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How to make 8,1,2-*closo*-MC₂B₉ metallocarboranes**

Wing Y. Man, Sergey Zlatogorsky, Hugo Tricas, David Ellis, Georgina M. Rosair, and Alan J. Welch*

Abstract: Three examples of the rare 8,1,2-*closo*-MC₂B₉ isomeric form of an icosahedral metallocarborane have been accidentally isolated as trace products in reactions. Seeking to understand how these were formed we considered both the nature of the reactions that were being undertaken and the nature of the co-products. This led us to propose a mechanism for formation of the 8,1,2-*closo*-MC₂B₉ species which we then tested, leading to the first deliberate synthesis of an example of this isomer. Thus, deboronation of 4-(η -C₅H₅)-4,1,8-*closo*-CoC₂B₁₀H₁₂ selectively removes the B5 vertex to yield the dianion [nido-(η -C₅H₅)CoC₂B₉H₁₁]²⁻, oxidative closure of which affords 8-(η -C₅H₅)-8,1,2-*closo*-CoC₂B₉H₁₁ in moderate yield.

Heteroborane chemistry is dominated by the 12-vertex icosahedron.^[1] The nine isomeric possibilities for icosahedral MC₂B₉ metallocarboranes were summarised by Hughes *et al* in 2000^[2] and are illustrated in Figure 1. These workers also reviewed the results of a search for MC₂B₉ species by isomer on the Cambridge Structural Database and reported the first example of a 2,1,12-*closo*-MC₂B₉ compound. More than a decade later we have undertaken a new database search^[3] (M = any metal) yielding 804 examples of 3,1,2-*closo*-MC₂B₉ species, 43 examples of 2,1,8-, 42 examples of 2,1,7-, 9 examples of 4,1,2- and 3 examples of 2,1,12-*closo*-MC₂B₉ compounds. Thus there are four “missing” isomers, 2,1,9-, 9,1,7-, 8,1,2- and 9,1,2-*closo*-MC₂B₉ (the last three of which, uniquely, have no C atoms in the metal-bonded face) that are yet to be crystallographically confirmed. Moreover, as far as we are aware there is only one report of the synthesis of these four “missing” isomers, as follows;^[4] in 1972 Hawthorne *et al* reported that 2-(η -C₅H₅)-2,1,9-*closo*-CoC₂B₉H₁₁ and 9-(η -C₅H₅)-9,1,7-*closo*-CoC₂B₉H₁₁ (and their C,C'-dimethyl analogues) are formed from isomerisation of the appropriate 3,1,2-*closo*-CoC₂B₉ species at ca. 650°C in the gas phase, whilst the tethered compounds 1,2- μ -(CH₂)₃-8-(η -C₅H₅)-8,1,2-*closo*-CoC₂B₉H₉ and 1,2- μ -(CH₂)₃-9-(η -C₅H₅)-9,1,2-*closo*-CoC₂B₉H₉ are formed from the isomerisation of 1,2- μ -(CH₂)₃-3-(η -C₅H₅)-3,1,2-*closo*-CoC₂B₉H₉ under similar conditions, with all structures assigned principally on the basis of spectroscopic analysis.

How might one prepare these four “missing” isomers by conventional chemistry? In particular, how might one prepare an 8,1,2-*closo*-MC₂B₉ species in which the two cage carbon atoms

