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5628Icosahedral metallocarborane/carborane species
derived from 1,1'-bis(*o*-carborane) \ddagger Gobika Thiripuranathar, Wing Y. Man, Cesar Palmero, Antony P. Y. Chan,
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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*-C₂B₉H₁₀]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 {CoCp}²⁺ fragment also affords a 3,1,2-MC₂B₉-1',2'-C₂B₁₀ product [1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-3-Cp-3,1,2-*closo*-CoC₂B₉H₁₀] (**4**), but if CoCl₂/NaCp is used followed by oxidation the result is the 2,1,8-CoC₂B₉-1',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 metallocarboranes. 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.

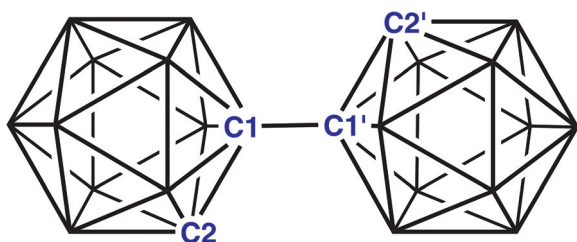
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Introduction

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

Fig. 1 1,1'-bis(*o*-carborane).

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‡ Electronic supplementary information (ESI) available: Table S1; ¹¹B NMR chemical shifts for key reference compounds. Tables S2–S5; computational models. CCDC 1042151–1042155 (salt [BTMA][1] and compounds 2–5, respectively). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00081e

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)^{3,4} 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)₃Na₂]²⁺ 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)₃Na₂]²⁺ 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 $[7,9\text{-nido-C}_2\text{B}_{10}\text{H}_{12}]^{2-}$ affording $[\mu_{9,10}\text{-CH}_2\text{-7-nido-CB}_{10}\text{H}_{11}]^{-}$.¹²

Prior to our recent research^{13,14} the only metallacarboranes derived from bis(carboranes) of which we are aware are two 2,1,8-MC₂B₉-1',2'-C₂B₁₀ species^{15,16} and two bis(metallacarboranes),¹⁷ one of 3,1,2-MC₂B₉-3',1',2'-MC₂B₉ geometry and the other of 3,1,2-MC₂B₉-2',1',8'-MC₂B₉ geometry.¹⁸

Recently we explored the consequences of 4e reduction and metallation of bis(*o*-carborane). Reduction and metallation with $\{\text{Ru}(p\text{-cymene})\}^{2+}$ fragments (*p*-cymene = $\eta\text{-C}_{10}\text{H}_{14}$, 1-ⁱPr,4-MeC₆H₄) 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 $\{\text{CoCp}\}^{2+}$ fragments (Cp = $\eta\text{-C}_5\text{H}_5$) afforded racemic and meso diastereoisomers of the 13-vertex metallacarborane/13-vertex metallacarborane species $[1\text{-}(1'\text{-}4'\text{-Cp-}4',1',6'\text{-}closo\text{-CoC}_2\text{B}_{10}\text{H}_{11})\text{-}4\text{-Cp-}4,1,6\text{-}closo\text{-CoC}_2\text{B}_{10}\text{H}_{11}]$.¹⁴

In this contribution we report the monodeboronation and subsequent metallation with $\{\text{ML}\}$ fragments (L = η -bonded polyene) of 1,1'-bis(*o*-carborane) leading to 12-vertex metallacarborane/12-vertex carborane products with both non-isomerised $[1\text{-}(1'\text{-}1',2'\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})\text{-}3\text{-L-}3,1,2\text{-}closo\text{-MC}_2\text{B}_9\text{H}_{10}]$ and isomerised $[8\text{-}(1'\text{-}1',2'\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})\text{-}2\text{-L-}2,1,8\text{-}closo\text{-MC}_2\text{B}_9\text{H}_{10}]$ 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 $[7\text{-}(1'\text{-}1',2'\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})\text{-}7,8\text{-nido}\text{-C}_2\text{B}_9\text{H}_{11}]^{-}$ (**[1]⁻**), as either the $[\text{HNMe}_3]^+$ or $[\text{BTMA}]^+$ salt (BTMA = benzyltrimethylammonium) in good yields. The ¹H NMR spectrum of **[1]⁻** shows, in addition to the resonances associated with the appropriate cation, two CH_{cage} resonances of equal integral at δ ca. 4.4 and 2.0 ppm. The former is assigned to the $\{closo\text{-C}_2\text{B}_{10}\}$ component and the latter to the $\{nido\text{-C}_2\text{B}_9\}$ component with reference to the spectra of 1,1'-bis(*o*-carborane) and $[7,8\text{-nido}\text{-C}_2\text{B}_9\text{H}_{12}]^{-}$.¹⁹

