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

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Abstract: Three examples of the rare 8,1,2-closo-MC₂B₉ isomeric form of an icosahedral metallacarborane 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-(η⁵-C₅H₅)-1,8-closo-CoC₂B₉H₁₂ selectively removes the B₅ vertex to yield the dianion [nido-(η⁵-C₅H₅)CoC₂B₉H₁₁]⁻; oxidative closure of which affords 8-(η⁵-C₅H₅)-8,1,2-closo-CoC₂B₉H₁₁ in moderate yield.

Heteroborane chemistry is dominated by the 12-vertex icosahedral.[1] The nine isomeric possibilities for icosahedral MC₂B₉ metallacarboranes 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- and 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-(η⁵-C₅H₅)-2,1,9-closo-CoC₂B₉H₁₁ and 9-(η⁵-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. 850°C in the gas phase, whilst the tethered compounds 1,2-µ-(CH₂)₂-8-(η⁵-C₅H₅)-8,1,2-closo-CoC₂B₉H₉ and 1,2-µ-(CH₂)₉-9-(η⁵-C₅H₅)-9,1,2-closo-CoC₂B₉H₉ are formed from the isomerisation of 1,2-µ-(CH₂)₂-3-(η⁵-C₅H₅)-3,1,2-closo-CoC₂B₉H₁₃ 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 metallacarboranes are the kinetic products of metallation of the corresponding dianion ([7,8-nido-C₅B₉]⁻ and [7,9-nido-C₅B₉]⁻); 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.[6] Deboronation of 1,12-closo-C₂B₁₀ affords [2,9-nido-C₂B₉]⁻; 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-C₂B₁₀H₁₃ and M(NMe₂)₃ (M = Ta, Nb).[8] 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[9]) 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 metallacarboranes.

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.
Reduction (Na/THF, naphthalene [catalytic]) of 1,8-Ph$_2$-(p-cymene)-4,1,8-closo-Ru$_2$C$_9$B$_2$H$_{10}$ followed by treatment with 0.5 equivalents of [Ru(η-C$_5$H$_5$)$_2$Cl$_2$] and work-up in air resulted in isolation of the known compounds 1,6-Ph$_2$-(p-cymene)-4,1,6-closo-Ru$_2$C$_9$B$_2$H$_{10}$ and 1,12-Ph$_2$-(p-cymene)-4,1,12-closo-Ru$_2$C$_9$B$_2$H$_{10}$, the new 12-vertex species 1,2-Ph$_2$-6-(p-cymene)-8,1,2-closo-Ru$_2$C$_9$B$_2$H$_{12}$ (1), the new 14-vertex diruthenacarborane 1-(p-cymene)-2,10-Ph$_2$-14-(η$_2$-C$_5$H$_5$)$_2$-1,14,2,10-closo-Ru$_2$C$_9$B$_2$H$_{12}$ (2) and the new 13-vertex diruthenacarborane 1,6-Ph$_2$-(η$_2$-C$_5$H$_5$)$_2$-5-(p-cymene)-4,5,1,6-closo-Ru$_2$C$_9$B$_2$H$_{12}$ (3) as well as partial recovery of the starting material. Products were characterised by mass spectrometry, $^1$H and $^{13}$B 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 $^{11}$B($^1$H) NMR spectrum of 1 consists of four resonances with relative integrals 2:2:1:4. Time-averaged C, molecular symmetry was confirmed by only one doublet from the methyl protons of the Pr group. Compound 1 is the first crystallographically-proven example of a 8,1,2-closo-M$_2$C$_5$B$_3$ species.