are not tethered together? It is a challenging problem because there is no obvious synthetic route. 3,1,2- and 2,1,7-*closo*-MC₂B₉ metallocarboranes are the kinetic products of metallation of the corresponding dianion ([7,8-*nido*-C₂B₉]²⁻ and [7,9-*nido*-C₂B₉]²⁻, respectively, these dianions resulting from deboronation of 1,2-*closo*-C₂B₁₀ and 1,7-*closo*-C₂B₁₀ carboranes),^[5] whilst 2,1,8- and 4,1,2-species are afforded by thermal isomerisation reactions.^[4,6] Deboronation of 1,12-*closo*-C₂B₁₀ affords [2,9-*nido*-C₂B₉]²⁻, metallation of which gives 2,1,12-*closo*-MC₂B₉,^[7] although Hughes's original 2,1,12-*closo*-MC₂B₉ compound was afforded by direct reaction between 2,9-*nido*-C₂B₉H₁₃ and M(NMe₂)₅ (M = Ta, Nb).^[2] Thus, it would appear likely that any attempts to prepare 8,1,2-*closo*-MC₂B₉ species must involve thermal isomerisation (as reported by Hawthorne *et al*^[4]) but in the absence of a C,C' tether the cage carbon atoms would be very unlikely either to remain or become adjacent under thermolysis conditions. Is there another way?

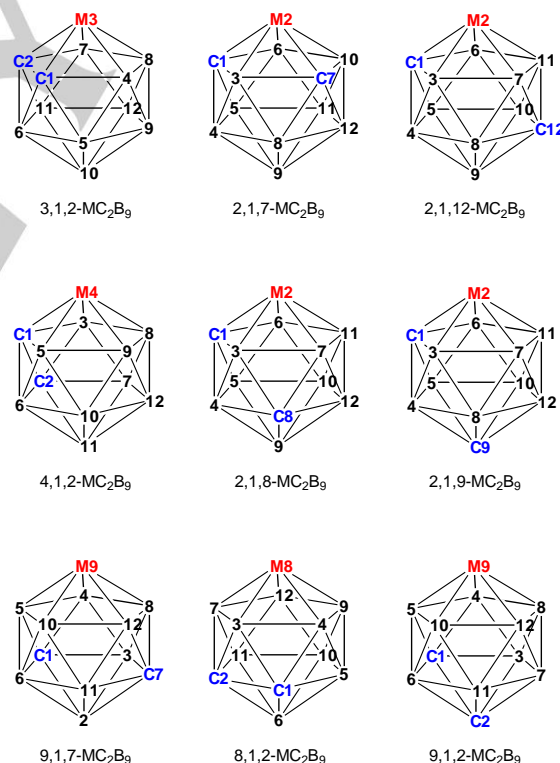


Figure 1. The nine isomers of icosahedral MC₂B₉ metallocarboranes.

It turns out that there is – we have serendipitously isolated and then structurally characterised three examples of 8,1,2-*closo*-MC₂B₉ species without C,C' tethers, and consideration of the reactions in which these were formed together with their co-products has led us to propose and then confirm a rational route to such species.

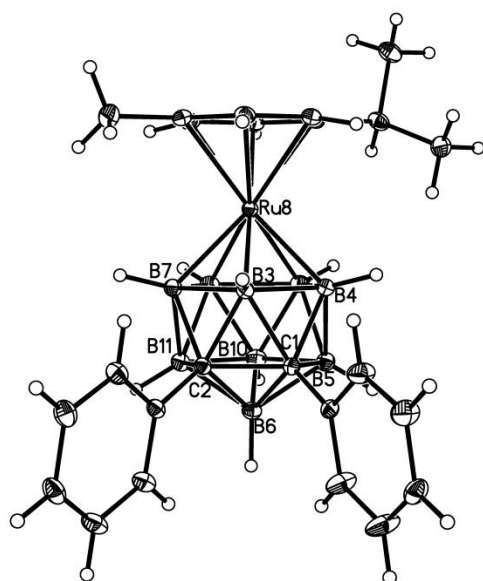
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Reduction (Na/THF, naphthalene [catalytic]) of 1,8-Ph₂-4-(*p*-cymene)-4,1,8-*closo*-RuC₂B₁₀H₁₀,^[9] followed by treatment with 0.5 equivalents of [Ru(η-C₆H₆)Cl₂]₂ and work-up in air resulted in isolation of the known compounds 1,6-Ph₂-4-(*p*-cymene)-4,1,6-*closo*-RuC₂B₁₀H₁₀^[9] and 1,12-Ph₂-4-(*p*-cymene)-4,1,12-*closo*-RuC₂B₁₀H₁₀,^[9] the new 12-vertex species 1,2-Ph₂-8-(*p*-cymene)-8,1,2-*closo*-RuC₂B₉H₉ (**1**), the new 14-vertex diruthenacarborane 1-(*p*-cymene)-2,10-Ph₂-14-(η-C₆H₆)-1,14,2,10-*closo*-Ru₂C₂B₉H₉ (**2**) and the new 13-vertex diruthenacarborane 1,6-Ph₂-4-(η-C₆H₆)-5-(*p*-cymene)-4,5,1,6-*closo*-Ru₂C₂B₉H₉ (**3**) as well as partial recovery of the starting material. Products were characterised by mass spectrometry, ¹H and ¹¹B NMR spectroscopies and X-ray diffraction (see Supporting Information for experimental, spectroscopic and crystallographic details of all new compounds reported in this paper), and the structure of **1** is shown in Figure 2. The ¹¹B{¹H} NMR spectrum of **1** consists of four resonances with relative integrals 2:2:1:4. Time-averaged C_s



