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

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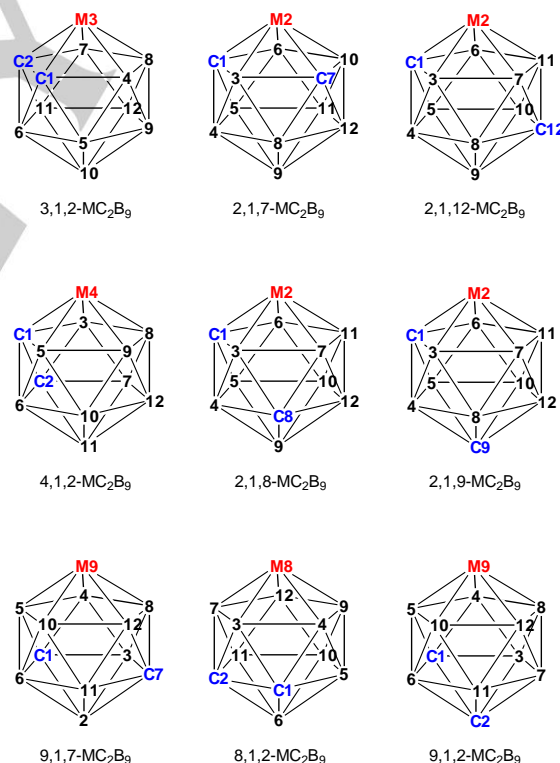# How to make 8,1,2-*closo*-MC$_2$B$_9$ metallacarboranes**

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-MC$_2$B$_9$ 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-MC$_2$B$_9$ species which we then tested, leading to the first deliberate synthesis of an example of this isomer. Thus, deboronation of 4-(η-C$_5$H$_5$)-4,1,8-closo-CoC$_2$B$_{10}$H$_{12}$ selectively removes the B5 vertex to yield the dianion [nido-(η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$]$^{2-}$, oxidative closure of which affords 8-(η-C$_5$H$_5$)-8,1,2-closo-CoC$_2$B$_9$H$_{11}$ in moderate yield.*

Heteroborane chemistry is dominated by the 12-vertex icosahedron.[1] The nine isomeric possibilities for icosahedral MC$_2$B$_9$ 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 MC$_2$B$_9$ species by isomer on the Cambridge Structural Database and reported the first example of a 2,1,12-*closo*-MC$_2$B$_9$ 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$_2$B$_9$ 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*-MC$_2$B$_9$ compounds. Thus there are four "missing" isomers, 2,1,9-, 9,1,7- 8,1,2- and 9,1,2-*closo*-MC$_2$B$_9$ (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$_5$H$_5$)-2,1,9-*closo*-CoC$_2$B$_9$H$_{11}$ and 9-(η-C$_5$H$_5$)-9,1,7-*closo*-CoC$_2$B$_9$H$_{11}$ (and their C,C′-dimethyl analogues) are formed from isomerisation of the appropriate 3,1,2-*closo*-CoC$_2$B$_9$ species at *ca.* 650ºC in the gas phase, whilst the tethered compounds 1,2-μ-(CH$_2$)$_3$-8-(η-C$_5$H$_5$)-8,1,2-*closo*-CoC$_2$B$_9$H$_9$ and 1,2-μ-(CH$_2$)$_3$-9-(η-C$_5$H$_5$)-9,1,2-*closo*-CoC$_2$B$_9$H$_9$ are formed from the isomerisation of 1,2-μ-(CH$_2$)$_3$-3-(η-C$_5$H$_5$)-3,1,2-*closo*-CoC$_2$B$_9$H$_9$ 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*-MC$_2$B$_9$ species in which the two cage carbon atoms

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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$_2$B$_9$ metallacarboranes are the kinetic products of metallation of the corresponding dianion ([7,8-*nido*-C$_2$B$_9$]$^{2-}$ and [7,9-*nido*-C$_2$B$_9$]$^{2-}$, respectively, these dianions resulting from deboronation of 1,2-*closo*-C$_2$B$_{10}$ and 1,7-*closo*-C$_2$B$_{10}$ carboranes),[5] whilst 2,1,8- and 4,1,2-species are afforded by thermal isomerisation reactions.[4,6] Deboronation of 1,12-*closo*-C$_2$B$_{10}$ affords [2,9-*nido*-C$_2$B$_9$]$^{2-}$, metallation of which gives 2,1,12-*closo*-MC$_2$B$_9$,[7] although Hughes's original 2,1,12-*closo*-MC$_2$B$_9$ compound was afforded by direct reaction between 2,9-*nido*-C$_2$B$_9$H$_{13}$ and M(NMe$_2$)$_5$ (M = Ta, Nb).[2] Thus, it would appear likely that any attempts to prepare 8,1,2-*closo*-MC$_2$B$_9$ 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 MC$_2$B$_9$ metallacarboranes.