The ¹¹B{¹H} NMR spectrum of **[1]⁻** consists of a 1:1:1:5:2:3:2:1:1:1:1 pattern between δ -4 and -36 ppm. A ¹¹B{¹H}-¹¹B{¹H} COSY spectrum of $[\text{HNMe}_3][\mathbf{1}]$ in (CD₃)₂CO was obtained in an attempt to assign these resonances to $\{closo\text{-C}_2\text{B}_{10}\}$ or $\{nido\text{-C}_2\text{B}_9\}$ components. By analogy with the spectra of $[7,8\text{-nido}\text{-C}_2\text{B}_9\text{H}_{12}]^{-}$ ¹⁹ and 1,2-*closo*-C₂B₁₀H₁₂,²⁰ it seems reasonable to suggest that the two highest frequency resonances are due to the $\{closo\text{-C}_2\text{B}_{10}\}$ cage and the four lowest frequency resonances are due to the $\{nido\text{-C}_2\text{B}_9\}$ cage, but beyond this it was not possible to deconvolute the entire spectrum of **[1]⁻** unambiguously.

The salt $[\text{HNMe}_3][\mathbf{1}]$ is a convenient starting point for the synthesis of MC₂B₉-C₂B₁₀ products by deprotonation then

metallation, following the protocol established for the first metallacarborane by Hawthorne *et al.*²¹

Following deprotonation of $[\text{HNMe}_3][\mathbf{1}]$ with *n*-BuLi in THF and addition of $[\text{RuCl}_2(p\text{-cymene})]_2$, yellow $[1\text{-}(1'\text{-}1',2'\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})\text{-}3\text{-}(p\text{-cymene})\text{-}3,1,2\text{-}closo\text{-RuC}_2\text{B}_9\text{H}_{10}]$ (**2**) and colourless $[8\text{-}(1'\text{-}1',2'\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})\text{-}2\text{-}(p\text{-cymene})\text{-}2,1,8\text{-}closo\text{-RuC}_2\text{B}_9\text{H}_{10}]$ (**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 ¹H spectrum of a freshly-prepared CDCl₃ solution of **2** are CH_{cage} resonances at δ 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 ¹H NMR spectrum of **2** also confirms overall molecular asymmetry with two integral-3 doublets (and not one integral-6 doublet) for the CH(CH₃)₂ protons of the *p*-cymene ligand. The ¹¹B{¹H} NMR spectrum of **2** consists of ten resonances between δ 2.8 and -17.2 with relative integrals 1:1:2:1:2:2:4:2:1:3 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 δ 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, δ 2.63, as arising from CH_{cage} in the $\{\text{RuC}_2\text{B}_9\}$ portion of **3**. Once again the resonances due to the *p*-cymene ligand reveal the overall molecular structure to be asymmetric. In the ¹¹B{¹H} NMR spectrum of **3** are ten resonances between δ -1.0 and -20.4 with integrals in the relative ratios 2:2:1:2:1:6:2:1:1:1.

In addition to $\{\text{Ru}(\text{arene})\}^{2+}$ a common transition-metal fragment in metallacarborane chemistry is $\{\text{CoCp}\}$. There are two different ways to introduce this fragment to afford a CpCoC₂B_x metallacarborane, (i) reaction of the $[\text{C}_2\text{B}_x]^{2-}$ dianion with CoCl₂/NaCp (*i.e.* *in situ* generation of the $\{\text{CoCp}\}$ fragment) followed by oxidation (Co^{II} → Co^{III})²³ or (ii) reaction of the $[\text{C}_2\text{B}_x]^{2-}$ dianion with $[\text{CpCo}(\text{CO})\text{I}_2]$ (*i.e.* using a “pre-formed” $\{\text{CoCp}\}$ fragment).²⁴ In reaction with $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ both approaches lead to exactly the same product, but we have found that this is *not* the case starting from **[1]⁻**.

Deprotonation of $[\text{HNMe}_3][\mathbf{1}]$ followed by addition of $[\text{CpCo}(\text{CO})\text{I}_2]$ affords, on work-up, the isomer $[1\text{-}(1'\text{-}1',2'\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})\text{-}3\text{-Cp-}3,1,2\text{-}closo\text{-CoC}_2\text{B}_9\text{H}_{10}]$ (**4**) as an orange solid. Microanalysis and mass spectrometry confirm the molecular formula. In the ¹H NMR spectrum are three singlets at δ 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 ¹¹B NMR spectrum are nine resonances in a 1:1:5:1:2:5:2:1:1 pattern, lying between δ 6.5 and -15.9 ppm.



