_{10}\text{H}_{10}$ (**2**), previously prepared by the thermolysis of **1** at 180 °C,^[7] and the other is the unique 4,1,11-isomer 1,11- Ph_2 -4-(*p*-cymene)-4,1,11-*closo*- $\text{RuC}_2\text{B}_{10}\text{H}_{10}$ (**3**).

Compound **3** was initially characterized by mass spectrometry and ^1H and ^{11}B NMR spectroscopies. In the ^1H NMR spectrum, only a single doublet for the Me resonances of the *i*Pr groups and two clean doublets for the *p*-cymene ring protons are present, indicative of a molecule with C_s symmetry. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum appears as a 4:1:1:2:2 pattern between $\delta = +11$ and -25 ppm, a much wider range than that displayed for 4-(*p*-cymene)-4,1,10-*closo*- $\text{RuC}_2\text{B}_{10}\text{H}_{12}$ ($\delta = -2$ to -17 ppm).^[6] The structural identity of **3** was ultimately confirmed by a crystallographic study (Figure 1).^[9]

The cage of **3** has the anticipated docosahedral architecture with the Ru atom at vertex 4 and the C atoms, unequivocally identified by their attached Ph groups, at vertices 1 and 11. The cage has effective C_s symmetry, which must be attained in solution on the NMR timescale by rotation or libration of the *p*-cymene ligand.

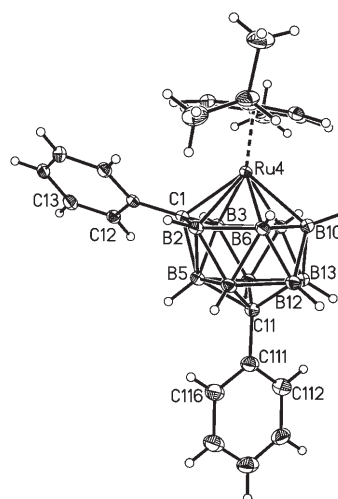


Figure 1. Perspective view of compound **3**. Selected bond lengths [Å]: Ru4-C1 2.1727(19), Ru4-B2 2.319(2), Ru4-B6 2.262(2), Ru4-B10 2.253(2), Ru4-B7 2.281(2), Ru4-B3 2.298(2).

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Metalation traps a reduced carborane and allows its structure to be determined; the *nido* carborane simply has the structure of the metallacarborane minus the metal vertex. We have recently demonstrated that isomerization *before* metalation is more facile than isomerization *after* metalation,^[10] and thus the isolation of three products from the reduction and metalation of 1,12-Ph₂-1,12-*closo*-C₂B₁₀H₁₀ implies more than one reduced species, possibly related by a series of isomerizations. To investigate this further we have repeated the reduction/metalation process at low temperature.

At -78°C metalation of the reduced 1,12-Ph₂-1,12-*closo*-C₂B₁₀H₁₀ species affords four isolatable compounds. In common with the room-temperature reaction, **3** (ca. 3%) and **1** (less than 1%) are formed, but uniquely at low temperature are isolated 1,12-Ph₂-4-(*p*-cymene)-4,1,12-*closo*-RuC₂B₁₀H₁₀ (**4**, ca. 2%), a known isomer previously prepared by the thermolysis of **1** or **2**, and the new species 1,10-Ph₂-4-(*p*-cymene)-4,1,10-*closo*-RuC₂B₁₀H₁₀ (**5**, less than 1%), ironically the expected product in the initial synthesis.

Both the ¹H and ¹¹B NMR spectra of **5** at 298 K are consistent with time-averaged molecular C_s symmetry, but there is clear evidence that the *p*-cymene ligand undergoes somewhat restricted rotation about the Ru4⋯B11 axis since the aromatic protons appear as a broad featureless signal in the ¹H NMR spectrum. At 218 K this signal is resolved into four distinct doublets and, in addition, two doublets are observed for the *i*Pr Me groups. At 353 K the aromatic protons appear as two doublets and the *i*Pr Me groups as one doublet. In contrast to **3**, the range of the ¹¹B NMR spectrum is relatively narrow, $\delta = 0$ to -14 ppm, consistent with a 4,1,10-RuC₂B₁₀ isomer. This molecular architecture was confirmed by crystallographic analysis (Figure 2).

