Icosahedral metallacarborane/carborane species derived from 1,1′-bis(o-carborane)†‡

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Examples of singly-metallated derivatives of 1,1′-bis(o-carborane) have been prepared and spectroscopically and structurally characterised. Metallation of [7-(1′,1′,2′-closo-C2B10H11)-7,8-nido-C2B4H10]2− with a (Ru(p-cymene))2+ fragment affords both the unisomerised species [1-(1′,1′,2′-closo-C2B10H11)-3-(p-cymene)-3,1,2-closo-RuC2B9H10] (2) and the isomerised [8-(1′,1′,2′-closo-C2B10H11)-2-(p-cymene)-2,1,8-closo-RuC2B9H10] (3), and 2 is easily transformed into 3 with mild heating. Metallation with a pre-formed (Co Cp)2+ fragment also affords a 3,1,2-MC2B9−1,2′-C2B10 product [1-(1′,1′,2′-closo-C2B9H11)-3-Cp,3,1,2-closo-CoC2B9H10] (4), but if CoCl2/NaCp is used followed by oxidation the result is the 2,1,8-CocC2B9-1′,2′-C2B10 species [8-(1′,1′,2′-closo-C2B10H11)-2-Cp,2,1,8-closo-CoC2B9H10] (5). Compound 4 does not convert into 5 in refluxing toluene, but does do so if it is reduced and then reoxidised, perhaps highlighting the importance of the basicity of the metal fragment in the isomerisation of metallacarboranes. A computational study of 1,1′-bis(o-carborane) is in excellent agreement with a recently-determined precise crystallographic study and establishes that the (1′,2′-closo-C2B10H11) fragment is electron-withdrawing compared to H.

Introduction

1,1′-Bis(o-carborane), the trivial name for [1-(1′,1′,2′-closo-C2B10H11)-1,2-closo-C2B10H11] (Fig. 1), is the simplest bis(carborane) species, comprising two ortho-carborane units connected by a C–C bond.1 It was first synthesised by insertion of diacetylene into B10 frameworks2 but it is also produced from the CuCl2-mediated coupling reactions of mono- or di-lithiated salts of ortho-carborane,3 although yields by this route are somewhat compromised by the additional formation of C–B and B–B linked isomers. CuCl2-coupling was also used to make 1,1′-bis(m-carborane)4 and 1,1′-bis(p-carborane),4,5 the latter an important starting point for the construction of “carborods”, rigid-rod oligomers of para-carborane. Ref. 5(a) also notes that 1,1′-bis(p-carborane) can be prepared by CuCl-coupling, an idea subsequently used by Xie to afford an improved yield of 1,1′-bis(o-carborane).6

Although 1,1′-bis(o-carborane) has been known for many years, its chemistry remains underdeveloped. Double deprotonation forms a dianionic chelating ligand which has been used to complex a variety of transition-metal cations7 and also an {AsMe} fragment.8 Mono- and di-deboronation (single and double “decapitation”, respectively) of 1,1′-bis(o-carborane) has also been reported.9 In addition, 1,1′-bis(o-carborane) has been reduced with both 2e and 4e.10 In solution, [PPh3Me]+ and [(15-crown-5)Na]+ salts of the 2e reduced species are identical, whilst in the solid state the anion of the [PPh3Me]+ salt has two partially-open 4-atom CBCB faces11 and the anion of the [(15-crown-5)Na]+ salt has one 4-atom CBCB face which is partially-open and one 5-atom CBCBB face which is rather more open.10 Double protonation of the 4e reduced form and subsequent work-up caused the linking C atoms to adopt bridging positions on B–B edges above nido 11-vertex
cages, in a similar manner to the protonation and work-up of $[7,9$-nido-C$_{2}$B$_{10}$H$_{12}]^{2-}$ affording $[\nu_{0,10}$-CH$_{2}$-$7$-nido-CB$_{10}$H$_{12}]^{+}$.

Prior to our recent research$^{15,14}$ the only metallacarboranes derived from bis(carboranes) of which we are aware are two 2,1,8-MC$_{2}$B$_{3}$-1',2'-C$_{2}$B$_{10}$ species$^{15,16}$ and two bis(metallacarboranes),$^{17}$ one of 3,1,2-MC$_{2}$B$_{3}$-3',1'-2'MC$_{2}$B$_{3}$ geometry and the other of 3,1,2-MC$_{2}$B$_{3}$-2',1',8'-MC$_{2}$B$_{3}$ geometry.$^{18}$