To our surprise, treatment of deprotonated $[\text{HNMe}_3][\mathbf{1}]$ with $\text{CoCl}_2/\text{NaCp}$ followed by aerial oxidation yielded an isomer of $\mathbf{4}$, the 2,1,8-1',2' species $[\text{8}-(1'-1',2'-\text{closo-C}_2\text{B}_{10}\text{H}_{11})\text{-2-Cp-2,1,8-closo-CoC}_2\text{B}_9\text{H}_{10}]$ ($\mathbf{5}$). This yellow product has, as well as the expected singlet for the Cp protons, cage CH resonances at lower frequency than in $\mathbf{4}$, δ 3.59 and 2.73. In $\mathbf{4}$ the $\{\text{CoC}_2\text{B}_9\}$ part of the molecule has a 3,1,2-CoC₂ heteroatom pattern whilst in $\mathbf{5}$ it is 2,1,8-CoC₂. In the corresponding reference compound $[\text{3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_{11}]$ the cage CH atoms resonate at δ 4.08 (CDCl₃) and in $[\text{2-Cp-2,1,8-closo-CoC}_2\text{B}_9\text{H}_{11}]$ they resonate at δ 2.73 and 2.47,²⁵ on the basis of which we tentatively assign the signal at δ 2.73 in $\mathbf{5}$ to the $\{2,1,8\text{-CoC}_2\text{B}_9\}$ fragment. The ¹¹B NMR spectrum of $\mathbf{5}$ 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 $\mathbf{4}$ a trace amount of $\mathbf{5}$ is also detected (see Experimental) and that in the synthesis of $\mathbf{5}$ a trace amount of $\mathbf{4}$ is observed.

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

When $[\mathbf{1}]^{2-}$ is treated with $[\text{CpCo}(\text{CO})\text{I}_2]$ a $\{\text{Co}^{\text{III}}\text{Cp}\}^{2+}$ fragment is introduced to the dianion, affording the non-isomerised $\mathbf{4}$. However, when $[\mathbf{1}]^{2-}$ is treated with $\text{CoCl}_2/\text{NaCp}$ the reacting fragment is $\{\text{Co}^{\text{II}}\text{Cp}\}^+$. This generates the 19e monoanion $[\text{CpCo}^{\text{II}}(\text{C}_2\text{B}_9\text{H}_{10})(\text{C}_2\text{B}_{10}\text{H}_{11})]^-$, which is then oxidised to the 18e, isomerised, Co^{III} species $\mathbf{5}$. We therefore added one equivalent of electrons to $\mathbf{4}$ at room temperature and, after stirring for one hour, oxidised the product aerially. Only $\mathbf{5}$ was detected by ¹H and ¹¹B NMR spectroscopies. This strongly implies that in the bulk synthesis of $\mathbf{5}$, a $[\text{3,1,2-CoC}_2\text{B}_9\text{-1',2'-C}_2\text{B}_{10}]^-$ species is formed first (as would be expected from the reaction between a $\{\text{CoCp}\}^+$ cation and a $[\text{7,8-C}_2\text{B}_9\text{-1',2'-C}_2\text{B}_{10}]^{2-}$ 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 $\mathbf{2}$ 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 $\mathbf{2}$, $\mathbf{4}$ and $\mathbf{5}$ we attempted to identify which ¹¹B resonances were due to which part of the molecule ($\{\text{MC}_2\text{B}_9\}$ or $\{\text{C}_2\text{B}_{10}\}$) from ¹¹B{¹H}-¹¹B{¹H} COSY spectra but, as was the case with $[\mathbf{1}]^-$, it proved impossible to do this unambiguously. In Table 1 we list the weighted average ¹¹B chemical shifts, $\langle\delta(^{11}\text{B})\rangle$, of the conjoined species 1,1'-bis(*o*-carborane), $\mathbf{2}$, $\mathbf{4}$ and $\mathbf{5}$ along with those of their "components", $[\text{1,2-closo-C}_2\text{B}_{10}\text{H}_{12}]$,²⁰ $[\text{3-}(p\text{-cymene})\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_{11}]$,²⁶ $[\text{3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_{11}]$ ²³ and $[\text{2-Cp-2,1,8-closo-CoC}_2\text{B}_9\text{H}_{11}]$.²⁵

Table 1 Weighted average ¹¹B NMR chemical shifts, $\langle\delta(^{11}\text{B})\rangle$, for conjoined cage compounds and their "components".^a All spectra recorded in CDCl₃ at room temperature