molecular symmetry was confirmed by only one doublet from the methyl protons of the ⁱPr group. Compound **1** is the first crystallographically-proven example of a 8,1,2-*closo*-MC₂B₉ species.

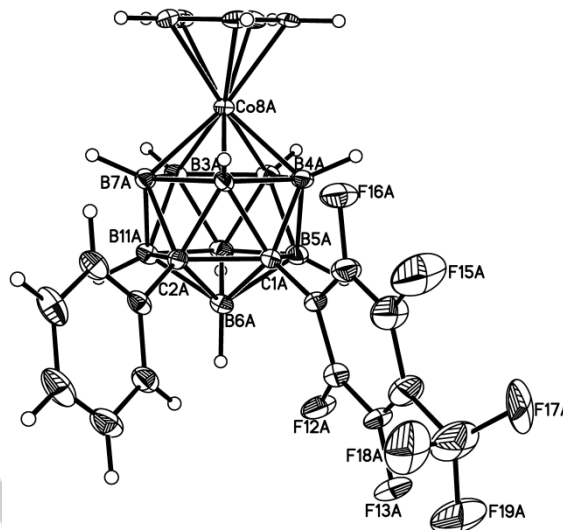
Figure 2. Compound **1**. Ru8–B 2.1421(13)–2.1947(13), C1–C2 1.6881(16) Å.

Compound **2** could potentially result from reduction and metallation of 1,12-Ph₂-4-(*p*-cymene)-4,1,12-*closo*-RuC₂B₁₀H₁₀.^[10] Dimetallacarboranes with 4,5,1,6-*closo*-M₂C₂B₉ architectures have previously been prepared by polyhedral substitution of 4,1,6-*closo*-MC₂B₁₀ species,^[11] by thermolysis of 4,5,2,3-*closo*-M₂C₂B₉ species^[12] or by reduction of 3,1,2-*closo*-MC₂B₉ compounds followed by thermolysis of the reduced species then metallation.^[12] We believe that the fact that we began with a 4,1,8-*closo*-MC₂B₁₀ compound and that one of the products is the 4,5,1,6-*closo*-M₂C₂B₉ species **3** are both relevant to the mechanism of formation of **1**.

There are >40 years between the first (and, prior to this publication, only) report of a 8,1,2-*closo*-MC₂B₉ compound^[4] and crystallographic proof of this architecture in compound **1**. Having waited so long however, like the proverbial London buses, two

more examples of the same isomer were isolated soon afterwards by different but related chemistry.