Recently we explored the consequences of 4e reduction and metallation of bis(o-carborane). Reduction and metallation with $\{Ru(p-cymene)\}^{2+}$ fragments ($p$-cymene = $\eta$_5-C$_{10}$H$_{14}$, $\eta$_1-Me$_2$MeC$_{6}$H$_{14}$) led unexpectedly to a 13-vertex metallacarborane-12/vertex carborane species and cleavage of an aromatic C-C bond under ambient conditions.$^{13}$ Reduction and metallation with $\{CoCp\}^{2+}$ fragments ($Cp = \eta$-1-iPr,4-MeC$_6$H$_4$) led unexpectedly to a 13-vertex metallacarborane species $[1-(1'4'5'-6'$-closo-CoC$_2$B$_{10}$H$_{11})_4]$-4-Cp.4,1,6-closo-CoC$_2$B$_{10}$H$_{11}$.$^{14}$

In this contribution we report the monodeboronation and subsequent metallation with $\{ML\}$ fragments ($L = \eta$-bonded polyene) of 1,1'-bis(o-carborane) leading to 12-vertex metallacarborane-12/vertex carborane products with both non-isomerised $[1-(1'4'5'-6'$-closo-CoC$_2$B$_{10}$H$_{11})_4]$-1,3-1,2-closo-MC$_2$B$_{10}$H$_{12}$ and isomerised $[8-(1'4'5'-6'$-closo-CoC$_2$B$_{10}$H$_{11})_4]$-2,1,2,1,8-closo-MC$_2$B$_{10}$H$_{12}$ architectures. We describe detailed spectroscopic and structural studies of these products and investigate the isomerisation between them.

### Results and Discussion

Monodeboronation of 1,1'-bis(o-carborane) with one equivalent of KOH in refluxing EtOH, according to the procedure outlined by Hawthorne et al.$^9$ followed by cation metathesis, afforded the anion $[7-(1'4'5'$-6'$-closo-CoC$_2$B$_{10}$H$_{12})_7]^{-}$ ($[1]^{-}$), as either the [HNMe$_3$]$^+$ or [BTMA]$^+$ salt (BTMA = benzyltrimethylammonium) in good yields. The $^1$H NMR spectrum of $[1]^{-}$ shows, in addition to the resonances associated with the appropriate cation, two CH$_{cage}$ resonances of equal integral at $\delta$ ca. 4.4 and 2.0 ppm. The former is assigned to the $\{close$-C$_{2}$B$_{10}\}$ component and the latter to the $\{nido$-C$_{2}$B$_{10}\}$ component with reference to the spectra of 1,1'-bis(o-carborane) and $[7,8$-nido-C$_{2}$B$_{10}$H$_{12}]^{2-}$.$^{19}$

The $^{11}$B($^1$H) NMR spectrum of $[1]^{-}$ consists of a 1 : 1 : 1 : 1 : 5 : 3 : 2 : 1 : 1 : 1 : 1 : 1 pattern between $\delta$ $-4$ and $-36$ ppm. A $^{11}$B($^1$H)$_{11}$/$^1$H($^1$H) COSY spectrum of [HNMe$_3$]$[1]$ in CD$_3$CO was obtained in an attempt to assign these resonances to $\{close$-C$_{2}$B$_{10}\}$ or $\{nido$-C$_{2}$B$_{10}\}$ components. By analogy with the spectra of $[7,8$-nido-C$_{2}$B$_{10}$H$_{12}]^{-}$ and 1,2-closo-C$_{2}$B$_{10}$H$_{12}$,$^{20}$ it seems reasonable to suggest that the two highest frequency resonances are due to the $\{close$-C$_{2}$B$_{10}\}$ cage and the four lowest frequency resonances are due to the $\{nido$-C$_{2}$B$_{10}\}$ cage, but beyond this it was not possible to deconvolute the entire spectrum of $[1]^{-}$ unambiguously.

The salt [HNMe$_3$]$[1]$ is a convenient starting point for the synthesis of MC$_2$B$_{3}$C$_2$B$_{10}$ products by deprotonation then metallation, following the protocol established for the first metallacarborane by Hawthorne et al.$^{21}$

Following deprotonation of [HNMe$_3$]$[1]$ with n-BuLi in THF and addition of [RuCl$_3$(p-cymene)]$_2$, yellow $[1-(1'4'5'-6'$-closo-CoC$_2$B$_{10}$H$_{11})_3]$-3-(p-cymene)-3,1,2-closo-RuC$_2$B$_{10}$H$_{10}$ (2) and colourless $[8-(1'4'5'$-6'$-closo-CoC$_2$B$_{10}$H$_{11})_4]$-2-(p-cymene)-2,1,8-closo-RuC$_2$B$_{10}$H$_{10}$ (3) were isolated in yields of 8 and 19%, respectively. Both compounds were initially characterised by elemental microanalysis and EI mass spectrometry, the latter clearly showing the molecular ion peaks as a characteristic envelope due to the two naturally-occurring boron isotopes.