Compound	$\langle\delta(^{11}\text{B})\rangle$
1,1'-bis(<i>o</i> -carborane)	-8.9
$[\text{1}-(1'-1',2'-\text{closo-C}_2\text{B}_{10}\text{H}_{11})\text{-3-}(p\text{-cymene})\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_{10}]$ ($\mathbf{2}$)	-9.1
$[\text{1}-(1'-1',2'-\text{closo-C}_2\text{B}_{10}\text{H}_{11})\text{-3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_{10}]$ ($\mathbf{4}$)	-6.7
$[\text{8}-(1'-1',2'-\text{closo-C}_2\text{B}_{10}\text{H}_{11})\text{-2-Cp-2,1,8-closo-CoC}_2\text{B}_9\text{H}_{10}]$ ($\mathbf{5}$)	-7.9
1,2-closo-C ₂ B ₁₀ H ₁₂	-10.7
3-(<i>p</i> -cymene)-3,1,2-closo-RuC ₂ B ₉ H ₁₁	-10.5
3-Cp-3,1,2-closo-CoC ₂ B ₉ H ₁₁	-7.3
2-Cp-2,1,8-closo-CoC ₂ B ₉ H ₁₁	-7.7

^a For 1,1'-bis(*o*-carborane), 1,2-closo-C₂B₁₀H₁₂, 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).

Although the spectra of 1,1'-bis(*o*-carborane)^{3,6} and all these "components" have been reported previously we have re-measured some of them here in CDCl₃ for internal consistency. Note that we have not included compound $\mathbf{3}$ in this Table since its $\{\text{MC}_2\text{B}_9\}$ component, $[\text{2-}(p\text{-cymene})\text{-2,1,8-closo-RuC}_2\text{B}_9\text{H}_{11}]$, is not currently known.

These data show that when 1,1'-bis(*o*-carborane) and the metallocarborane-carborane species $\mathbf{2}$, $\mathbf{4}$ and $\mathbf{5}$ are "constructed" from their constituent parts the $\langle\delta(^{11}\text{B})\rangle$ value for the "product" lies to high frequency of the (weighted) average of that of the two "components". For $\mathbf{5}$ the $\langle\delta(^{11}\text{B})\rangle$ value is very close (and slightly to low frequency of) to that for the metallocarborane component, whilst for 1,1'-bis(*o*-carborane), $\mathbf{2}$ and $\mathbf{4}$ the $\langle\delta(^{11}\text{B})\rangle$ 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 of $[\text{1,2-closo-C}_2\text{B}_{10}\text{H}_{12}]$ 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

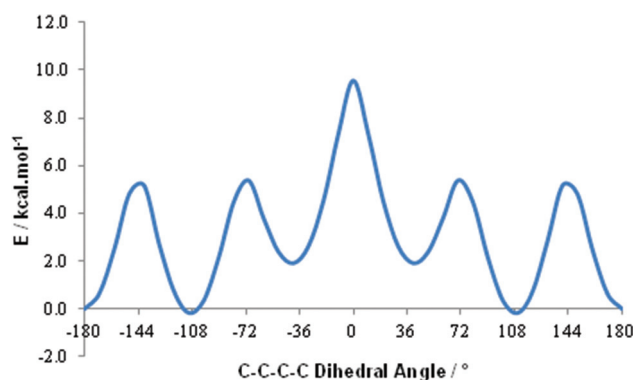


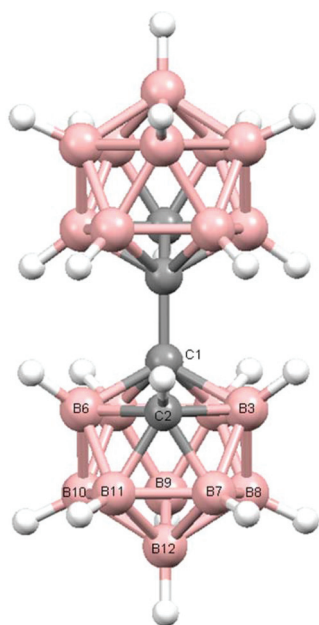
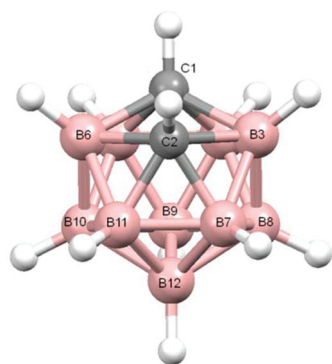
Fig. 2 Plot of energy vs. dihedral angle for 1,1'-bis(*o*-carborane) from DFT calculation where the C2-C1-C1'-C2' torsion angle was subjected to a relaxed scan from -180° to 0° and the resulting data points mirrored to illustrate full 360° rotation.



