Metallacarboranes

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How to Make 8,1,2-*closo*-MC_2B_9 Metallacarboranes**

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Abstract: *Three examples of the rare 8,1,2-closo-MC_2B_9 isomeric form of an icosahedral metallacarborane have been isolated as unexpected 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 coproducts. This led us to propose a mechanism for the formation of the 8,1,2-closo-MC_2B_9 species. The mechanism was then tested, leading to the first deliberate synthesis of an example of this isomer. Thus, deboronation of 4-(η-C_5H_5)-4,1,8-closo-$CoC_2B_{10}H_{12}$ selectively removes the B5 vertex to yield the dianion [nido-(η-C_5H_5)$CoC_2B_9H_{11}$]$^{2-}$, oxidative closure of which affords 8-(η-C_5H_5)-8,1,2-closo-$CoC_2B_9H_{11}$ in moderate yield.*

Heteroborane chemistry is dominated by the 12-vertex icosahedron.[1] The nine isomeric possibilities for icosahedral MC_2B_9 metallacarboranes were summarized by Hughes et al. in 2000[2] and are illustrated in Figure 1. This group also reviewed the results of a search for MC_2B_9 species by isomer on the Cambridge Structural Database and reported the first example of a 2,1,12-*closo*-MC_2B_9 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*-MC_2B_9 species, 43 examples of 2,1,8-, 42 examples of 2,1,7-, nine examples of 4,1,2-, and three examples of 2,1,12-*closo*-MC_2B_9 compounds. Thus there are four "missing" isomers, 2,1,9-, 9,1,7-, 8,1,2-, and 9,1,2-*closo*-MC_2B_9 (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-C_5H_5)-2,1,9-*closo*-$CoC_2B_9H_{11}$ and 9-(η-C_5H_5)-9,1,7-*closo*-$CoC_2B_9H_{11}$ (and their C,C′-dimethyl analogues) are formed from isomerization of the appropriate 3,1,2-*closo*-CoC_2B_9 species at ca. 650 °C in the gas phase, whilst the tethered compounds 1,2-μ-$(CH_2)_3$-8-(η-C_5H_5)-8,1,2-*closo*-$CoC_2B_9H_9$ and 1,2-μ-$(CH_2)_3$-9-(η-C_5H_5)-9,1,2-*closo*-$CoC_2B_9H_9$ are formed from the isomerization of 1,2-μ-$(CH_2)_3$-3-(η-C_5H_5)-3,1,2-*closo*-$CoC_2B_9H_9$ under similar conditions, with all structures assigned principally on the basis of spectroscopic analysis.

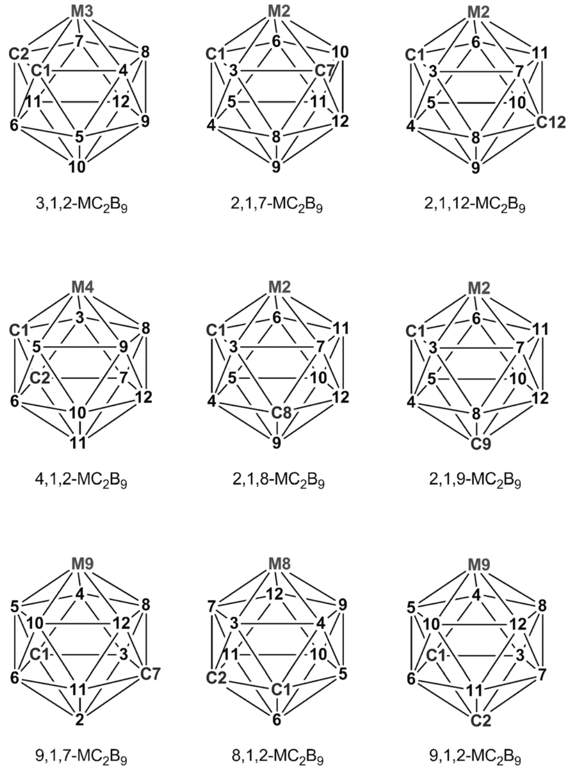
3,1,2-MC_2B_9 2,1,7-MC_2B_9 2,1,12-MC_2B_9
4,1,2-MC_2B_9 2,1,8-MC_2B_9 2,1,9-MC_2B_9
9,1,7-MC_2B_9 8,1,2-MC_2B_9 9,1,2-MC_2B_9