In the $^1$H spectrum of a freshly-prepared CDCl$_3$ solution of 2 are CH$_{cage}$ resonances at $\delta$ 4.03 and 3.91 but these are too close to each other to speculate which is due to the carborane and which is due to the ruthenacarborane. The $^1$H NMR spectrum of 2 also confirms overall molecular asymmetry with two integral-3 doublets (and not one integral-6 doublet) for the CH$_2$CF$_3$ protons of the p-cymene ligand. The $^{11}$B($^1$H) NMR spectrum of 2 consists of ten resonances between $\delta$ 2.8 and $-17.2$ with relative integrals 1 : 1 : 2 : 1 : 2 : 4 : 2 : 1 : 3 from high frequency to low frequency.

With time, solutions of 2 show clear evidence for a slow transformation of 2 into an isomer 3, a compound which was originally isolated along with 2 from the initial reaction. A THF solution of 2 heated to reflux for two hours reveals its complete conversion to 3, with 58% of the compound being recovered following work-up involving thin layer chromatography (TLC). In 3 there is a significantly greater separation of the CH$_{cage}$ resonances, which now appear at $\delta$ 3.64 and 2.63. Since only the ruthenacarborane part of 2 has changed in its isomerisation into 3 we tentatively assign the lower frequency resonance, $\delta$ 2.63, as arising from CH$_{cage}$ in the {RuC$_2$B$_{10}$}$_2$ portion of 3. Once again the resonances due to the p-cymene ligand reveal the overall molecular structure to be asymmetric. In the $^{11}$B($^1$H) NMR spectrum of 3 are ten resonances between $\delta$ $-1.0$ and $-20.4$ with integrals in the relative ratios 2 : 2 : 1 : 2 : 1 : 6 : 2 : 1 : 1 : 1.

In addition to $\{Ru(arene)\}^{2+}$ a common transition-metal fragment in metallacarborane chemistry is $\{CoCp\}$. There are two different ways to introduce this fragment to a CPoCo$_2$B$_{5}$ metallacarborane, (i) reaction of the [C$_2$B$_{10}$]$_2$-dianion with CoCl$_2$/NaCp (i.e. in situ generation of the $\{CoCp\}$ fragment) followed by oxidation (Co$^{II}$ $\rightarrow$ Co$^{III}$)$^{23}$ or (ii) reaction of the [C$_2$B$_{10}$]$_2$-dianion with [Co(CO)$_3$]$_2$ (i.e. using a ‘preformed’ $\{CoCp\}$ fragment).$^{24}$ In reaction with [C$_2$B$_{10}$H$_{11}]_2$ both approaches lead to exactly the same product, but we have found that this is not the case starting from $[1]^{-}$.

Deprotonation of [HNMe$_3$]$[1]$ followed by addition of [CpCo(CO)$_3$]$_2$ affords, on work-up, the isomer $[1-(1'4'$-closo-C$_{2}$B$_{10}$H$_{11})_3]$-3-Cp,3,1,2-closo-CoC$_2$B$_{10}$H$_{10}$ (4) as an orange solid. Microanalysis and mass spectrometry confirm the molecular formula. In the $^1$H NMR spectrum are three singlets at $\delta$ 5.86 (5H, Cp), 4.24 (1H) and 4.03 (1H), the last two relatively broad and arising from the cage CH atoms. In the $^{11}$B NMR spectrum are nine resonances in a 1 : 1 : 5 : 1 : 2 : 5 : 2 : 1 : 1 pattern, lying between $\delta$ 6.5 and $-15.9$ ppm.
To our surprise, treatment of deprotonated [HNMe₃]⁺ with CoCl₂/NaCp followed by aerial oxidation yielded an isomer of 4, the 2,1,8-1′,2′ species [8-[1′-1′,2′-closo-C₂B₉H₁₀]-2-Cp-2,1,8-closo-CoC₂B₉H₁₁] (5). This yellow product has, as well as the expected singlet for the Cp protons, cage CH resonances at lower frequency than in 4, δ 3.59 and 2.73. In 4 the {CoC₂B₉} part of the molecule has a 3,1,2-CoC₂ heteroatom pattern whilst in 5 it is 2,1,8-CoC₂. In the corresponding reference compound [3-Cp-3,1,2-closo-CoC₂B₉H₁₁] the cage CH atoms resonate at δ 4.08 (CDCl₃) and in [2-Cp-2,1,8-closo-CoC₂B₉H₁₁] they resonate at δ 2.73 and 2.47, in 5 on the basis of which we tentatively assign the signal at δ 2.73 in 5 to the {2,1,8-CoC₂B₉} fragment. The ¹¹B NMR spectrum of 5 reveals eleven resonances between δ 1.7 and −17.7 in a 1:2:1:1:1:2:6:1:2:1:1 pattern of integrals. Note that in the synthesis of 4 a trace amount of 5 is also detected (see Experimental) and that in the synthesis of 5 a trace amount of 4 is observed.