Compound 2 could potentially result from reduction and metallation of 1,12-Ph$_2$-(p-cymene)-4,1,12-closo-Ru$_2$C$_9$B$_2$H$_{10}$. Dimetalacarboranes with 4,5,1,6-closo-M$_2$C$_5$B$_3$ architectures have previously been prepared by polyhedral subrogation of 4,1,6-closo-M$_2$C$_5$B$_3$ species by thermolysis of 4,5,2,3-closo-M$_2$C$_5$B$_3$ species or by reduction of 3,1,2-closo-M$_2$C$_5$B$_3$ compounds followed by thermolysis of the reduced species then metallation. We believe that the fact we began with a 4,1,8-closo-M$_2$C$_5$B$_3$ compound that one of the products is the 4,5,1,6-closo-M$_2$C$_5$B$_3$ 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-M$_2$C$_5$B$_3$ compound 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′-F$_2$CClF$_2$)-2-Ph-1,2-closo-C$_5$B$_2$H$_{10}$ followed by treatment with Na[C$_5$H$_5$]Co affords, on work-up, three isolatable products: the 4,5,1,6-closo-M$_2$C$_5$B$_3$ compound 1,6-Ph$_2$-(p-cymene)-4,1,6-closo-Ru$_2$C$_9$B$_2$H$_{10}$ and the unique ortho-phenylene bridging species 1,4-μ-[(η$_2$-C$_5$H$_5$)$_2$]-4′-F$_2$CClF$_2$-6-Ph-4,1,6-closo-Co$_2$C$_9$B$_2$H$_{12}$ (4) (the unique ortho-phenylene bridging species 1,4-μ-[(η$_2$-C$_5$H$_5$)$_2$]-4′-F$_2$CClF$_2$-6-Ph-4,1,6-closo-Co$_2$C$_9$B$_2$H$_{12}$ (5) and the 8,1,2-closo-M$_2$C$_5$B$_3$ compound 1-(4′-F$_2$CClF$_2$)-2-Ph-8-(η$_2$-C$_5$H$_5$)$_2$-8,1,2-closo-Co$_2$C$_9$B$_2$H$_{12}$ (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-M$_2$C$_5$B$_3$ co-product. The isolation of 5 suggests that reduction and metallation of 1-(4′-F$_2$CClF$_2$)-2-Ph-1,2-closo-C$_5$B$_2$H$_{10}$ produces first a 4,1,6-closo-Co$_2$C$_9$B$_2$H$_{12}$ 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 1,8,14-intermediates.

The third 8,1,2-closo-M$_2$C$_5$B$_3$ metallocarborane, 1-(1′-1′,2′-closo-C$_5$B$_2$H$_{10}$)-8-(η$_2$-C$_5$H$_5$)$_2$-8,1,2-closo-C$_5$B$_2$H$_{10}$ (7) was isolated in trace amount during the 2-e reduction and metallation (Na[C$_5$H$_5$]CoCl$_2$) of bis(ortho-carborane), 1-(1′-1′,2′-closo-C$_5$B$_2$H$_{10}$)-1,2-closo-C$_5$B$_2$H$_{11}$ Co-products are 1-(1′-1′,2′-closo-C$_5$B$_2$H$_{11}$)-4-(η$_2$-C$_5$H$_5$)-4,1,8-closo-Co$_2$C$_9$B$_2$H$_{12}$ (8), 1-(1′-1′,2′-closo-C$_5$B$_2$H$_{11}$)-4-(η$_2$-C$_5$H$_5$)-4,1,12-closo-Co$_2$C$_9$B$_2$H$_{12}$ (9) and the known compounds, the rac and meso diastereoisomers of 1-(1′-1′,-4′-1″,6′-closo-Co$_2$C$_9$B$_2$H$_{11}$)-4-(η$_2$-C$_5$H$_5$)-4,1,6-closo-Co$_2$C$_9$B$_2$H$_{12}$ (10). 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-M$_2$C$_5$B$_3$ species is once more one of the co-products we do not observe a 4,5,1,6-closo-M$_2$C$_5$B$_3$ species in this reaction, but we anticipate that such...
a product would suffer severe steric crowding having a $\text{C}_2\text{B}_2\text{H}_1$ substituent on a cage C atom adjacent to two $(\eta^1\text{C}_2\text{H}_2)$C vertices. The common denominators in all these reactions affording 8,1,2-closo-MC$_2$B$_3$ compounds appear to be 4,1,8-closo-MC$_2$B$_3$ species (as either precursor or co-product) and 4,5,1,6-closo-MC$_2$B$_3$ 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$_2$B$_3$ compounds to be advanced.