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(*o*-carborane) found that the non-linking C atom is equally disordered between vertices 2 and 3 (and, by symmetry, 2' and 3').¹ This means that in the crystal any one molecule of 1,1'-bis(*o*-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

Table 2 Natural atomic charges in 1,2-*closo*-C₂B₁₀H₁₂ and 1,1'-bis(*o*-carborane) (180° conformation) by DFT calculation. H atoms carry the same number as the B or C to which they are bonded

Atom	Charge
(a) 1,2- <i>closo</i> -C ₂ B ₁₀ H ₁₂	
C1, C2	-0.56
B3, B6	+0.13
B4, B5, B7, B11	-0.03
B8, B10	-0.19
B9, B12	-0.17
H1, H2	+0.36
H3, H6	+0.08
H4, H5, H7, H11	+0.10
H8, H10	+0.11
H9, H12	+0.10
(b) 1,1'-bis(<i>o</i> -carborane)	
C1	-0.31
C2	-0.51
B3, B6	+0.15
B4, B5	-0.01
B7, B11	-0.01
B8, B10	-0.18
B9	-0.16
B12	-0.14
H2	+0.32
H3, H6	+0.08
H4, H5	+0.08
H7, H11	+0.09
H8, H10	+0.10
H9	+0.10
H12	+0.09



In Table 2 we list the natural charges for atoms in [1,2-*closo*-C₂B₁₀H₁₂] and 1,1'-bis(*o*-carborane), the latter in the 180° conformation. In [1,2-*closo*-C₂B₁₀H₁₂] 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(*o*-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*-C₂B₁₀H₁₂] by a {1',2'-*closo*-C₂B₁₀H₁₁} 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 -0.36 in [1,2-*closo*-C₂B₁₀H₁₂] to precisely zero in 1,1'-bis(*o*-carborane).²⁷ In brief the {1',2'-*closo*-C₂B₁₀H₁₁} substituent is electron-withdrawing compared to H. This conclusion is consistent with our analysis of the $\langle\delta(^{11}\text{B})\rangle$ values for 1,1'-bis(*o*-carborane) and for 2.

Salt [BTMA][1] and compounds 2–5 were also studied crystallographically. In [BTMA][1] (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-RuC₂B₉-1',2'-C₂B₁₀ species 2, its 2,1,8-RuC₂B₉-1',2'-C₂B₁₀ analogue 3, and the equivalent cobalt species 4 and 5 are presented in

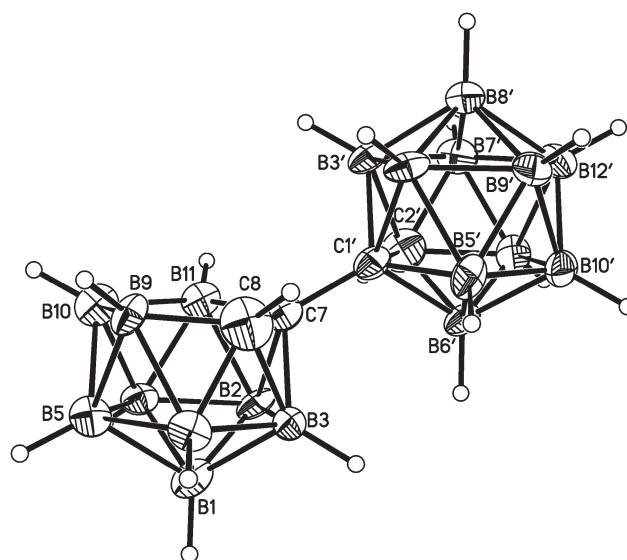


Fig. 3 Perspective view of the anion in the salt [BTMA][1] and atom numbering scheme. In the unprimed cage there is partial disorder of B3, part of which appears as the 12th atom of an icosahedron (not shown for clarity); partial occupancies are B3 0.548(10) and B12 0.452(10). The H atom bridging on the open face of the unprimed cage was not located. Displacement ellipsoids are drawn at the 40% probability level except for H atoms.



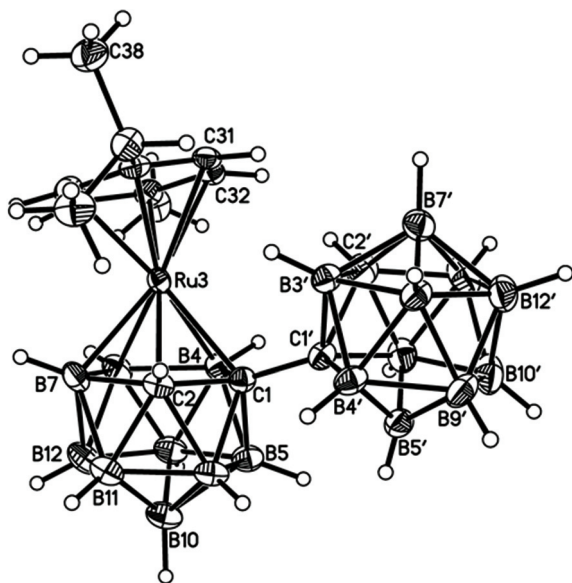


Fig. 4 Perspective view of compound 2 and atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level except for H atoms.