Reduction of 1-(4'-F₃CC₆F₄)-2-Ph-1,2-*closo*-C₂B₁₀H₁₀^[13] followed by treatment with Na[C₅H₅]/CoCl₂ affords, on work-up, three isolatable products: the 4,5,1,6-*closo*-M₂C₂B₉ compound 1-Ph-4,5-(η-C₅H₅)₂-6-(4'-F₃CC₆F₄)-4,5,1,6-*closo*-Co₂C₂B₉H₉ (**4**), the unique *ortho*-phenylene bridging species 1,4-μ-[2'-(C₅H₄)-4'-F₃CC₆F₃]-6-Ph-4,1,6-*closo*-Co₂B₁₀H₁₀ (**5**) and the 8,1,2-*closo*-



MC₂B₉ compound 1-(4'-F₃CC₆F₄)-2-Ph-8-(η-C₅H₅)-8,1,2-*closo*-Co₂B₉H₉, (**6**). All three compounds were characterised spectroscopically and crystallographically and the structure of **6** is shown in Figure 3.

Figure 3. Compound **6** (molecule A). Co8–B 2.008(3)–2.072(3), C1–C2 1.720(4) Å (molecule A); Co8–B 2.005(3)–2.081(3), C1–C2 1.718(4) Å (molecule B).

Again we note the formation of a 4,5,1,6-*closo*-M₂C₂B₉ co-product. The isolation of **5** suggests that reduction and metallation of 1-(4'-F₃CC₆F₄)-2-Ph-1,2-*closo*-C₂B₁₀H₁₀ produces first a 4,1,6-*closo*-Co₂B₁₀ species and we have already demonstrated that 4,1,6- compounds with fluorinated aryl substituents can readily isomerise to 4,1,12- isomers, but such 4,1,6- to 4,1,12-isomerisations are known to go via 4,1,8- intermediates.^[14]

The third 8,1,2-*closo*-MC₂B₉ metallocarborane, 1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-8-(η-C₅H₅)-8,1,2-*closo*-C₂B₉H₁₀ (**7**) was isolated in trace amount during the 2-*e* reduction and metallation (Na[C₅H₅]/CoCl₂) of bis(*ortho*-carborane), 1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-1,2-*closo*-C₂B₁₀H₁₁.^[15] Co-products are 1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-4-(η-C₅H₅)-4,1,8-*closo*-Co₂B₁₀H₁₁ (**8**), 1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-4-(η-C₅H₅)-4,1,12-*closo*-Co₂B₁₀H₁₁ (**9**) and the known compounds, the *rac* and *meso* diastereoisomers of 1-[1'-4'-(η-C₅H₅)-4',1',6'-*closo*-Co₂B₁₀H₁₁]-4-(η-C₅H₅)-4,1,6-*closo*-Co₂B₁₀H₁₁.^[16] Again, product identities were confirmed spectroscopically and in some cases crystallographically; see Supporting Information. The molecular structure of compound **7** is shown in Figure 4. Although a 4,1,8-*closo*-MC₂B₁₀ species is once more one of the co-products we do not observe a 4,5,1,6-*closo*-M₂C₂B₉ species in this reaction, but we anticipate that such

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a product would suffer severe steric crowding having a $C_2B_{10}H_{11}$ substituent on a cage C atom adjacent to two $(\eta-C_5H_5)Co$ vertices.

The common denominators in all these reactions affording 8,1,2-*closo*- MC_2B_9 compounds appear to be 4,1,8-*closo*- MC_2B_{10} species (as either precursor or co-product) and 4,5,1,6-*closo*- $M_2C_2B_9$ species (as co-product if not too crowded to form) and this allows a feasible mechanism for the formation of 8,1,2-*closo*- MC_2B_9 compounds to be advanced.

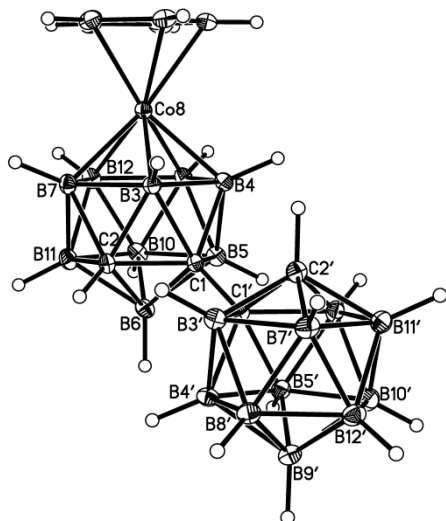


Figure 4. Compound **7**. Co8–B 2.0122(17)–2.2.0726(19), C1–C2 1.640(2), C1–C1' 1.527(2), C1'–C2' 1.650(2) Å.