Thus, the reduction and metalation of 1,12-Ph₂-1,12-*closo*-C₂B₁₀H₁₀ affords, in total, five isomeric 4,1,*x*-MC₂B₁₀ metallacarboranes. In an attempt to understand this result we have investigated the reduction of 1,12-*closo*-C₂B₁₀H₁₂ using DFT calculations.^[11] Note that this has been the subject of a previous computational study but at only the HF level.^[12]

Our results are summarized in Figure 3 (note that in the figure constant labelling is used to help follow atom movement). Two sequential one-electron reductions of 1,12-*closo*-C₂B₁₀H₁₂ initially result in alternative highly distorted dianion intermediates **A** (+97.1 kcal mol⁻¹ relative to 1,12-*closo*-C₂B₁₀H₁₂) and **B** (+92.6 kcal mol⁻¹). Species **A** and **B** are

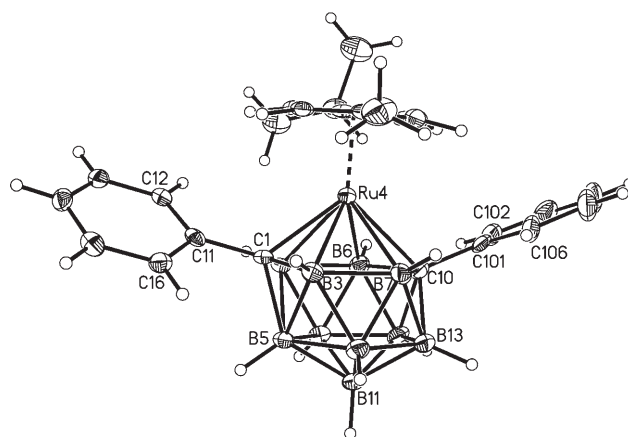


Figure 2. Perspective view of compound **5**. Selected bond lengths [Å]: Ru4-C1 2.195(3), Ru4-B2 2.330(4), Ru4-B6 2.268(4), Ru4-C10 2.262(3), Ru4-B7 2.257(4), Ru4-B3 2.303(4).

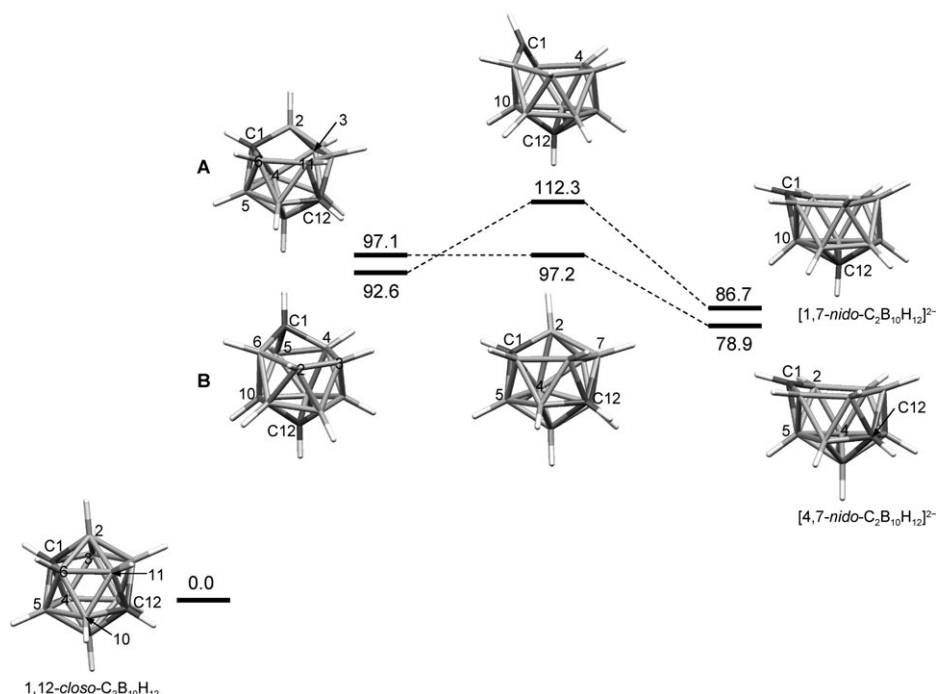
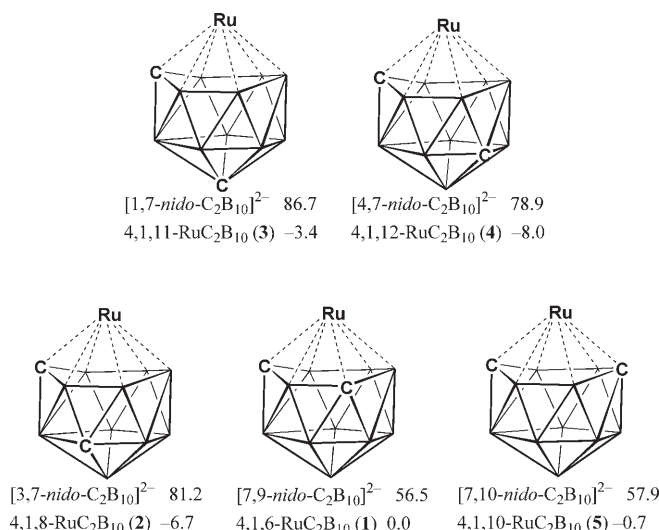


Figure 3. Computed profiles for the reduction of 1,12-*closo*-C₂B₁₀H₁₂. C atoms are dark gray and B atoms are light gray. Calculated energies in kcal mol⁻¹.