Figure 1. The nine isomers of icosahedral MC_2B_9 metallacarboranes.

How might one prepare these four "missing" isomers by conventional chemistry? In particular, how might one prepare an 8,1,2-*closo*-MC_2B_9 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*-MC_2B_9 metallacarboranes are the kinetic products of metalation of the corresponding dianion ([7,8-*nido*-C_2B_9]$^{2-}$ and [7,9-*nido*-C_2B_9]$^{2-}$, respectively; these dianions result from deboronation of 1,2-*closo*-C_2B_{10} and 1,7-*closo*-C_2B_{10} carboranes),[5] whilst 2,1,8- and 4,1,2-species are afforded by thermal isomerization reactions.[4,6] Deboronation of 1,12-*closo*-C_2B_{10} affords [2,9-*nido*-C_2B_9]$^{2-}$, metalation of which gives 2,1,12-*closo*-MC_2B_9,[7] although Hughes's original 2,1,12-*closo*-MC_2B_9 compound was afforded by direct reaction between 2,9-*nido*-$C_2B_9H_{13}$ and $M(NMe_2)_5$ (M = Ta, Nb).[2] Thus, it would appear likely that any attempts to prepare 8,1,2-*closo*-MC_2B_9 species must involve thermal isomerization (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?

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It turns out that there is: We have serendipitously isolated and then structurally characterized three examples of 8,1,2-*closo*-MC_2B_9 species without C,C′ tethers, and consideration of the reactions in which these were formed together with their coproducts has led us to propose and then confirm a rational route to such species.

Reduction (Na/THF, naphthalene [catalytic]) of 1,8-Ph_2-4-(*p*-cymene)-4,1,8-*closo*-$RuC_2B_{10}H_{10}$,[8] followed by treatment with 0.5 equivalents of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ and work-up in air resulted in isolation of the known compounds 1,6-Ph_2-4-(*p*-cymene)-4,1,6-*closo*-$RuC_2B_{10}H_{10}$[9] and 1,12-Ph_2-4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{10}$,[8] the new 12-vertex species 1,2-Ph_2-8-(*p*-cymene)-8,1,2-*closo*-$RuC_2B_9H_9$ (**1**), the new 14-vertex diruthenacarborane 1-(*p*-cymene)-2,10-Ph_2-14-(η-C_6H_6)-1,14,2,10-*closo*-$Ru_2C_2B_{10}H_{10}$ (**2**), and the new 13-vertex diruthenacarborane 1,6-Ph_2-4-(η-C_6H_6)-5-(*p*-cymene)-4,5,1,6-*closo*-$Ru_2C_2B_9H_9$ (**3**) as well as partial recovery of the starting material. Products were characterized by mass spectrometry, ^1H and ^{11}B NMR spectroscopies, and *X*-ray diffraction (see the 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 $^{11}B\{^1H\}$ NMR spectrum of **1** shows 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 *i*Pr group. Compound **1** is the first crystallographically proven example of a 8,1,2-*closo*-MC_2B_9 species.