Given that the 3,1,2-RuC₂B₉-1′,2′-C₂B₁₀ species 2 easily transforms to its isomer 2,1,8-RuC₂B₉-1′,2′-C₂B₁₀, 3 on heating to reflux in THF to thermally isomerise the 3,1,2-CoC₂B₉-1′,2′-C₂B₁₀ species 4, expecting it to convert into 2,1,8-CoC₂B₉-1′,2′-C₂B₁₀ 5. However, even in refluxing toluene for five hours there is no evidence that 4 converts into 5 by thermolysis. We later show from crystallographic studies that, at least as far as we can tell, compounds 2 and 4 suffer similar degrees of intramolecular steric crowding, implying that the different isomerisation characteristics of 2 and 4 cannot be explained by steric factors.

When [1]⁻ is treated with [CpCo(CO)₂]Cl a [Co⁴⁺Cl]²⁺ fragment is introduced to the dianion, affording the non-isomerised 4. However, when [1]⁻ is treated with CoCl₂/NaCp the reacting fragment is [Co⁵⁺Cl]⁻. This generates the 19e monoanion [CpCo⁴⁺[C₂B₁₀H₁₀]⁻[C₂B₉H₁₁]]⁻, which is then oxidised to the 18e, isomerised, Co⁴⁺ species 5. We therefore added one equivalent of electrons to 4 at room temperature and, after stirring for one hour, oxidised the product aerily. Only 5 was detected by ¹H and ¹¹B NMR spectroscopies. This strongly implies that in the bulk synthesis of 5, a [3,1,2-CoC₂B₉-1′,2′-C₂B₁₀]⁻⁻ species is formed first (as would be expected from the reaction between a [CoC₃]³⁺ cation and a [7,8-C₂B₁₀-1′,2′-C₂B₁₀]⁻⁻ anion) and that this 19e anionic intermediate then isomerises before it is oxidised. Taken together with the facile isomerisation of the 3,1,2-RuC₂B₉-1′,2′-C₂B₁₀ p-cymene species 2 these observations highlight that the basicity of the metal fragment, and not just its steric bulk, might be important in effecting a 3,1,2-MC₂B₉ to 2,1,8-MC₂B₉ isomerisation.

For compounds 2, 4 and 5 we attempted to identify which ¹¹B resonances were due to which part of the molecule (MC₂B₉) or (C₂B₁₀) from ¹¹B{¹H}-¹¹B{¹H} COSY spectra but, as was the case with [1]⁻, it proved impossible to do this unambiguously. In Table 1 we list the weighted average ¹¹B chemical shifts, <δ(¹¹B)>, of the conjoined species 1,1′-bis(o-carborane), 2, 4 and 5 along with those of their “components”, [1,2-closo-C₂B₉H₁₀], [3-p-cymene]-3,1,2-closo-RuC₂B₉H₁₁, [3-Cp-3,1,2-closo-CoC₂B₉H₁₁] and [2-Cp-2,1,8-closo-CoC₂B₉H₁₁] . Although the spectra of 1,1′-bis(o-carborane), 1,2-closo-RuC₂B₉H₁₁, 3-[p-cymene]-3,1,2-closo-RuC₂B₉H₁₁, 3-Cp-3,1,2-closo-CoC₂B₉H₁₁ and 2-Cp-2,1,8-closo-CoC₂B₉H₁₁ individual ¹¹B chemical shifts are given in Table S1 (ESI).

| Compound | <δ(¹¹B)> |
|----------|---------|
| 1,1′-bis(o-carborane) | 7.7 |
| 1,2-closo-RuC₂B₉H₁₁ | 10.5 |
| 3-[p-cymene]-3,1,2-closo-RuC₂B₉H₁₁ | 7.3 |
| 3-Cp-3,1,2-closo-CoC₂B₉H₁₁ | 7.7 |
| 2-Cp-2,1,8-closo-CoC₂B₉H₁₁ | 7.7 |

For 1,1′-bis(o-carborane), 1,2-closo-RuC₂B₉H₁₁, 3-[p-cymene]-3,1,2-closo-RuC₂B₉H₁₁, 3-Cp-3,1,2-closo-CoC₂B₉H₁₁ and 2-Cp-2,1,8-closo-CoC₂B₉H₁₁ individual ¹¹B chemical shifts are given in Table S1 (ESI).

These data show that when 1,1′-bis(o-carborane) and the metallacarborane-carborane species 2, 4 and 5 are “constructed” from their constituent parts the <δ(¹¹B)> value for the “product” lies to high frequency of the (weighted) average of that of the two “components”. For 5 the <δ(¹¹B)> value is very close (and slightly to low frequency of) that for the metallacarborane component, whilst for 1,1′-bis(o-carborane), 2 and 4 the <δ(¹¹B)> value is actually to high frequency of that of both components.

