Metallacarboranes

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

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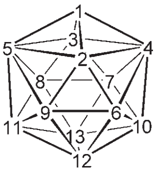
Thirteen-vertex heteroboranes generally adopt the docosahedral architecture predicted for the (as yet) unknown species $[B_{13}H_{13}]^{2-}$,[1] although the first 13-vertex carborane[2] and some MC_2B_{10} metallacarboranes[3] adopt an alternative henicosahedral structure. In the docosahedron (Scheme 1), 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*-$C_2B_{10}H_{12}$ 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*-$C_2B_{10}H_{12}$ or its *C,C*-dimethyl analogue.[6]



Scheme 1. Numbering scheme for the docosahedron.

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*-$RuC_2B_{10}H_{10}$. We also describe a computational study of the reduction of 1,12-*closo*-$C_2B_{10}H_{12}$ 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 ([{Ru(*p*-cymene)Cl_2}$_2$]) of 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ affords 1,6-Ph_2-4-(*p*-cymene)-4,1,6-*closo*-$RuC_2B_{10}H_{10}$ (**1**)[8] as the major product instead of the expected 4,1,10-RuC_2B_{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*-$RuC_2B_{10}H_{10}$ (**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*-$RuC_2B_{10}H_{10}$ (**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 $^{11}B\{^1H\}$ 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*-$RuC_2B_{10}H_{12}$ ($\delta = -2$ 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.

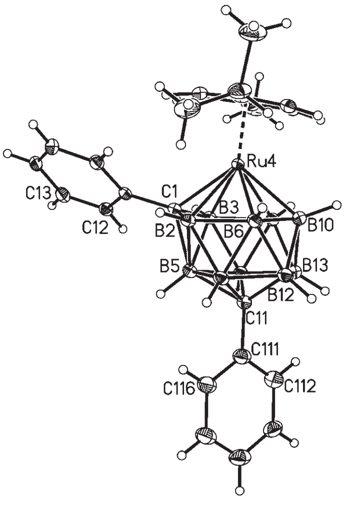


Figure 1. Perspective view of compound **3**. Selected bond lengths [Å]: Ru4-C1 2.1727(19), Ru4-B2 2.319(2), Ru4-B6 2.262(2), Ru4-B10 2.253(2), Ru4-B7 2.281(2), Ru4-B3 2.298(2).

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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-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ 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-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ 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-Ph_2-4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{10}$ (**4**, ca. 2 %), a known isomer previously prepared by the thermolysis of **1** or **2**, and the new species 1,10-Ph_2-4-(*p*-cymene)-4,1,10-*closo*-$RuC_2B_{10}H_{10}$ (**5**, less than 1 %), ironically the expected product in the initial synthesis.

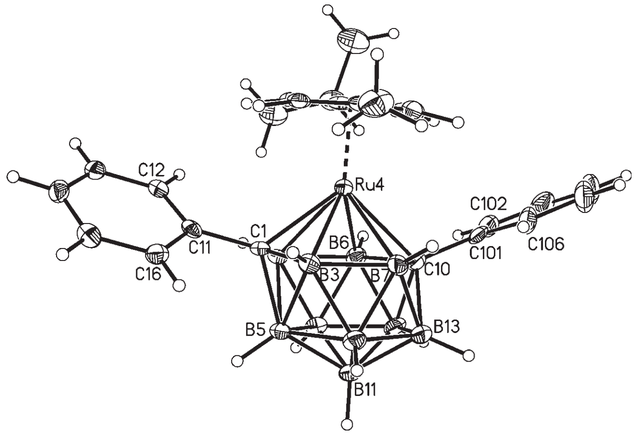


Figure 2. Perspective view of compound **5**. Selected bond lengths [Å]: Ru4-C1 2.195(3), Ru4-B2 2.330(4), Ru4-B6 2.268(4), Ru4-C10 2.262(3), Ru4-B7 2.257(4), Ru4-B3 2.303(4).

Both the ^1H and ^{11}B 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 ^{11}B NMR spectrum is relatively narrow, $\delta = 0$ to −14 ppm, consistent with a 4,1,10-RuC_2B_{10} isomer. This molecular architecture was confirmed by crystallographic analysis (Figure 2).

