Bis(carboranes) Very Important Paper

Deutsche Ausgabe: DOI: 10.1002/ange.201600635
Internationale Ausgabe: DOI: 10.1002/anie.201600635

Carborane Substituents Promote Direct Electrophilic Insertion over Reduction–Metalation Reactions

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Abstract: *Two-electron reduction of 1,1′-bis(o-carborane) followed by reaction with [Ru(η-mes)Cl$_2$]$_2$ affords [8-(1′-1′,2′-closo-C$_2$B$_{10}$H$_{11}$)-4-(η-mes)-4,1,8-closo-RuC$_2$B$_{10}$H$_{11}$]. Subsequent two-electron reduction of this species and treatment with [Ru(η-arene)Cl$_2$]$_2$ results in the 14-vertex/12-vertex species [1-(η-mes)-9-(1′-1′,2′-closo-C$_2$B$_{10}$H$_{11}$)-13-(η-arene)-1,13,2,9-closo-Ru$_2$C$_2$B$_{10}$H$_{11}$] by direct electrophilic insertion, promoted by the carborane substituent in the 13-vertex/12-vertex precursor. When arene = mesitylene (mes), the diruthenium species is fluxional in solution at room temperature in a process that makes the metal–ligand fragments equivalent. A unique mechanism for this fluxionality is proposed and is shown to be fully consistent with the observed fluxionality or nonfluxionality of a series of previously reported 14-vertex dicobaltacarboranes.*

The chemistry of bis(carboranes), two carborane units joined together by a conventional two-center two-electron bond, is highly topical. In principle, bis(carboranes) have the capacity to undergo similar reactions to single-cage carboranes but with two important differences, specifically 1) reactivity at a single cage is likely to be significantly influenced by the presence of a large, electron-withdrawing substituent and 2) the reaction could occur at both cages and such reactivity could be either isolated or cooperative. An interesting example of this second point is provided by the following: four-electron reduction of 1,1′-bis(*o*-carborane), the trivial name for [1-(1′-1′,2′-*closo*-C$_2$B$_{10}$H$_{11}$)-1,2-*closo*-C$_2$B$_{10}$H$_{11}$], followed by metalation with {CoCp$^+$} fragments (Cp = cyclopentadienyl), and finally Co^{II}→Co^{III} oxidation, leads to the anticipated racemic and *meso* diastereoisomers of the 13-vertex cobaltacarborane/13-vertex cobaltacarborane species [1-(1′-4′-Cp-4′,1′,6′-*closo*-CoC$_2$B$_{10}$H$_{11}$)-4-Cp-4,1,6-*closo*-CoC$_2$B$_{10}$H$_{11}$].[1] In marked contrast, four-electron reduction of 1,1′-bis(*o*-carborane) followed by metalation with {Ru(*p*-cymene)$^{2+}$} fragments (*p*-cymene = 1-^{i}Pr-4-Me-C$_6$H$_4$) affords a unique 13-vertex ruthenacarborane/12-vertex carborane species. In this molecule, the Ru atom in the expanded cage is bonded to an exopolyhedral {Ru(*p*-cymene)} unit by a Ru–Ru bond bridged by a [μ-σ,η^3:η^3,σ-C$_6$]$^{2-}$ "flyover" ligand formed by the room-temperature reductive cleavage of an arene, the origin of this reduction being the pendant carborane dianion.[2]

References [1] and [2] represent the only reports to date of the reduction and subsequent metalation of bis(carboranes) and, although they describe very different outcomes, in both cases both carborane units were fully reduced (by the addition of two electrons) before metalation. Herein we describe the results of the reduction of only a single cage of 1,1′-bis(*o*-carborane) followed by metalation, and the consequences of repeating this process. We found that unique linked heteroborane species are produced, one subset of which displays unexpected fluxionality that is traced to the formation of a transition-state polyhedron with an unprecedented disk shape.