A shift to higher frequency of the average ¹¹B resonance implies, overall, that the B nuclei in these last two conjoined cages are deshielded, and therefore δ₊, relative to those in the individual components. A comparative computational study [1,2-closo-C₂B₁₀H₁₂] and 1,1′-bis(o-carborane) supports this conclusion. By DFT calculation we find effectively no preference in 1,1′-bis(o-carborane) between conformations with C₂-C₁-C₁′-C₂′ torsion angles of 108° and 180° (Fig. 2). In terms
of only the electronic energy the 108° conformation is favoured by 0.2 kcal mol⁻¹, whereas if zero point energy is included the 180° conformation is preferred by 0.5 kcal mol⁻¹. The barrier to free rotation about the C1–C1’ bond is only ca. 10 kcal mol⁻¹, corresponding to a transition state at a C2–C1–C1’–C2’ torsion angle of 0°. Computational models are listed in the ESI.‡ It is very satisfying to note that our recent definitive crystallographic study of 1,1′-bis(ο-carborane) found that the non-linking C atom is equally disordered between vertices 2 and 3 (and, by symmetry, 2′ and 3′). This means that in the crystal any one molecule of 1,1′-bis(ο-carborane) is equally likely to have a C–C–C–C torsion angle of 180° (C2–C1–C1′–C2′) or 108° (C3–C1–C1′–C2′), in perfect agreement with the results of the DFT study. The computed C1–C1’ distance in the 180° conformation is 1.542 Å, and in the 108° conformation it is 1.540 Å. Experimentally C1–C1’ is 1.5339(11) Å.¹

In Table 2 we list the natural charges for atoms in [1,2-closo-C₈B₉H₁₂] and 1,1′-bis(ο-carborane), the latter in the 180° conformation. In [1,2-closo-C₈B₉H₁₂] the C atoms carry a charge of −0.56 and the B atoms an average charge of −0.06. H bonded to C is +0.36 whilst the average charge of H bonded to B is +0.10. In 1,1′-bis(ο-carborane) the negative charge on both C atoms decreases (C1, the substituted atom, −0.31; C2, −0.51) and the B atoms are also less negative (average charge −0.04). The remaining C-bonded H atom carries a charge of +0.32 and the average charge on H bound to B is +0.09. Thus substitution of one of the C-bound H atoms in [1,2-closo-C₈B₉H₁₂] by a {1′,2′-closo-C₈B₉H₁₁} unit causes all the polyhedral atoms (both C and B) in the original cage to become less negatively charged. At the same time there is an opposite, but smaller, change in the charges on the H atoms bonded to the polyhedral atoms, which become slightly less positively charged. The overall charge on the {C₂B₁₀H₁₁} fragment changes from −1.06 in [1,2-closo-C₈B₉H₁₂] to precisely zero in 1,1′-bis(ο-carborane).² Seven in brief the {1′,2′-closo-C₈B₉H₁₁} substituent is electron-withdrawing compared to H. This conclusion is consistent with our analysis of the <δ¹(B)> values for 1,1′-bis(ο-carborane) and for 2.

Salt [BTMA][I] and compounds 2–5 were also studied crystallographically. In [BTMA][I] (Fig. 3) the C₂B₁₀ cage is ordered but the C₂B₉ cage is disordered with positions 3 and 12 partially occupied by boron. The second C atom of the nido cage is ordered, however, and the C₈–C₇–C1–C2’ torsion angle is 177.2(6)°. The linking C7–C1’ bond length is 1.514(9) Å.

Perspective views of single molecules of the 3,1,2-RuC₂B₅–1′,2′-C₈B₁₀ species 2, its 2,1,8-RuC₂B₅–1′,2′-C₈B₁₀ analogue 3, and the equivalent cobalt species 4 and 5 are presented in
Since compounds 2, 4 and 5 are composed of \(\{3,1,2\text{-closo-RuC}_2B_9\}\) (compound 2), \(\{3,1,2\text{-closo-CoC}_2B_9\}\) (compound 4) and \(\{2,1,8\text{-closo-CoC}_2B_9\}\) (compound 5) icosahedra conjoined to \(\{1,2\text{-closo-C}_2B_{10}\}\) icosahedra, and all these individual components have previously been studied crystallographically, we have used the Structure Overlay tool in Mercury\textsuperscript{28} to calculate individual atom and overall fragment root-mean-square (rms) misfits between the components of 2, 4 and 5 and the corresponding literature molecules (there is currently no structural study of a 2-(arene)-2,1,8\text{-closo-RuC}_2B_9H_{11} species in the literature and so a similar exercise cannot be undertaken for compound 3). The results, summarised in Table 3, clearly show that for the \(\{3,1,2\text{-MC}_2B_9\}\) fragments the greatest misfit is at the metal vertex, ca. 0.08–0.09 Å, and that the misfit at C1 (the position of substitution) is also relatively large, ca. 0.06–0.08 Å. The overall misfit for \(\{3,1,2\text{-MC}_2B_9\}\) is typically 0.038–0.040 Å. In contrast the misfit for the \(\{2,1,8\text{-MC}_2B_9\}\) fragment is considerably less with an overall misfit of only 0.012 Å, the greatest individual misfit, 0.025 Å, occurring at C8 (the position of substitution) and no other
atom having a misfit >0.018 Å. The \{C_{2}B_{9}\} fragments fit better with their reference molecule, the overall misfit here being 0.02–0.03 Å, and it is always C1’ or C2’ that has the largest individual misfit, typically 0.05–0.06 Å.