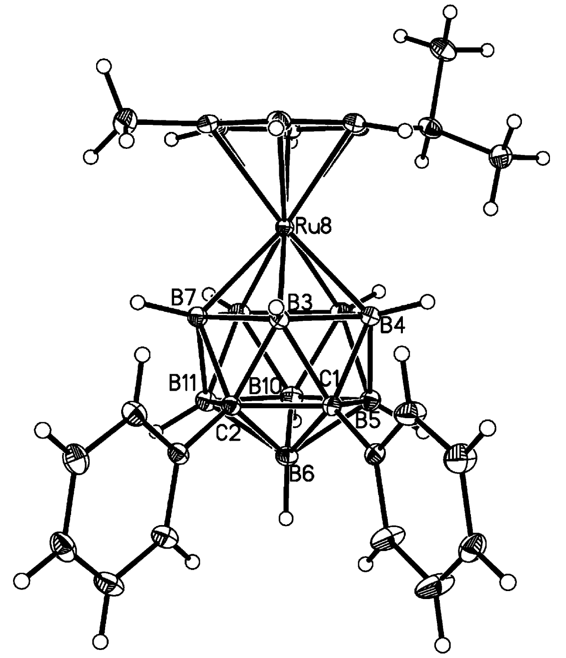

Figure 2. Compound **1**. Ru8–B 2.1421(13)–2.1947(13), C1–C2 1.6881(16) Å.

Compound **2** could potentially result from reduction and metalation of 1,12-Ph_2-4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{10}$.[10] Dimetallacarboranes with 4,5,1,6-*closo*-$M_2C_2B_9$ architectures have previously been prepared by polyhedral subrogation of 4,1,6-*closo*-MC_2B_{10} species,[11] by thermolysis of 4,5,2,3-*closo*-$M_2C_2B_9$ species,[12] or by reduction of 3,1,2-*closo*-MC_2B_9 compounds followed by thermolysis of the reduced species and then metalation.[12] We believe that the facts that we began with a 4,1,8-*closo*-MC_2B_{10} compound and that one of the products is the 4,5,1,6-*closo*-$M_2C_2B_9$ species **3** are both relevant to the mechanism of formation of **1**.

There are more than 40 years between the first (and, prior to this publication, only) report of a 8,1,2-*closo*-MC_2B_9 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′-$F_3CC_6F_4$)-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$[13] followed by treatment with $Na[C_5H_5]/CoCl_2$ affords, on work-up, three isolatable products: the 4,5,1,6-*closo*-$M_2C_2B_9$ compound 1-Ph-4,5-(η-C_5H_5)$_2$-6-(4′-$F_3CC_6F_4$)-4,5,1,6-*closo*-$Co_2C_2B_9H_9$ (**4**), the unique *ortho*-phenylene bridging species 1,4-μ-[2′-(C_5H_4)-4′-$F_3CC_6F_3$]-6-Ph-4,1,6-*closo*-$CoC_2B_{10}H_{10}$ (**5**), and the 8,1,2-*closo*-MC_2B_9 compound 1-(4′-$F_3CC_6F_4$)-2-Ph-8-(η-C_5H_5)-8,1,2-*closo*-$CoC_2B_9H_9$ (**6**). All three compounds were characterized spectroscopically and crystallographically and the structure of **6** is shown in Figure 3.

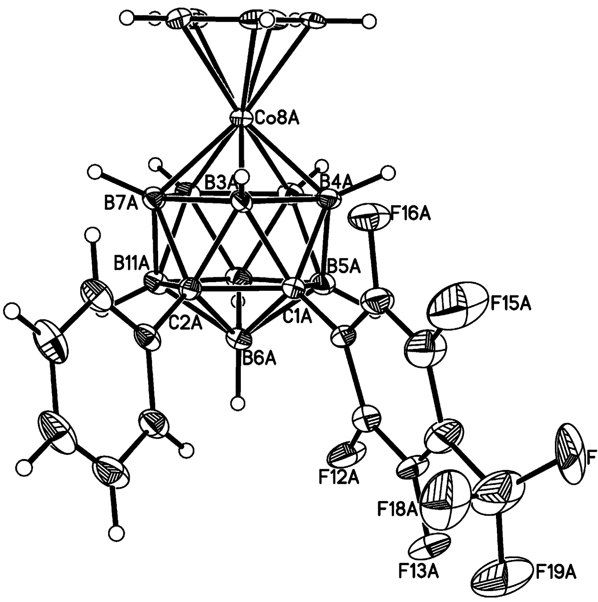

Figure 3. Compound **6** (molecule A). Co8–B 2.008(3)–2.072(3), C1–C2 1.720(4) Å (molecule A); Co8–B 2.005(3)–2.081(3), C1–C2 1.718(4) Å (molecule B).