Reduction of 1,1′-bis(*o*-carborane) with two equivalents of Na[C$_{10}$H$_8$] in THF followed by addition of 0.5 equivalents of [Ru(η-C$_6$H$_6$)Cl$_2$]$_2$ or [Ru(η-*p*-cymene)Cl$_2$]$_2$ affords the 13-vertex ruthenacarborane/12-vertex carborane species [1-(1′-1′,2′-*closo*-C$_2$B$_{10}$H$_{11}$)-4-(η-arene)-4,1,6-*closo*-RuC$_2$B$_{10}$H$_{11}$] (**1** and **2**, respectively) as the only isolable products following work-up involving preparative TLC. Compounds **1** and **2** were fully characterized spectroscopically and crystallographically, with CH and BH vertices distinguished in the crystallographic studies by the vertex–centroid distance[3] and boron–hydrogen distance[4] methods (see the Supporting Information for experimental, spectroscopic, and crystallographic details of all new compounds). The structure of **2** is shown in Figure 1.

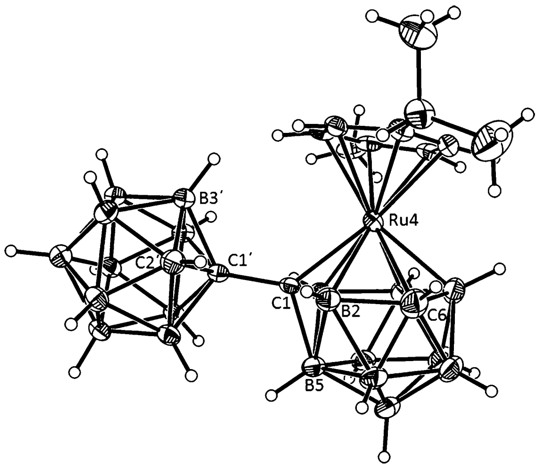

Figure 1. Structure of compound **2**. Ru4–C1 2.205(3), Ru4–B2 2.310(3), Ru4–C6 2.274(3), Ru4–B10 2.241(4), Ru4–B7 2.259(3), Ru4–B3 2.308(3), Ru4–arene 2.188(3)–2.328(3), C1–C1′ 1.529(4) Å. Thermal ellipsoids for Figures 1, 3, and 4 drawn at the 50% probability level except for H atoms.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201600635. CCDC 1447581–1447588 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

Compounds **1** and **2** are composed of a 13-vertex docosahedral 4,1,6-RuC_2B_{10} ruthenacarborane[5] bonded to an icosahedral C_2B_{10} carborane through a C1-C1′ bond. As such, they originate from metalation of a $[7,9\text{-}nido\text{-}C_2B_{10}]^{2-}$ unit, thus suggesting that the dianion resulting from two-electron reduction of 1,1′-bis(*o*-carborane), which has a formal negative charge on each cage,[6] must be in equilibrium in solution with at least a small amount of a $[nido\text{-}C_2B_{10}]^{2-}$–($closo\text{-}C_2B_{10}$) species, as shown in Figure 2.

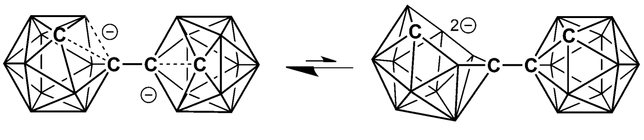

Figure 2. Suggested equilibrium between (left) the two-electron reduced form of 1,1′-bis(*o*-carborane) established by Hawthorne[6] and (right) a form in which one cage is fully reduced and the other not reduced.