It turns out that there is – we have serendipitously isolated and then structurally characterised three examples of 8,1,2-*closo*-MC$_2$B$_9$ 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_2-4-(p-cymene)-4,1,8-$closo$-$RuC_2B_{10}H_{10}$,[8] followed by treatment with 0.5 equivalents of [Ru(η-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-$closo$-$Ru_2C_2B_9H_9$ (**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 characterised by mass spectrometery, ^1H and ^{11}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 $^{11}B\{^1H\}$ NMR spectrum of **1** consists of four resonances with relative integrals 2:2:1:4. Time-averaged C_s
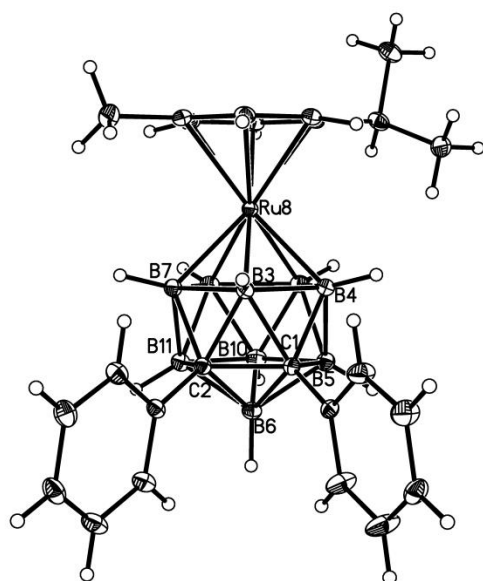
molecular symmetry was confirmed by only one doublet from the methyl protons of the ^{i}Pr group. Compound **1** is the first crystallographically-proven example of a 8,1,2-$closo$-MC_2B_9 species.

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 metallation 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 then metallation.[12] We believe that the fact 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 >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-$closo$-
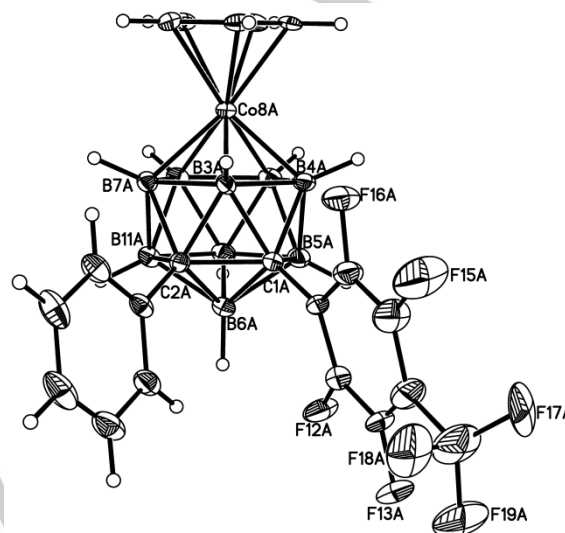
MC_2B_9 compound 1-(4′-$F_3CC_6F_4$)-2-Ph-8-(η-C_5H_5)-8,1,2-$closo$-$CoC_2B_9H_9$, (**6**). All three compounds were characterised spectroscopically and crystallographically and the structure of **6** is shown in Figure 3.

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-$closo$-$M_2C_2B_9$ co-product. The isolation of **5** suggests that reduction and metallation 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 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-$closo$-MC_2B_9 metallacarborane, 1-(1′-1′,2′-$closo$-$C_2B_{10}H_{11}$)-8-(η-C_5H_5)-8,1,2-$closo$-$C_2B_9H_{10}$ (**7**) was isolated in trace amount during the 2-e reduction and metallation (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] Co-products 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 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 co-products 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.

The common denominators in all these reactions affording 8,1,2-*closo*-MC$_2$B$_9$ compounds appear to be 4,1,8-*closo*-MC$_2$B$_{10}$ species (as either precursor or co-product) and 4,5,1,6-*closo*-M$_2$C$_2$B$_9$ 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$_2$B$_9$ compounds to be advanced.
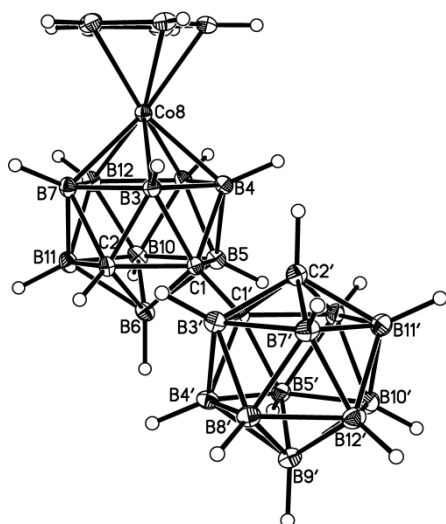
Figure 4. Compound **7**. Co8–B 2.0122(17)-2.2.0726(19), C1–C2 1.640(2), C1–C1′ 1.527(2), C1′–C2′ 1.650(2) Å.