topologically equivalent with both four- and five-atom open faces. For **A** the open faces result from cleavage of the C1-B3, B2-B6, and B2-B11 connections, whilst for **B** the C1-B2, C1-B3, and B5-B6 bonds are broken. From **A**, a transition state with a B2-B4 connection is located only 0.1 kcal mol⁻¹ above the intermediate, which then collapses by a diamond-square-diamond transformation (breaking C1-B4 and forming B2-B5) and breaking of the B2-B7 connection to form [4,7-*nido*-C₂B₁₀H₁₂]²⁻ with an energy of +78.9 kcal mol⁻¹ relative to the starting carborane. From intermediate **B** the C1-B4 connection breaks to yield a transition state at

+ 112.3 kcal mol⁻¹ that ultimately collapses by formation of the C1–B10 connection to [1,7-*nido*-C₂B₁₀H₁₂]²⁻ at + 86.7 kcal mol⁻¹.

Thus the *nido* species predicted by theory are [1,7-*nido*-C₂B₁₀H₁₂]²⁻ and [4,7-*nido*-C₂B₁₀H₁₂]²⁻. In the case of diphenylcarborane, metalation of these species with a {(*p*-cymene)Ru}²⁺ fragment successfully explains the formation of compounds **3** and **4**, respectively. To account for **1**, **2**, and **5** we assume that the [1,7-*nido*-C₂B₁₀]²⁻ and/or [4,7-*nido*-C₂B₁₀]²⁻ species first isomerize to the [7,9-*nido*-C₂B₁₀]²⁻, [3,7-*nido*-C₂B₁₀]²⁻, and [7,10-*nido*-C₂B₁₀]²⁻ forms, respectively. Scheme 2 summarizes the five isomeric [C₂B₁₀H₁₂]²⁻ dianions



Scheme 2. Without Ru: the five isomeric [*nido*-C₂B₁₀]²⁻ carboranes (upper line); calculated energies (in kcal mol⁻¹) are for C=CH (all other vertices are BH) and are relative to 1,12-*closo*-C₂B₁₀H₁₂. With Ru: the five experimental metallacarboranes **1**–**5** derived from these *nido* carboranes (C=CPh, Ru={(*p*-cymene)Ru}, lower line); calculated energies (in kcal mol⁻¹) are for C=CH and Ru={(η -C₆H₅)Ru} and are relative to that for the 4,1,6-RuC₂B₁₀ isomer.

and their calculated stabilities (DFT, in kcal mol⁻¹ relative to 1,12-*closo*-C₂B₁₀H₁₂). As anticipated, the isomers with both cage C atoms in the open face (the 7,9- and 7,10-forms) are the most stable. The mechanisms by which [1,7-*nido*-C₂B₁₀H₁₂]²⁻ and [4,7-*nido*-C₂B₁₀H₁₂]²⁻ might rearrange to the other isomers shown in Scheme 2 will be the subject of a future computational study.^[13]

We have previously shown that whilst compound **1** is resistant to isomerization in refluxing toluene,^[8] at 180 °C it isomerizes to a mixture of **2** and **4**.^[7] In contrast, both **3** and **5** isomerize in refluxing toluene; **5** converts into **4**, thus mirroring the behavior of its non-phenylated analogue,^[6] whilst **3** isomerizes to **2**, somewhat surprisingly in terms of the cage C–C separations (from crystallographic determinations) of 3.24 (**3**) and 2.79 Å (**2**).^[7] However, the directions of all these isomerizations are fully consistent with the calculated energies of (η -C₆H₅)RuC₂B₁₀H₁₂ in its various 4,1,*x*-RuC₂B₁₀ isomeric forms, also shown in Scheme 2 (DFT, in kcal mol⁻¹ relative to 4-(η -C₆H₅)-4,1,6-*closo*-RuC₂B₁₀H₁₂).^[14]

In conclusion, we have isolated and characterized the first example of a 4,1,11-MC₂B₁₀ 13-vertex metallacarborane and have shown that this is one of five isomeric metallacarboranes formed upon metalation of reduced 1,12-Ph₂-1,12-*closo*-C₂B₁₀H₁₀. We have studied the reduction of 1,12-*closo*-C₂B₁₀H₁₂ computationally and have shown that the [1,7-*nido*-C₂B₁₀]²⁻ and [4,7-*nido*-C₂B₁₀]²⁻ anions result. We have suggested that these *nido* carboranes then isomerize to three other isomers, and that metalations of all these account for the five metallacarboranes isolated. It therefore appears that the reduction of *para* carborane is much more complicated than previous studies have suggested.^[6,7,15] The importance of the [1,7-*nido*-C₂B₁₀]²⁻ and [4,7-*nido*-C₂B₁₀]²⁻ anions, in which one cage carbon atom is *not* located in the open face, could be particularly significant.

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Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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