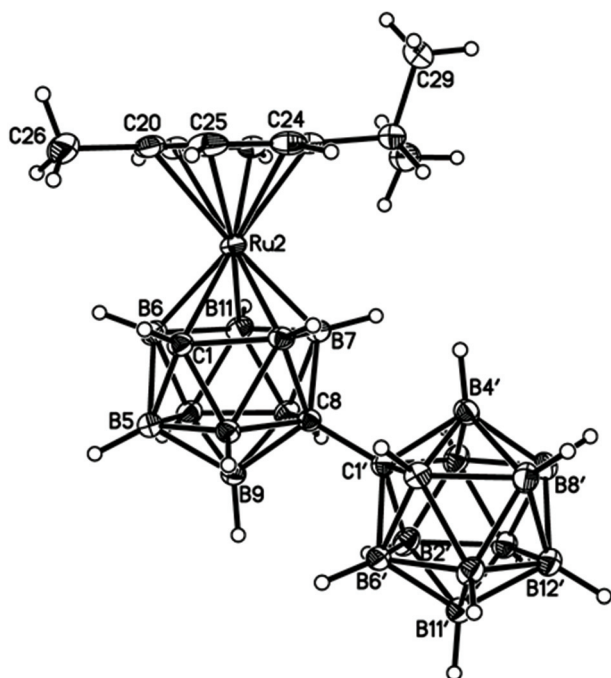


Fig. 5 Perspective view of compound 3 and atom numbering scheme. Position 2' is $0.446(19)B + 0.554(19)C$, with complementary occupations at position 3'. Displacement ellipsoids as for Fig. 4.

Fig. 4–7, respectively. Since compounds 2, 4 and 5 are composed of $\{3,1,2\text{-closo-Ru}_2\text{C}_2\text{B}_9\}$ (compound 2), $\{3,1,2\text{-closo-Co}_2\text{C}_2\text{B}_9\}$ (compound 4) and $\{2,1,8\text{-closo-Co}_2\text{C}_2\text{B}_9\}$ (compound 5) icosahedra conjoined to $\{1,2\text{-closo-C}_2\text{B}_{10}\}$ icosahedra, and all these individual components have previously been studied crystallographically, we have used the *Structure Overlay* tool in

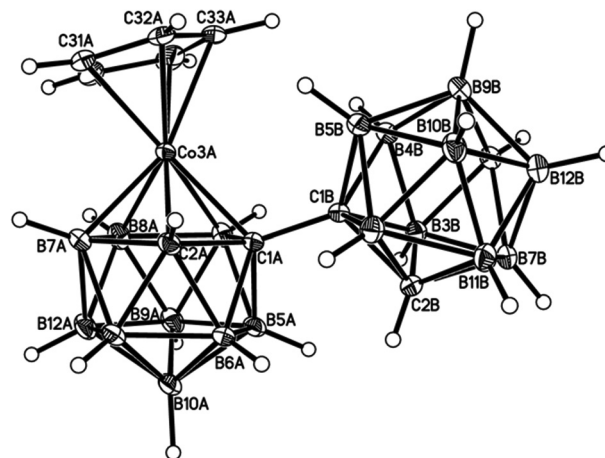


Fig. 6 Perspective view of one of two crystallographically-independent molecules (molecule AB) of compound 4 and atom numbering scheme. Displacement ellipsoids as for Fig. 4.

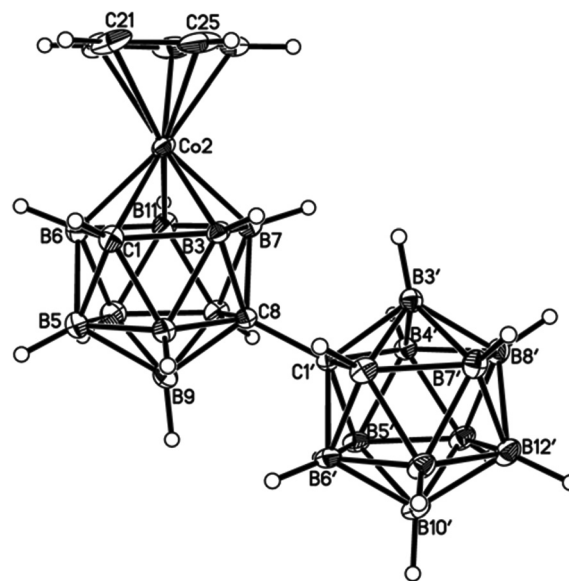


Fig. 7 Perspective view of compound 5 and atom numbering scheme. Displacement ellipsoids as for Fig. 4.