In contrast, metalation of two-electron-reduced 1,1′-bis(*o*-carborane) with 0.5 equivalents of $[Ru(\eta\text{-mes})Cl_2]_2$ (mes = mesitylene = 1,3,5-$Me_3C_6H_3$) affords [8-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-(η-mes)-4,1,8-*closo*-$RuC_2B_{10}H_{11}$] (**3**). In compound **3** the 13-vertex ruthenacarborane has isomerized to a 4,1,8-RuC_2B_{10} architecture (Figure 3) and the carborane substituent is now bound to the degree-5 (i.e., 5-connected with respect to the polyhedron) atom C8, in contrast to the situation in **1** and **2** where carborane is bound to the degree-4 C1.[7] The isomerization is presumably the result of otherwise untenable steric interaction between the mes and carborane substituents. Strong circumstantial evidence for this conclusion is that in **1** and **2** the arene ring is bent away from the carborane substituent, subtending angles of 10.57(17) and 12.56(11)° respectively with the plane through atoms B5, B9, B12, B13, and B8, and that related sterically driven isomerizations have been noted in 12-vertex metallacarborane/12-vertex carborane analogues.[8]

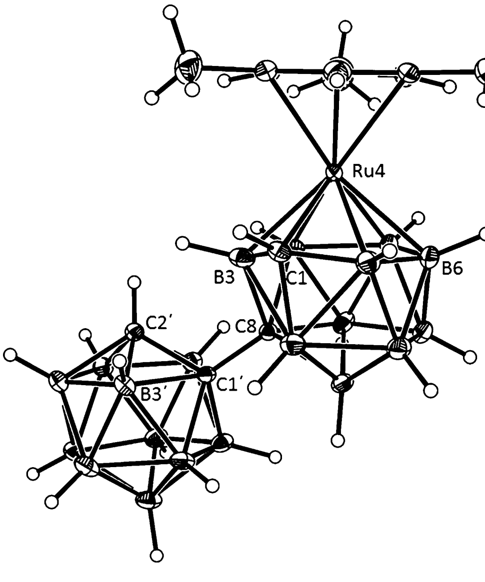

Figure 3. Structure of compound **3**. The molecule is partially disordered and only the major component is shown. Ru4–C1 2.1364(18), Ru4–B2 2.295(2), Ru4–B6 2.2775(18), Ru4–B10 2.2568(19), Ru4–B7 2.2726(19), Ru4–B3 2.2462(18), Ru4–arene 2.2228(17)–2.3017(18), C8–C1′ 1.5369(17) Å.

The formation of a 4,1,8-RuC_2B_{10} metallacarborane in **3** offers the opportunity for a second reduction–metalation sequence, since, unlike 4,1,6-MC_2B_{10} species, 4,1,8- and 4,1,12-13-vertex metallacarboranes are known to be susceptible to two-electron reduction. Thus reduction–metalation of 4,1,8-MC_2B_{10} affords 1,14,2,9-$MM'C_2B_{10}$ compounds whilst reduction–metalation of 4,1,12-MC_2B_{10} leads to 1,14,2,10-$MM'C_2B_{10}$ products, both having bicapped hexagonal antiprismatic structures and isolated as both homo- and heterobimetallic species.[9] However, unlike these single-cage precursors, compound **3** has two potential sites for reduction and metalation, the 13-vertex ruthenacarborane and the 12-vertex carborane, and it is not possible to predict a priori which would be expanded.

The reaction of **3** with two equivalents of $Na[C_{10}H_8]$ in THF followed by addition of 0.5 equivalents of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$, $[Ru(\eta\text{-}p\text{-cymene})Cl_2]_2$, or $[Ru(\eta\text{-mes})Cl_2]_2$ affords in each case two new compounds, namely a 14-vertex $Ru_2C_2B_{10}$/12-vertex C_2B_{10} species (compounds **4**, **6**, and **8**, respectively) as the major product, and a 13-vertex $Ru_2C_2B_9$/12-vertex C_2B_{10} species (compounds **5**, **7**, and **9**, respectively) as a minor coproduct. Compounds **5**, **7**, and **9** all feature a 4,5,1,6-$Ru_2C_2B_9$ docosahedron with a carborane substituent bound to the C6 atom. In the case of **5** and **7**, the Ru atoms are distinguished by their different η-arene ligands, thus showing that in both cases the second Ru vertex is adjacent to both cage C atoms. This result allows us to speculate that the mechanism by which **5**, **7**, and **9** are formed is the same as that we recently proposed to rationalize the formation of 4,5,1,6-$M_2C_2B_9$ species as minor coproducts in the synthesis of 8,1,2-MC_2B_9 compounds, namely loss of the degree-6 $\{BH\}^{2+}$ unit from a 4,1,8-MC_2B_{10} precursor and its replacement by a metal dication fragment.[10]