To test this hypothesis we first treated 4-$(\eta^1\text{C}_2\text{H}_2)$-4,1,8-closo-CoC$_2$B$_3$H$_2$ with 1 equivalent of KOH in EtOH to effect deliberate deboronation, isolating the product [(nido-$(\eta^1\text{C}_2\text{H}_2)$CoC$_2$B$_3$)$_2$] as its $[\text{CH}_3\text{CH}_2\text{NEt}]^-$ salt, 10. A crystallographic study of 10 confirmed deboronation at the B5 position. Having established this we then treated $[\text{HNMe}_2][\text{nido-}(\eta^1\text{C}_2\text{H}_2)$CoC$_2$B$_3$H$_2]$ with excess NaH in THF for 3 hr and aerily oxidised the resulting species. This afforded, as the only chromatographically-mobile products, 8-$(\eta^1\text{C}_2\text{H}_2)$-8,1,2-closo-CoC$_2$B$_3$H$_2$ (12) and 2-$(\eta^1\text{C}_2\text{H}_2)$-2,1,8-closo-CoC$_2$B$_3$H$_1$ (13) in 8% yield and trace amount, respectively. (10) Compound 12, the 8,1,2-closo-MC$_2$B$_3$ species with H atoms as the only cage substituents and the classic $(\eta^1\text{C}_2\text{H}_2)$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-$(\eta^1\text{C}_2\text{H}_2)$-3,1,2-closo-CoC$_2$B$_3$H$_1$ but was only characterised spectroscopically. (15)

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$_2$B$_3$ species.

In conclusion, the first examples of metallacarboranes with 8,1,2-closo-MC$_2$B$_3$ architectures to be crystallographically characterised, compounds 1, 6 and 7, are reported. They are, moreover, the first crystallographically-confirmed MC$_2$B$_3$ 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$_2$B$_3$ compounds by B5 deboronation of 4,1,8-closo-MC$_2$B$_3$ precursors followed by oxidative closure, and successfully tested this proposal to prepare...
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8-(η₆-C₆H₁₂)-8,1,2-closo-CoC₆B₈H₄⁺ (12)

Using DFT calculations Perekalin and Kudinov [21] and later King et al. [22] have calculated the relative stabilities of all nine closo-MC₆B₈ isomers; whilst the single most important factor is maximal separation of the C atoms, isomers with B₆ metal-bonded faces are more stable than analogues with C₂B₆ faces, e.g. 9,1,7-is calculated to be more stable than 2,1,7-closo-MC₆B₈ and 8,1,2-is calculated to be more stable than 3,1,2-closo-MC₆B₈. [21]

Presumably the previous dearth of examples of 8,1,2-closo-MC₆B₈ species was therefore due to a lack of a suitable kinetic pathway, a problem we believe we have now overcome.

**Keywords:** metallacarborane • synthesis • structure • isomer • icosahedron

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[10] a) W. J. Evans, M. F. Hawthorne, J. Chem. Soc., Chem. Commun. 1974, 38-39; b) A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair, A. J. Welch, Dalton Trans. 2013, 42, 671-679. Alternatively, it is possible that [1-(p-cymene)-2,9-Ph₂-1,2,9-nidoRuC₆B₈H₄]⁺ the reduced form of 1,8-Ph₂-4-(p-cymene)-1,8-closo-RuC₆B₈H₄ isomerises to the 1,2,10 isomer of the diание which is then metallated to afford compound 2.
[18] The relative amounts of 12 and 13 afforded by this process are dependent on the precise experimental conditions (see Supporting information for details). However, we have conclusively established that under the conditions employed the two species are formed by separate routes.
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.