We propose that the precursor to 8,1,2-*closo*- MC_2B_9 compounds is the corresponding 13-vertex 4,1,8-*closo*- MC_2B_{10} species. It would be anticipated that in such 4,1,8- compounds the unique degree-6 boron atom B5 is susceptible to deboronation in the presence of a suitable nucleophile (possibly OH^- from a trace of water). As shown in Figure 5, loss of $\{B5H\}^{2+}$ affords a $[nido-MC_2B_9]^{2-}$ ion which could then either be metallated if in the presence of a suitable metal dication to afford a 4,5,1,6-*closo*- $M_2C_2B_9$ species or could undergo oxidative closure to afford a 8,1,2-*closo*- MC_2B_9 product.

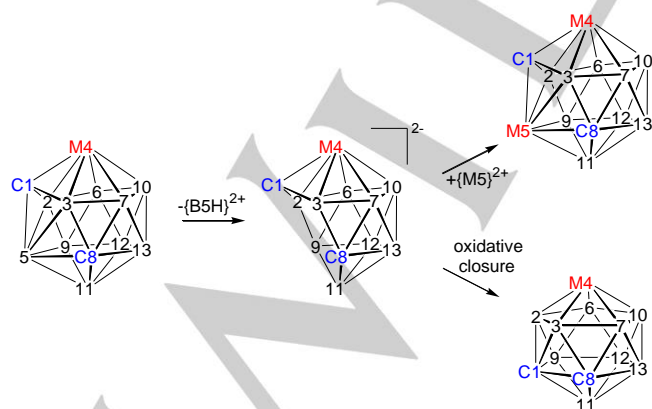


Figure 5. Suggested mechanism for the formation of 8,1,2-*closo*- MC_2B_9 species from 4,1,8-*closo*- MC_2B_{10} precursors. To aid following the process the atom numbering has been preserved throughout. Initial loss of a $\{B5H\}^{2+}$ unit affords the [4,1,8-*nido*- MC_2B_9] $^{2-}$ dianion (properly numbered the [2,7,9-*nido*- MC_2B_9] $^{2-}$

dianion). Metallation of this affords a 4,5,1,6-*closo*- $M_2C_2B_9$ species (properly numbered 4,5,1,6-*closo*- $M_2C_2B_9$) whilst oxidative closure (involving a diamond-square diamond transformation of the 1342 face and the formation of 1–8, 1–11 and 1–9 connectivities) affords the 4,1,8-*closo*- MC_2B_9 icosahedron (properly numbered 8,1,2-*closo*- MC_2B_9).

To test this hypothesis we first treated 4- $(\eta-C_5H_5)$ -4,1,8-*closo*- $CoC_2B_{10}H_{12}$ [17] with 1 equivalent of KOH in EtOH to effect deliberate deboronation, isolating the product $[nido-(\eta-C_5H_5)CoC_2B_9H_{12}]^-$ as its $[C_6H_5CH_2NEt_3]^+$ salt, **10**. A crystallographic study of **10** confirmed deboronation at the B5 position. Having established this we then treated $[HNMe_3][nido-(\eta-C_5H_5)CoC_2B_9H_{12}]$ (**11**) with excess NaH in THF for 3 hr and aeri ally oxidised the resulting species. This afforded, as the only chromatographically-mobile products, 8- $(\eta-C_5H_5)$ -8,1,2-*closo*- $CoC_2B_9H_{11}$ (**12**) and 2- $(\eta-C_5H_5)$ -2,1,8-*closo*- $CoC_2B_9H_{11}$ (**13**) in 8% yield and trace amount, respectively.[18] Compound **12**, the 8,1,2-*closo*- MC_2B_9 species with H atoms as the only cage substituents and the classic $\{(\eta-C_5H_5)Co\}$ metal fragment, is reported for the first time. Compound **13** was reported in Hawthorne's 1972 paper as one of the products of gas phase thermolysis of 3- $(\eta-C_5H_5)$ -3,1,2-*closo*- $CoC_2B_9H_{11}$ but was only characterised spectroscopically.[4]