The structure of compound **6**, as representative of those of the major products **4**, **6**, and **8**, has two important features (Figure 4). Firstly, it is the original 13-vertex ruthenacarborane, and not the 12-vertex carborane, of **3** that has been expanded. Secondly, the 14-vertex diruthenacarborane, whilst structurally based on a bicapped hexagonal antiprism, does not have the anticipated 1,14,2,9-$Ru_2C_2B_{10}$ architecture. Rather it is 1,13,2,9-$Ru_2C_2B_{10}$ with the newly added Ru atom in the degree-5 vertex 13 and the C_2B_{10} substituent at C9. Thus, for example, compound **6** is formally [1-(η-mes)-9-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-13-(η-*p*-cymene)-1,13,2,9-*closo*-$Ru_2C_2B_{10}H_{11}$].

We have previously[4] rationalized the formation of 1,13,2,9-$M_2C_2B_{10}$ and related asymmetric 14-vertex dimetallacarboranes by direct electrophilic insertion (DEI)[11] of a cationic metal fragment into an effectively *closo* monoanionic metallacarborane cage, in contrast to formal two-electron reduction followed by metalation. Whilst reduction–metalation of 4,1,8-MC_2B_{10} leads to 1,14,2,9-$MM'C_2B_{10}$ species, DEI of 4,1,8-MC_2B_{10} affords a 1,13,2,9-$MM'C_2B_{10}$

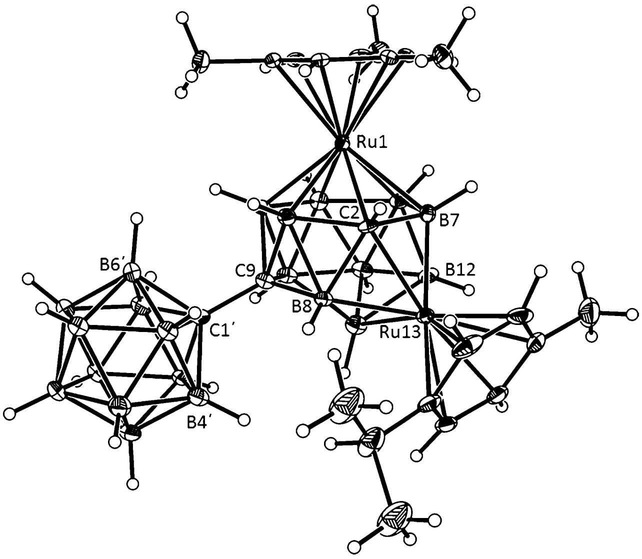

Figure 4. Structure of compound **6**. Ru1–C2 2.248(3), Ru1–B3 2.190(4), Ru1–B4 2.238(4), Ru1–B5 2.262(4), Ru1–B6 2.260(4), Ru1–B7 2.299(4), Ru1–arene 2.221(3)–2.308(3), Ru13–C2 2.188(3), Ru13–B7 2.226(4), Ru13–B12 2.153(4), Ru13–B14 2.222(4), Ru13–B8 2.105(4), Ru13–arene 2.238(4)–2.321(4), C9–C1′ 1.542(5) Å.

product. Thus we conclude that when two electrons are added to compound **3**, they are partitioned one to each cage and that the resulting species, a monoanionic RuC_2B_{10} cage linked to a monoanionic C_2B_{10} cage, reacts in this form with the incoming electrophilic metal cation to result in DEI. Since the predominant product from two-electron reduction of 4,1,8-MC_2B_{10} species with only H substituents followed by metalation is 1,14,2,9-$MM'C_2B_{10}$,[9c] we conclude that the electron-withdrawing carborane substituent in **3** is responsible for promoting DEI over classic reduction–metalation.