Mercury²⁸ 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-*closo*- $\text{Ru}_2\text{C}_2\text{B}_9\text{H}_{11}$ 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 $\{3,1,2\text{-MC}_2\text{B}_9\}$ 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 $\{3,1,2\text{-MC}_2\text{B}_9\}$ is typically 0.038–0.040 Å. In contrast the misfit for the $\{2,1,8\text{-MC}_2\text{B}_9\}$ 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



Table 3 Rms deviations (Å) between the {MC₂B₉} and {C₂B₁₀} "components" of compounds **2**, **4** and **5** and these fragments in reference single cage compounds

Compound 2 ^a	Compound 4 (C-D) ^b			Compound 4 (C-D) ^b			Compound 5 ^c		
	{RuC ₂ B ₉ }	{C ₂ B ₁₀ }	Dev.	{CoC ₂ B ₉ }	{C ₂ B ₁₀ }	Dev.	{CoC ₂ B ₉ }	{C ₂ B ₁₀ }	Dev.
C1	0.066	C1'	0.054	C1	C1'	0.076	C1	C1'	0.004
C2	0.036	C2'	0.056	C2	C2'	0.037	Co2	C2'	0.012
Ru3	0.083	B3'	0.039	Co3	B3'	0.091	B3	B3'	0.006
B4	0.033	B4'	0.012	B4	B4'	0.025	B4	B4'	0.006
B5	0.025	B5'	0.047	B5	B5'	0.020	B5	B5'	0.008
B6	0.038	B6'	0.017	B6	B6'	0.037	B6	B6'	0.010
B7	0.008	B7'	0.008	B7	B7'	0.012	B7	B7'	0.018
B8	0.016	B8'	0.009	B8	B8'	0.006	C8	B8'	0.025
B9	0.009	B9'	0.009	B9	B9'	0.011	B9	B9'	0.000
B10	0.025	B10'	0.005	B10	B10'	0.019	B10	B10'	0.005
B11	0.013	B11'	0.017	B11	B11'	0.009	B11	B11'	0.016
B12	0.006	B12'	0.013	B12	B12'	0.015	B12	B12'	0.005
Overall	0.038	Overall	0.030	Overall	Overall	0.039	Overall	Overall	0.012

^a The reference {RuC₂B₉} compound is 3-(*p*-cymene)-3,1,2-*c*-*closo*-RuC₂B₉H₁₁ (ref. 26). CCDC refcode ODOGAQ. ^b The reference {CoC₂B₉} compound is 3-Cp-3,1,2-*c*-*closo*-CoC₂B₉H₁₁ (ref. 45). CCDC refcode DUBDIN. ^c The reference {CoC₂B₉} compound is 2-Cp-2,1,8-*c*-*closo*-CoC₂B₉H₁₁ (ref. 25). CCDC refcode NOWMIX00. ^d In all cases the reference {C₂B₁₀} compound is 1,2-*c*-*closo*-C₂B₁₀H₁₂ (ref. 46). CCDC refcode TOKGJJ. We arbitrarily used the molecule containing C13 and C14 (CCDC numbering) matching C13 with C1'.

atom having a misfit >0.018 Å. The {C₂B₁₀} 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-MC₂B₉-1',2'-C₂B₁₀ structures is a pronounced bend-back of the arene or Cp ligand in a direction away from the C₂B₁₀ 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 θ , the dihedral angle between the plane of the ligand C atoms (arene or Cp) and the plane defined by B5B6B11B12B9 (the lower pentagonal belt usually taken as the reference plane in 3,1,2-MC₂B₉ icosahedra).²⁹ For **2** θ is 16.08(9)° whilst for **4** θ 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 CoC₂B₉ cage and second letter to the C₂B₁₀ 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 than 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-MC₂B₉-1',2'-C₂B₁₀ compounds **3** and **5** significant intramolecular steric crowding is removed since the C₂B₁₀ substituent to the MC₂B₉ cage is now at position 8 and so not adjacent to the metal atom. Consequently the arene or Cp ring plane lies effectively parallel to the lower pentagonal belt, now the C8B4B5B10B12 plane [θ is only 0.27(5)° in **3** and 2.19(7)° in **5**], 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 metallocarboranes has precedent in the literature.³⁰ Thus, as already has 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-MC₂B₉ to 2,1,8-MC₂B₉ 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 metallocarborane/carborane compounds, MC₂B₉-C₂B₁₀, derived from single deboronation and