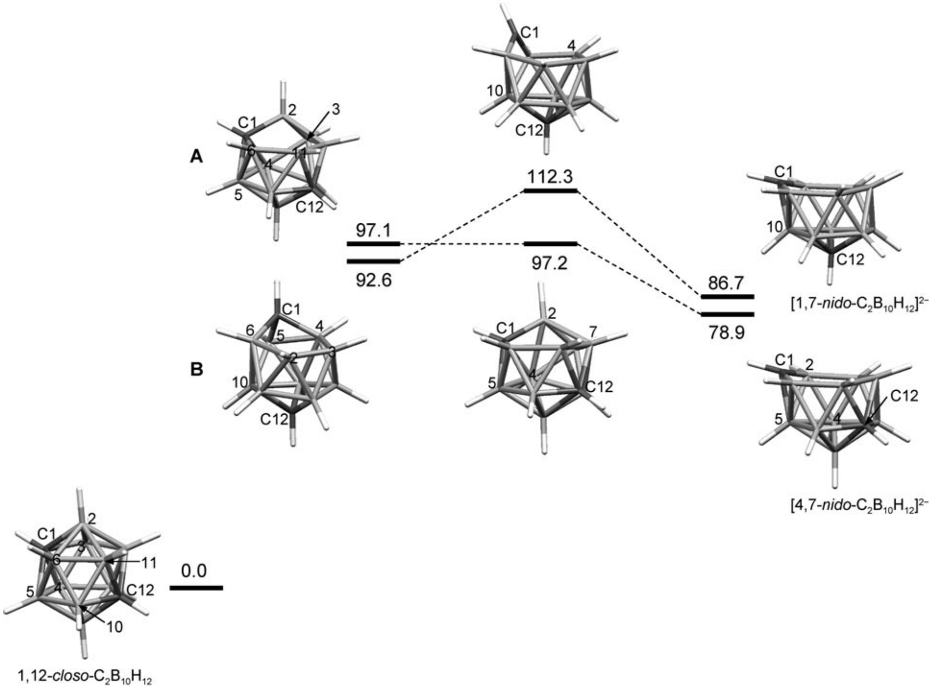


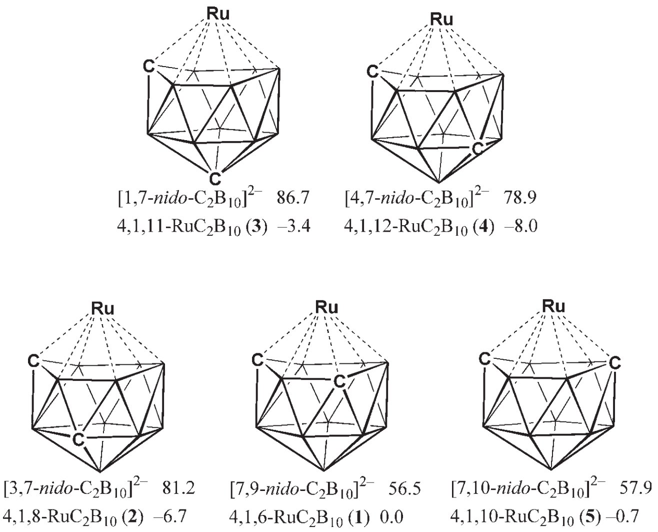
Figure 3. Computed profiles for the reduction of 1,12-*closo*-$C_2B_{10}H_{12}$. C atoms are dark gray and B atoms are light gray. Calculated energies in kcal mol^{-1}.

Thus, the reduction and metalation of 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ affords, in total, five isomeric 4,1,*x*-MC_2B_{10} metallacarboranes. In an attempt to understand this result we have investigated the reduction of 1,12-*closo*-$C_2B_{10}H_{12}$ 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*-$C_2B_{10}H_{12}$ initially result in alternative highly distorted dianion intermediates **A** (+97.1 kcal mol^{-1} relative to 1,12-*closo*-$C_2B_{10}H_{12}$) and **B** (+92.6 kcal mol^{-1}). Species **A** and **B** are 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 $[4,7\text{-}nido\text{-}C_2B_{10}H_{12}]^{2-}$ 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*-$C_2B_{10}H_{12}$]$^{2-}$ at $+86.7$ kcal mol^{-1}.

Thus the *nido* species predicted by theory are [1,7-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ and [4,7-*nido*-$C_2B_{10}H_{12}$]$^{2-}$. 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*-C_2B_{10}]$^{2-}$ and/or [4,7-*nido*-C_2B_{10}]$^{2-}$ species first isomerize to the [7,9-*nido*-C_2B_{10}]$^{2-}$, [3,7-*nido*-C_2B_{10}]$^{2-}$, and [7,10-*nido*-C_2B_{10}]$^{2-}$ forms, respectively. Scheme 2 summarizes the five isomeric [$C_2B_{10}H_{12}$]$^{2-}$ dianions and their calculated stabilities (DFT, in kcal mol^{-1} relative to 1,12-*closo*-$C_2B_{10}H_{12}$). 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*-$C_2B_{10}H_{12}$]$^{2-}$ and [4,7-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ might rearrange to the other isomers shown in Scheme 2 will be the subject of a future computational study.[13]