It is clear from Fig. 4 and 6 that a consistent feature of the 3,1,2-MC_{2}B_{9}−1’,2’-C_{2}B_{10} structures is a pronounced bend-back of the arenic or Cp ligand in a direction away from the C_{2}B_{10} substituent on C1. This structural feature is undoubtedly the result of intramolecular steric crowding, which also likely contributes to the relatively large misfit values of the metal atoms in 2 and 4. The ligand bend-back is conveniently quantified by \( \theta \), the dihedral angle between the plane of the ligand C atoms (arenic or Cp) and the plane defined by B5B6B11B12B9 (the lower pentagonal belt usually taken as the reference plane in 3,1,2-MC_{2}B_{9} icosahedra).\(^{29}\) For 2 \( \theta \) is 16.08(9)° whilst for 4 \( \theta \) is 15.83(8)° (molecule A−B) and 16.34(8)° (molecule C−D; in 4 there are two crystallographically-independent molecules A−B and C−D where the first letter refers to the CoC_{2}B_{9} cage and second letter to the C_{2}B_{10} cage). C1−C1’ distances in 2 and 4 are 1.545(3), 1.549(2) (A−B) and 1.550(2) Å (C−D), respectively. All these are significantly longer that the C1−C1’ distance in 1,1’-bis(o-carborane), 1.5339(11) Å,\(^{1}\) again a reflection of the steric crowding in 2 and 4.

In the 2,1,8-MC_{2}B_{9}−1’,2’-C_{2}B_{10} compounds 3 and 5 significant intramolecular steric crowding is removed since the C_{2}B_{10} substituent to the MC_{2}B_{9} cage is now at position 8 and so not adjacent to the metal atom. Consequently the arenic or Cp ring plane lies effectively parallel to the lower pentagonal belt, now the C8B4B5B10B12 plane \([ \theta \text{ is only 0.27(5)}° \text{ in 3 and 2.19(7)}° \text{ in 5} \text{]}\) and the C8−C1’ distances are 1.5294(17) and 1.5329(16) Å, respectively, slightly shorter than or identical to the intercage C–C distance in 1,1’-bis(o-carborane).\(^{1}\)

The gross similarities between the structures of 2 and 4 (similar ligand bend-back angles, similar C−C1’ distances) imply that, to a first approximation, they are equally sterically crowded. However, whilst 2 is relatively easily isomerised to 3 by gentle heating, even prolonged heating to reflux of 4 in toluene does not convert it into 5; rather 4 has to be reduced to the anion \([4^-]\) which then isomerises (presumably to \([5^-]\)) at room temperature, affording 5 on aerial oxidation. This reduction-induced isomerisation of metallacarboranes has preceded in the literature.\(^{30}\) Thus, as already been noted, it appears that the basicity of the metal fragment, and not simply the steric crowding it affords, is important in determining the ease of 3,1,2-MC_{2}B_{9} to 2,1,8-MC_{2}B_{9} isomerisation in these species. Given that it is generally accepted that cobaltacarboranes are more susceptible to isomerisation than ruthenacarboranes, at least for 13-vertex species,\(^{31}\) this is an interesting observation and one that we will address more fully in future contributions.\(^{32}\)

### Conclusions

Examples of 12-vertex metallacarborane/carborane compounds, MC_{2}B_{9}−C_{2}B_{10}, derived from single deboronation and
then metallation of 1,1'-bis(o-carboline), have been prepared and characterised. Both non-isomerised 3,1,2-MC3B10H11,1,2'-C2B10H11 and isomerised 2,1,8-MC3B10H11,2'-C2B10H11 isomers have been isolated. For M = [Ru(p-cymene)] the isomerisation of the former to the latter is effected by gentle heating. In contrast, the non-isomerised form with M = {CoCp} does not isomerise in refluxing toluene but readily isomerises as the result of 1e reduction followed by reoxidation.

Experimental Synthesis

Experiments were performed under dry, oxygen free N2, using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. All solvents were freshly distilled under nitrogen from the appropriate drying agents immediately before use (CH2Cl2 [DCM], CaH2: THF and 40–60 petroleum ether; sodium wire) or were stored over 4 Å molecular sieves and were degassed (3 x freeze–pump–thaw cycles) before use. Preparative TLC employed 20 x 20 cm Kieselgel F254 glass plates. NMR spectra at 400.1 MHz (1H) or 128.4 MHz (13B) were recorded on a Bruker DRX-400 spectrometer from CDCl3 or (CD3)2CO solutions at room temperature. Electron impact mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. Elemental analyses were conducted using an Exeter CE-440 elemental analyser at Heriot-Watt University. The starting materials 1,1'-bis(o-carboline), [Ru(p-cymene)Cl3], [Ru[η-C5H5]Cl]34 and CpCo(CO)235 were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially.