The molecular structure of **12** is shown in Figure 6. Note that in compounds **7–10**, **12** and **13** at least one of the cage C atoms has only an H substituent, so it is particularly important that the cage C and cage B atoms are correctly distinguished in crystallographic studies. For this purpose we have used the recently reported VCD [19] and BHD [20] methods, both of which gave the same unambiguous results, allowing us to be completely confident that, for example, **7** and **12** are correctly described as 8,1,2-*closo*- MC_2B_9 species.

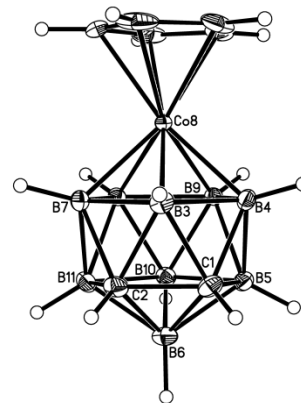


Figure 6. Compound **12** (molecule A). Co8–B 2.023(2)–2.079(2), C1–C2 1.621(3) Å (molecule A); Co8–B 2.018(2)–2.072(2), C1–C2 1.619(3) Å (molecule B).

In conclusion, the first examples of metallocarboranes with 8,1,2-*closo*- MC_2B_9 architectures to be crystallographically characterised, compounds **1**, **6** and **7**, are reported. They are, moreover, the first crystallographically-confirmed MC_2B_9 compounds of any isomeric type in which the metal is bonded to an all-boron ligand face. By considering the nature of the reactions and co-products from which they were isolated we have proposed a rational synthesis of 8,1,2-*closo*- MC_2B_9 compounds by B5 deboronation of 4,1,8-*closo*- MC_2B_{10} precursors followed by oxidative closure, and successfully tested this proposal to prepare

8-(η -C₅H₅)-8,1,2-*closo*-CoC₂B₉H₁₁ (**12**).

Using DFT calculations Perekalin and Kudinov^[21] and later King *et al*^[22] have calculated the relative stabilities of all nine *closo*-MC₂B₉ isomers; whilst the single most important factor is maximal separation of the C atoms, isomers with B₅ metal-bonded faces are more stable than analogues with C₂B₃ faces, *e.g.* 9,1,7- is calculated to be more stable than 2,1,7-*closo*-MC₂B₉ and 8,1,2- is calculated to be more stable than 3,1,2-*closo*-MC₂B₉.^[21] Presumably the previous dearth of examples of 8,1,2-*closo*-MC₂B₉ species was therefore due to a lack of a suitable kinetic pathway, a problem we believe we have now overcome.

Keywords: metallocarborane • synthesis • structure • isomer • icosahedron

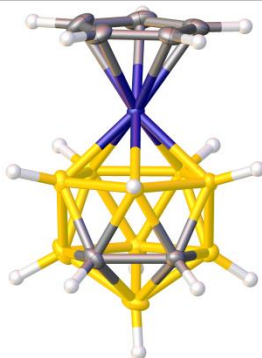
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More than 40 years after the only report of an 8,1,2-*closo*-MC₂B₉ species (only partially characterised), three further examples were accidentally discovered.

Consideration of the reactions in which they were formed together with their co-products led to a suggested mechanism which was tested and found to be successful. Thus the archetypal example, 8-(η -C₅H₅)-8,1,2-*closo*-CoC₂B₉H₁₁ was prepared and fully characterised.



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