[1,7-*nido*-C_2B_{10}]$^{2-}$ 86.7
4,1,11-RuC_2B_{10} (**3**) –3.4

[4,7-*nido*-C_2B_{10}]$^{2-}$ 78.9
4,1,12-RuC_2B_{10} (**4**) –8.0

[3,7-*nido*-C_2B_{10}]$^{2-}$ 81.2
4,1,8-RuC_2B_{10} (**2**) –6.7

[7,9-*nido*-C_2B_{10}]$^{2-}$ 56.5
4,1,6-RuC_2B_{10} (**1**) 0.0

[7,10-*nido*-C_2B_{10}]$^{2-}$ 57.9
4,1,10-RuC_2B_{10} (**5**) –0.7

Scheme 2. Without Ru: the five isomeric [*nido*-C_2B_{10}]$^{2-}$ 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*-$C_2B_{10}H_{12}$. 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-C_6H_6)Ru} and are relative to that for the 4,1,6-RuC_2B_{10} isomer.

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-C_6H_6)Ru$C_2B_{10}H_{12}$ in its various 4,1,*x*-RuC_2B_{10} isomeric forms, also shown in Scheme 2 (DFT, in kcal mol^{-1} relative to 4-(η-C_6H_6)-4,1,6-*closo*-Ru$C_2B_{10}H_{12}$).[14]

In conclusion, we have isolated and characterized the first example of a 4,1,11-MC_2B_{10} 13-vertex metallacarborane and have shown that this is one of five isomeric metallacarboranes formed upon metalation of reduced 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$. We have studied the reduction of 1,12-*closo*-$C_2B_{10}H_{12}$ computationally and have shown that the [1,7-*nido*-C_2B_{10}]$^{2-}$ and [4,7-*nido*-C_2B_{10}]$^{2-}$ 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*-C_2B_{10}]$^{2-}$ and [4,7-*nido*-C_2B_{10}]$^{2-}$ anions, in which one cage carbon atom is *not* located in the open face, could be particularly significant.

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[9] 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 semiempirically and structures were solved by direct and difference-Fourier methods. Refinement[16] was carried out by full-matrix least-squares analysis on F^2. Crystal data for **3**: $C_{24}H_{34}B_{10}Ru$, $M_r = 531.68$, monoclinic, space group $P2_1/n$, $a = 10.2946(6)$, $b = 15.9730(10)$, $c = 15.6391(9)$ Å, $\beta = 102.555(3)°$, $V = 2510.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.407$ Mg m^{-3}, $\mu = 0.638$ mm^{-1}, $F(000) = 1088$. Data to $\theta_{max} = 32.35°$ collected at 100(2) K on a Bruker X8 diffractometer using Mo$_{K\alpha}$ radiation. 8879 out of 54570 independent reflections, $R_1 = 0.0372$, $wR_2 = 0.0705$, $S = 0.994$ for data with $I > 2\sigma(I)$, largest peak 0.67 and deepest hole -0.61 e Å^{-3}. Crystal data for **5**: $C_{22}H_{33}B_{10}Ru$, $M_r = 531.68$, rhombohedral, space group $R\bar{3}$, $a = 36.095(3)$, $c = 10.0400(8)$ Å, $V = 11\,328.3(15)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.403$ Mg m^{-3}, $\mu = 0.636$ mm^{-1}, $F(000) = 4896$, $\theta_{max} = 25.43°$. 4589/45467 reflections, $R_1 = 0.0334$, $wR_2 = 0.0701$, $S = 1.003$, $I > 2\sigma(I)$, largest peak 0.81 and deepest hole -0.61 e Å^{-3}. CCDC-646529 (**3**) and CCDC-646530 (**5**) contain 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] The relative energies calculated for [7,9-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ and [7,10-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ provide a rationale for the unexpected 7,10→7,9 isomerization previously observed.[7] For completeness we have also calculated the energies (in kcal mol^{-1}) of [7,8-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ and [2,7-*nido*-$C_2B_{10}H_{12}$]$^{2-}$ (69.2 and 101.4, respectively, relative to 1,12-*closo*-$C_2B_{10}H_{12}$) and of the related metallacarboranes 4-(η-C_6H_6)-4,1,2-*closo*-$RuC_2B_{10}H_{12}$ and 4-(η-C_6H_6)-4,1,5-*closo*-$RuC_2B_{10}H_{12}$ (7.7 and 17.5, respectively, relative to 4-(η-C_6H_6)-4,1,6-*closo*-$RuC_2B_{10}H_{12}$). The relative instability of the 4,1,5-MC_2B_{10} species supports our contention that such an isomer is unlikely to be synthesized.

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