[HNMMe][7-(1’-1’,2’-closo-C3B10H11)-7,8-nido-C2B10H11] [HNMMe][1] and [BTM][7-(1’-1’,2’-closo-C3B10H11)-7,8-nido-C2B10H11] [BTM][1]. 1,1'-bis(o-carboline (0.50 g, 1.75 mmol) and KOH (0.09 g, 1.75 mmol) were heated in reflux in EtOH (30 mL) for 4 h. The solution was allowed to cool and the solvent removed to give a white oily residue. Distilled water (20 mL) was added, and the suspension filtered to give a slightly cloudy solution. To this was added an aqueous solution of either [HNMMe][Cl] (0.17 g, 1.8 mmol) or [BTM][Cl] (0.32 g, 1.8 mmol) resulting in the immediate precipitation of [HNMMe][7-(1’-1’,2’-closo-C3B10H11)-7,8-nido-C2B10H11] [HNMMe][1] or [BTM][7-(1’-1’,2’-closo-C3B10H11)-7,8-nido-C2B10H11] [BTM][1] as white solids. These were isolated by filtration, washed with H2O (3 x 20 mL) and dried in vacuo.

[HNMMe][1]: Yield 0.37 g, 64%. C14H32B19N requires C 32.5, H 9.6. Found for [HNMMe][1]: C 24.7, H 9.71, N 4.04%.

11B NMR [(CD3)2CO], δ 22.7 (1B), −22.8 (1B), −33.2 (1B), −35.5 (1B). 1H NMR [(CD3)2CO], δ 7.75–7.45 (m, 5H, C5H5), 4.75 (s, 2H, CH2), 4.35 (s, 1H, CHage), 3.35 (s, 9H, N(CH3)3), 1.95 (s, 1H, CHage).

[BTM][1]: Yield 0.55 g, 74%. C14H32B19N requires C 39.5, H 8.99, N 3.29. Found for [BTM][1]: C 41.5, H 9.15, N 3.25%.

11B NMR [(CD3)2CO], δ 22.7 (1B), −22.8 (1B), −33.2 (1B), −35.5 (1B).

Thermal isomerisation of 2. Compound 2 (0.024 g, 0.05 mmol) was dissolved in THF (20 mL) and the solution heated at reflux for 2 h. The solvent was removed and the product purified by preparative TLC using an eluent system of DCM–petroleum ether, 30:70, to afford a colourless band at Rf = 0.51 identified as 3 (0.014 g, 59%) by 1H and 11B NMR spectroscopies.

[1-(1’-1’,2’-closo-C3B10H11)-3-Cp,1,2-closo-CoC5B6H14] [4]. [HNMMe][1] (0.25 g, 0.74 mmol) was deprotonated with n-BuLi (0.60 mL of 2.5 M solution, 1.48 mmol) as above then frozen at −196 °C. To this was addedCoCo(CO)5 (0.30 g, 0.74 mmol) and the reaction mixture was allowed to warm to room temperature and stirred overnight. Following spot TLC* (DCM–petroleum ether, 30:70, Rf = 0.28) purification by column chromatography using the same eluent gave, on removal of solvent, an orange powder (0.038 g, 13%), subsequently identified as [1-(1’-1’,2’-closo-C3B10H11)-3-Cp,1,2-closo-CoC5B6H14] (4). C14H32B19Co requires C 27.1, H 6.57. Found for 4: C 26.5, H 6.67. 11B NMR [(CD3)2CO], δ 6.5 (1B), 2.5 (1B), −2.6 (5B), −4.4 (1B), −8.0 (2B), −9.7 (5B), −12.3 (2B), −14.2 (1B), −15.9 (1B). 1H
NMR [CDCl$_3$], $\delta$ 5.86 (s, 5H, C$_2$H$_5$), 4.24 (s, 1H, CH$_{cage}$), 4.03 (s, 1H, CH$_{cage}$). EIMS: envelope centred on $m/z$ 399 (M$^+$).

A trace amount of a yellow spot ($R_t = 0.34$) identified as [8-(1',2'-closo-C$_{2}B_{10}H_{11})-2$-Cp-2,1,8-closo-CoC$_{2}$B$_{10}H_{10}$] (5) was also observed and its identity confirmed via $^1$H NMR spectroscopy.

[8-(1',2'-closo-C$_{2}$B$_{10}H$_{11})-2$-Cp-2,1,8-closo-CoC$_{2}$B$_{10}$H$_{10}$] (5).

A trace amount of an orange spot ($R_t = 0.60$) identified as 4 was also observed and its identity confirmed via $^1$H NMR spectroscopy.