Although the di(mes) compound **8** is clearly asymmetric in the solid state, it is fluxional in solution at room temperature as we observe only one set of resonances for the mes ligands in the ^{1}H NMR spectrum (singlets at $\delta = 5.51$ ppm for $C_6\mathit{H}_3Me_3$ and $\delta = 2.13$ ppm for $C_6H_3\mathit{Me}_3$). Cooling the sample causes both resonances to decoalesce ($T_{\text{coalescence}} = 243$ K) and allows the activation energy for the fluxional process to be estimated as 50.8 kJ mol^{-1} (from the methyl signals) or 49.1 kJ mol^{-1} (aromatic signals).[12] This fluxionality is similar to that recently reported by us for the analogous species [1,13-Cp_2-1,13,2,9-*closo*-$Co_2C_2B_{10}H_{12}$] **I**. For this single-cage dicobaltacarborane, room-temperature NMR spectra suggested the onset of fluxionality,[4] and we have now performed a variable-temperature NMR study (see the Supporting Information). These experiments confirm a fluxional process where the two {CoCp} fragments are equivalent (by ^{1}H NMR spectroscopy)at high temperature, whilst maintaining inequivalent cage {CH} fragments. The activation energy for this process is estimated to be 55.3 kJ mol^{-1}. The ^{11}B NMR spectrum at high temperature appears as a 2:1:1:3:2:1 pattern of integrals from high frequency to low frequency, changing to a 1:1:1:1:1:1:1:2:1 pattern at low temperature.

Assuming that the resonance with an integration of three in the high-temperature ^{11}B NMR spectrum is a 2+1 coincidence, a mechanism for the fluxional process that fits the observed spectra is proposed in Figure 5. In this mechanism, the asymmetric 1,13,2,9-$M_2C_2B_{10}$ bicapped hexagonal antiprism is converted into a novel disk-shaped transition state (TS) with C_s symmetry by two diamond–square–diamond steps, breaking 9–14 and making 8–10, and breaking 2–8 and making 3–13. In the TS, the metal atoms are symmetry-related but the C atoms are symmetry-independent, and both C atoms are in favored degree-4 vertices.

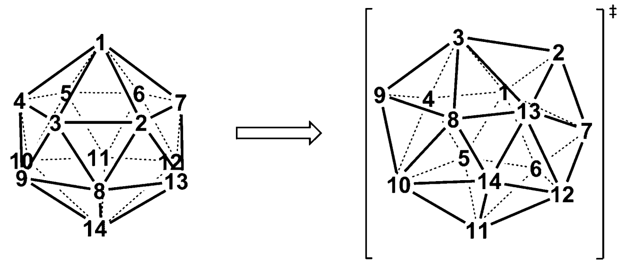

Figure 5. Suggested mechanism for conversion of a 1,13,2,9-$M_2C_2B_{10}$ bicapped hexagonal antiprism into a transition state with C_s symmetry (plane of paper).

Compound **I** is one of five similar asymmetric dicobaltacarboranes formed by DEI[4] but the only one that shows evidence of fluxionality in solution, so it is instructive to test the validity of our suggested fluxional mechanism on the other four compounds. In Table 1 we show whether each of these five compounds would have a C_s-symmetric transition state if the same mechanism was applied. The first column shows the 13-vertex precursor of the 14-vertex dicobaltacarborane. For the sake of completeness, in the second column there are two possibilities from three precursors since for 4,1,6-, 4,1,8-, and 4,1,12-MC_2B_{10} species the DEI could in principle be either "forwards" (metal inserting into the 1-2-9-11-5 pentagon) or "backwards" (metal inserting into 1-3-8-11-5), although not all possibilities have yet been isolated (shown in gray). Finally, in the third column, some of the products of the second column are renumbered to a common system in which the metal atoms are at vertices 1 and 13.