Again we note the formation of a 4,5,1,6-*closo*-$M_2C_2B_9$ coproduct. The isolation of **5** suggests that reduction and metalation of 1-(4′-$F_3CC_6F_4$)-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}$ produces first a 4,1,6-*closo*-CoC_2B_{10} species and we have already demonstrated that 4,1,6-compounds with fluorinated aryl substituents can readily isomerize to 4,1,12-isomers, but such 4,1,6- to 4,1,12-isomerizations are known to proceed via 4,1,8-intermediates.[14]

The third 8,1,2-*closo*-MC_2B_9 metallacarborane, 1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-8-(η-C_5H_5)-8,1,2-*closo*-$CoC_2B_9H_{10}$ (**7**), was isolated in trace amount during the 2-e reduction and metalation (Na[C_5H_5]/$CoCl_2$) of bis(*ortho*-carborane), 1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-1,2-*closo*-$C_2B_{10}H_{11}$.[15] Coproducts are 1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-(η-C_5H_5)-4,1,8-*closo*-$CoC_2B_{10}H_{11}$ (**8**), 1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-(η-C_5H_5)-4,1,12-*closo*-$CoC_2B_{10}H_{11}$ (**9**), and the known compounds, the *rac* and *meso* diastereoisomers of 1-[1′-4′-(η-C_5H_5)-4′,1′,6′-*closo*-$CoC_2B_{10}H_{11}$]-4-(η-C_5H_5)-4,1,6-*closo*-$CoC_2B_{10}H_{11}$.[16] Again, product identities were confirmed spectroscopically and in some cases crystallographically; see the Supporting Information. The molecular structure of compound **7** is shown in Figure 4. Although a 4,1,8-*closo*-MC_2B_{10} species is once more one of the coproducts, we do not observe a 4,5,1,6-*closo*-$M_2C_2B_9$ species in this reaction, but we anticipate that such a product would suffer severe steric crowding having a $C_2B_{10}H_{11}$ substituent on a cage C atom adjacent to two (η-C_5H_5)Co vertices.

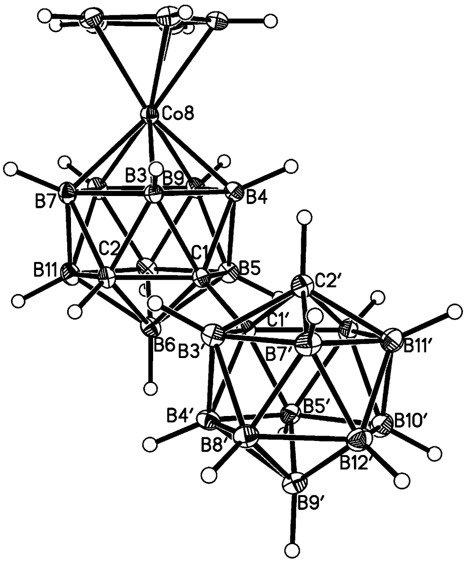

Figure 4. Compound **7**. Co8–B 2.0122(17)–2.0726(19), C1–C2 1.640(2), C1–C1′ 1.527(2), C1′–C2′ 1.650(2) Å.

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 coproduct) and 4,5,1,6-*closo*-$M_2C_2B_9$ species (as coproduct 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.

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 metalated 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.