We propose that the precursor to 8,1,2-*closo*-MC$_2$B$_9$ compounds is the corresponding 13-vertex 4,1,8-*closo*-MC$_2$B$_{10}$ 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$_2$B$_9$]$^{2-}$ 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$_2$C$_2$B$_9$ species or could undergo oxidative closure to afford a 8,1,2-*closo*-MC$_2$B$_9$ product.
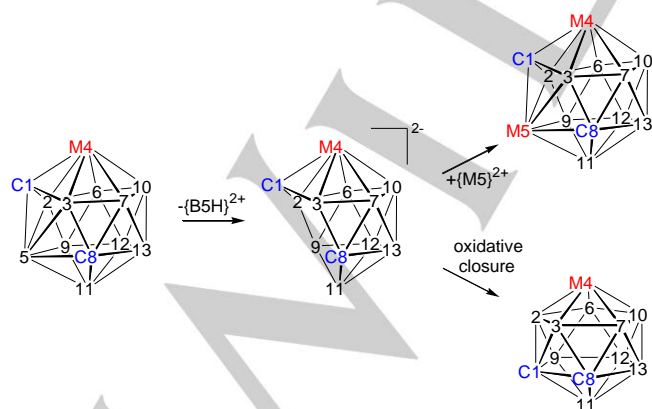

Figure 5. Suggested mechanism for the formation of 8,1,2-*closo*-MC$_2$B$_9$ species from 4,1,8-*closo*-MC$_2$B$_{10}$ precursors. To aid following the process the atom numbering has been preserved throughout. Initial loss of a {B5H}$^{2+}$ unit affords the [4,1,8-*nido*-MC$_2$B$_9$]$^{2-}$ dianion (properly numbered the [2,7,9-*nido*-MC$_2$B$_9$]$^{2-}$

dianion). Metallation of this affords a 4,5,1,8-*closo*-M$_2$C$_2$B$_9$ species (properly numbered 4,5,1,6-*closo*-M$_2$C$_2$B$_9$] 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$_2$B$_9$ icosahedron (properly numbered 8,1,2-*closo*-MC$_2$B$_9$).

To test this hypothesis we first treated 4-(η-C_5H_5)-4,1,8-*closo*-CoC$_2$B$_{10}$H$_{12}$ [17] with 1 equivalent of KOH in EtOH to effect deliberate deboronation, isolating the product [*nido*-(η-C_5H_5)CoC$_2$B$_9$H$_{12}$]⁻ as its [C$_6$H$_5$CH$_2$NEt$_3$]⁺ 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$_2$B$_9$H$_{12}$] (**11**) with excess NaH in THF for 3 hr and aerially oxidised the resulting species. This afforded, as the only chromatographically-mobile products, 8-(η-C_5H_5)-8,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ (**12**) and 2-(η-C_5H_5)-2,1,8-*closo*-CoC$_2$B$_9$H$_{11}$ (**13**) in 8% yield and trace amount, respectively.[18] Compound **12**, the 8,1,2-*closo*-MC$_2$B$_9$ 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$_2$B$_9$H$_{11}$ 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$_2$B$_9$ species.
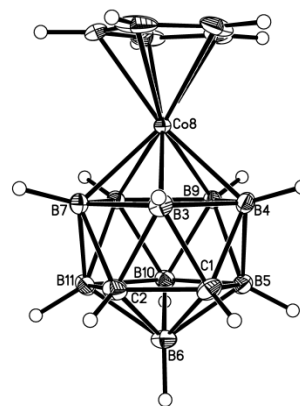
Figure 6. Compound **12** (molecule A). Co8–B 2.023(2)-2.079(2), C1–C2 1.621(3) Å (molecule A); Co8–B 2.018(2)-2.072(2), C1–C2 1.619(3) Å (molecule B).

In conclusion, the first examples of metallacarboranes with 8,1,2-*closo*-MC$_2$B$_9$ architectures to be crystallographically characterised, compounds **1**, **6** and **7**, are reported. They are, moreover, the first crystallographically-confirmed MC$_2$B$_9$ 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$_2$B$_9$ compounds by B5 deboronation of 4,1,8-*closo*-MC$_2$B$_{10}$ precursors followed by oxidative closure, and successfully tested this proposal to prepare

8-(η-C$_5$H$_5$)-8,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ (**12**).

Using DFT calculations Perekalin and Kudinov [21] and later King *et al* [22] have calculated the relative stabilities of all nine *closo*-MC$_2$B$_9$ 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$_2$B$_3$ faces, *e.g.* 9,1,7- is calculated to be more stable than 2,1,7-*closo*-MC$_2$B$_9$ and 8,1,2- is calculated to be more stable than 3,1,2-*closo*-MC$_2$B$_9$.[21] Presumably the previous dearth of examples of 8,1,2-*closo*-MC$_2$B$_9$ 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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Entry for the Table of Contents

COMMUNICATION

More than 40 years after the only report of an 8,1,2-*closo*-MC$_2$B$_9$ 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-C$_5$H$_5$)-8,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ was prepared and fully characterised.
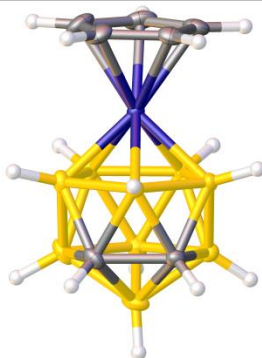
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Page No. – Page No.

How to make 8,1,2-*closo*-MC$_2$B$_9$ metallacarboranes