Attempted thermal isomerisation of 4. Compound 4 (0.038 g, 0.10 mmol) was dissolved in toluene (20 mL) and the solution heated at reflux for 5 h. The solvent was removed and the crude residue was submitted for $^1$H and $^{11}$B NMR spectroscopies, however there was no evidence that 4 had converted to 5. Preparative TLC using an eluent of DCM–petroleum ether, 30:70, led to the recovery of 4 (0.020 g, 53%).

Redox isomerisation of 4. To a solution of 4 (0.012 g, 0.030 mmol) in dry degassed THF (10 mL) was added a solution of sodium naphthalenide (1 mL of a 0.031 M solution in THF, 0.031 mmol). The reaction was allowed to stir under nitrogen for 1 h, oxidised using a water aspirator for 30 min, and solvent was removed in vacuo. Only compound 5 was identified by $^1$H and $^{11}$B NMR spectroscopies.

Crystallography

Diffraction-quality crystals of salt [BTMA][I] and compounds 2, 3, 4 and 5 were obtained by slow diffusion of a CH$_2$Cl$_2$ solution of the appropriate species and 40–60% petroleum ether at $-30$ °C. Intensity data for all except 4 were collected on a Bruker X8 APEXII diffractometer using Mo-K$_\alpha$ X-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Compound 4 afforded crystals too small for our in-house system and consequently data were collected at the National Crystallographic Service at the University of Southampton at 100 K on a Rigaku AFC12 diffractometer operating with Mo-K$_\alpha$ X-radiation. Indexing, data collection and absorption correction were performed using the APEXII suite of programs. Structures were solved by direct methods (SHELXS$^{37}$ or OLEX2$^{38}$) and refined by full-matrix least-squares (SHELXL$^{37}$).

A trace amount of a yellow spot ($R_t = 0.34$) identified as 4 was also observed and its identity confirmed via $^1$H NMR spectroscopy.

Table 4 Crystallographic data

| [BTMA][I] | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| Formula | C$_{23}$H$_{35}$B$_{19}$N | C$_{23}$H$_{35}$B$_{19}$Ru | C$_{23}$H$_{35}$B$_{19}$Co | C$_{23}$H$_{35}$B$_{19}$Co |
| $M$ | 425.84 | 509.88 | 509.88 | 398.62 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ | $P1$ |
| $a/\AA$ | 18.851(9) | 11.5653(7) | 10.9051(9) | 89.609(3) |
| $b/\AA$ | 10.002(4) | 15.1116(10) | 16.9528(14) | 85.554(3) |
| $c/\AA$ | 13.477(6) | 14.1229(9) | 13.8437(11) | 89.158(3) |
| $\alpha(\degree)$ | 90 | 90 | 90 | 90 |
| $\beta(\degree)$ | 97.068(13) | 91.611(4) | 105.039(4) | 85.554(3) |
| $\gamma(\degree)$ | 90 | 90 | 90 | 90 |
| $U/\AA^3$ | 2540(2) | 2467.2(3) | 2471.7(4) | 1994.3(2) |
| $Z$, $\rho(000)$ | 4 | 4 | 4 | 4 |
| $/\AA^{-3}$ | 4,1 | 4,1 | 4,1 | 4,1 |
| $D_{calc}/\text{Mg}^\text{m}^{-3}$ | 0.896 | 1.032 | 1.032 | 1.032 |
| $\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$ | 0.052 | 0.640 | 0.639 | 0.853 |
| $\theta_{max}(\degree)$ | 20.84 | 27.47 | 33.53 | 27.48 |
| Data measured | 14 879 | 34 686 | 52 456 | 26 471 |
| Unique data, $n$ | 2651 | 5604 | 9614 | 39102 |
| $R_{int}$ | 0.2172 | 0.0431 | 0.0388 | 0.0378 |
| $R$, Wyf (obs. data) | 0.0867, 0.1912 | 0.0309, 0.0689 | 0.0288, 0.0639 | 0.0334, 0.0821 |
| Variables | 308 | 373 | 374 | 649 |
| $E_{max}, E_{min}/e\text{ \AA}^{-3}$ | 0.27, -0.26 | 0.68, -0.71 | 0.96, -1.37 | 0.66, -0.34 |

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The anion in [BTMA][1] is partially disordered. The C2B10 cage is fully ordered but the C6B9 cage has one B atom disordered between two sites, B3 and B12, with SOFs 0.548(10) and 0.452(10) respectively. Atoms B3 and B12 were refined with an isotropic thermal parameter fixed at 0.03 Å2. There is also partial disorder in the H atoms were constrained to Cphenyl

Calculations

All geometries were optimised without constraints using Gaussian 03, Revision D.0141 employing the B3P86 functional42 and 6-31G** basis sets for B, C and H atoms.43 Analytical frequency calculations were used to confirm geometries as minima or transition states. The transition state was further characterised through IRC calculations.44

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Since 1,1′-bis(o-carborane) is neutral overall and symmetric about the C1–C1′ mid-point, the two halves individually must be neutral.