Table 1: The known (black text) and potential (gray text) isomers of $Cp_2Co_2C_2B_{10}H_{12}$ formed by DEI in the context of the isomerization mechanism shown in Figure 5.

Precursor	Product	Renumbered	C_s TS?	Fluxional?
4,1,6-	1,8,2,4-	1,13,3,7-	Yes	No; C3 degree-6
	1,13,2,4-	1,13,2,4-	No	No
4,1,8-	1,8,2,9-	1,13,7,8-	No	Not yet isolated
	1,13,2,9-	1,13,2,9-	Yes	Yes; C2, C9 degree-4
4,1,12-	1,8,2,10-	1,13,7,9-	Yes	Not yet isolated
	1,13,2,10-	1,13,2,10-	Yes	No; C10 degree-6
4,1,10-	1,8,2,5-	1,13,4,7	No	No

The 1,13,3,7- (1,8,2,4-) dicobaltacarborane would have a C_s-symmetric TS, but this involves one cage C atom, C3, in an unfavorable degree-6 vertex, so presumably the TS would have a relatively high energy. Thus the lack of fluxionality of this species in solution at room temperature is rationalized.

The nonfluxionality of the 1,13,2,10- isomer is similarly explained (C10 degree-6). The 1,13,2,4- and 1,13,4,7- (1,8,2,5-) species are also nonfluxional, which would be expected since in both cases the TS is asymmetric. For the same reason, the 1,13,7,8- (1,8,2,9-) isomer (not yet isolated) is predicted to be nonfluxional (note that the 1,13,4,7- TS and 1,13,7,8- TS are equivalent by symmetry). The remaining isomer not yet isolated, 1,13,7,9- (1,8,2,10-) might be expected to be fluxional at or near room temperature since the suggested mechanism predicts a C_s-symmetric TS in which C7 is degree-5 and C9 degree-4.

Finally we note that the experimentally estimated barrier for the fluxionality of the 1,13,2,9-$Co_2C_2B_{10}$ species **I** is about 5 kJ mol^{-1} higher than that estimated for the 1,13,2,9-$Ru_2C_2B_{10}$ species **3**. This result is fully consistent with the proposed mechanism for the fluxional process involving a TS in which the metal becomes more highly connected, since the more diffuse orbitals of a second-row metal are better suited to highly connected vertices. Similar observations have been made previously.[13]

In conclusion, we have shown that two-electron reduction of 1,1′-bis(*o*-carborane) followed by metalation with {Ru(mes)$^{2+}$} affords a 4,1,8-RuC_2B_{10} species with a carborane substituent. Upon further two-electron reduction, this substituent restricts the formal charge on the metallacarborane cluster to −1, thus promoting DEI on addition of a second metal fragment to lead to 1,13,2,9-$Ru_2C_2B_{10}$ species. The di(mes) species **8** is fluxional in solution at room temperature, and a mechanism is proposed that also rationalizes the fluxionality or lack of fluxionality in a series of $Cp_2Co_2C_2B_{10}H_{12}$ dicobaltacarboranes previously characterized. Future studies will be directed towards the isolation of the currently unknown 1,8,2,10-$Co_2C_2B_{10}$ isomer, predicted to be fluxional, and to a computational study of the proposed fluxional mechanism.

Acknowledgements

We thank the Engineering & Physical Sciences Research Council (EPSRC, project EP/I031545/1) for support. We also thank the EPSRC National Crystallographic Service at the University of Southampton for data collection from crystals of compound **4**.

Keywords: bis(carboranes) · fluxionality · metalation · metallacarboranes · two-electron reduction

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4596–4599
Angew. Chem. **2016**, *128*, 4672–4675

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Received: January 20, 2016