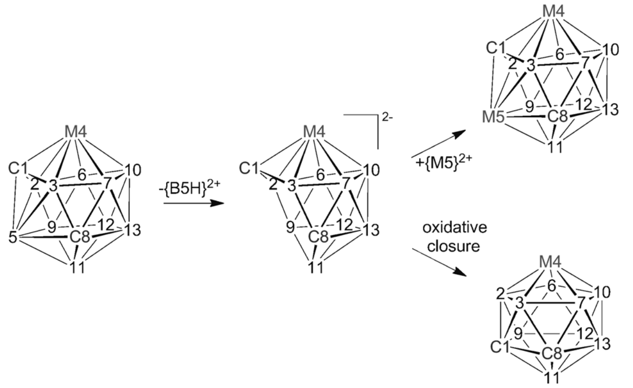

Figure 5. Suggested mechanism for the formation of 8,1,2-*closo*-MC_2B_9 species from 4,1,8-*closo*-MC_2B_{10} precursors. To aid following the process the atom numbering has been preserved throughout. Initial loss of a $\{B5H\}^{2+}$ unit affords the [4,1,8-*nido*-MC_2B_9]$^{2-}$ dianion (properly numbered the [2,7,9-*nido*-MC_2B_9]$^{2-}$ dianion). Metalation of this affords a 4,5,1,8-*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-(η-C_5H_5)-4,1,8-*closo*-$CoC_2B_{10}H_{12}$[17] with one equivalent of KOH in EtOH to effect deliberate deboronation, isolating the product [*nido*-(η-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*-(η-C_5H_5)$CoC_2B_9H_{12}$] (**11**) with excess NaH in THF for 3 h and aerially oxidized the resulting species. This afforded, as the only chromatographically mobile products, 8-(η-C_5H_5)-8,1,2-*closo*-$CoC_2B_9H_{11}$ (**12**) and 2-(η-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 {(η-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-(η-C_5H_5)-3,1,2-*closo*-$CoC_2B_9H_{11}$, but was only characterized 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 vertex–centroid distance (VCD)[19] and boron–hydrogen distance (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.

In conclusion, the first examples of metallacarboranes with 8,1,2-*closo*-MC_2B_9 architectures to be crystallographically characterized, 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 coproducts and the nature of the reactions from which they were isolated we have proposed a rational synthesis of 8,1,2-*closo*-MC_2B_9

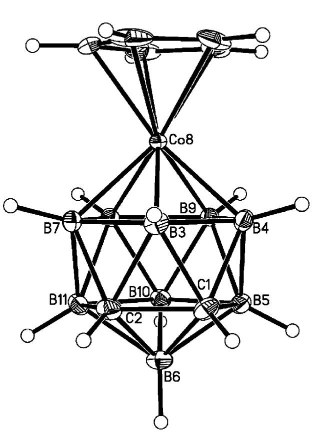

Figure 6. Compound **12** (molecule A). Co8–B 2.023(2)–2.079(2), C1–C2 1.621(3) Å (molecule A); Co8–B 2.018(2)–2.072(2), C1–C2 1.619(3) Å (molecule B).

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-C_5H_5)-8,1,2-*closo*-$CoC_2B_9H_{11}$ (**12**).

Using DFT calculations Perekalin and Kudinov[21] and later King et al.[22] have calculated the relative stabilities of all nine *closo*-MC_2B_9 isomers; whilst the single most important factor is maximal separation of the C atoms, isomers with B_5 metal-bonded faces are more stable than analogues with C_2B_3 faces, for example, 9,1,7- is calculated to be more stable than 2,1,7-*closo*-MC_2B_9 and 8,1,2- is calculated to be more stable than 3,1,2-*closo*-MC_2B_9.[21] Presumably the previous dearth of examples of 8,1,2-*closo*-MC_2B_9 species was therefore due to a lack of a suitable kinetic pathway, a problem we believe we have now overcome.

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Keywords: icosahedron · isomers · metallacarboranes · structure · synthesis

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