then metallation of 1,1'-bis(*o*-carborane), have been prepared and characterised. Both non-isomerised 3,1,2-MC₂B₉-1',2'-C₂B₁₀ and isomerised 2,1,8-MC₂B₉-1',2'-C₂B₁₀ 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 × freeze-pump-thaw cycles) before use. Preparative TLC employed 20 × 20 cm Kieselgel F₂₅₄ glass plates. NMR spectra at 400.1 MHz (¹H) or 128.4 MHz (¹¹B) were recorded on a Bruker DPX-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*-carborane),⁶ [Ru(*p*-cymene)Cl₂]₂,³³ [Ru(η-C₆H₆)Cl₂]₂³⁴ and CpCo(CO)I₂³⁵ were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially.

[HNMe₃][7-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-7,8-*nido*-C₂B₉H₁₁] ([HNMe₃][1]) and [BTMA][7-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-7,8-*nido*-C₂B₉H₁₁] ([BTMA][1]). 1,1'-bis(*o*-carborane) (0.50 g, 1.75 mmol) and KOH (0.09 g, 1.75 mmol) were heated to reflux in EtOH (30 mL) for 4 h. The solution was allowed to cool and the solvent removed to give a white oily residue. Deionised water (20 mL) was added, and the suspension filtered to give a slightly cloudy solution. To this was added an aqueous solution of either [HNMe₃]Cl (0.17 g, 1.8 mmol) or [BTMA]Cl (0.32 g, 1.8 mmol) resulting in the immediate precipitation of [HNMe₃][7-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-7,8-*nido*-C₂B₉H₁₁] ([HNMe₃][1]) or [BTMA][7-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-7,8-*nido*-C₂B₉H₁₁] ([BTMA][1]) as white solids. These were isolated by filtration, washed with H₂O (3 × 20 mL) and dried *in vacuo*.

[HNMe₃][1]: Yield 0.37 g, 64%. C₇H₃₂B₁₉N requires C 25.0, H 9.60, N 4.17. Found for [HNMe₃][1]: C 24.7, H 9.71, N 4.04%. ¹¹B{¹H} NMR [(CD₃)₂CO], δ -3.9 (1B), -6.0 (1B), -8.8 (1B), -10.4 (5B), -11.2 (sh., 2B), -13.5 (3B), -16.8 (2B), -19.0 (1B), -22.7 (1B), -33.9 (1B), -35.3 (1B). ¹H NMR [(CD₃)₂CO], δ 4.36 (s, 1H, CH_{cage}), 3.22 (s, 9H, N(CH₃)₃), 1.99 (s, 1H, CH_{cage}).

[BTMA][1]: Yield 0.55 g, 74%. C₁₄H₃₈B₁₉N requires C 39.5, H 8.99, N 3.29. Found for [BTMA][1]: C 41.5, H 9.15, N 3.25%. ¹¹B{¹H} NMR [(CD₃)₂CO], δ -4.2 (1B), -6.2 (1B), -9.0 (1B),

-10.6 (5B), -11.5 (sh., 2B), -13.8 (3B), -17.0 (2B), -19.2 (1B), -22.8 (1B), -33.2 (1B), -35.5 (1B). ¹H NMR [(CD₃)₂CO], δ 7.75–7.45 (m, 5H, C₆H₅), 4.75 (s, 2H, CH₂), 4.35 (s, 1H, CH_{cage}), 3.35 (s, 9H, N(CH₃)₃), 1.95 (s, 1H, CH_{cage}).

[1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-3-(*p*-cymene)-3,1,2-*closo*-RuC₂B₉H₁₀] (2) and [8-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-8-(*p*-cymene)-2,1,8-*closo*-RuC₂B₉H₁₀] (3). *n*-BuLi (0.48 mL of 2.5M solution, 1.2 mmol) was added dropwise to a cooled (0 °C) solution of [HNMe₃][1] (0.20 g, 0.60 mmol) in THF (20 mL) and the products stirred for 1 h. The pale yellow solution was frozen at -196 °C, [RuCl₂(*p*-cymene)]₂ (0.18 g, 0.30 mmol) added and the reaction mixture stirred overnight at room temperature. THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petroleum ether in a ratio of 30:70 afforded a yellow band (R_f = 0.47) subsequently identified as [1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-3-(*p*-cymene)-3,1,2-*closo*-RuC₂B₉H₁₀] (2) (0.024 g, 8%) and a colourless band (R_f = 0.51) identified as [8-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-2-(*p*-cymene)-2,1,8-*closo*-RuC₂B₉H₁₀] (3) (0.057 g, 19%).

2: C₁₄H₃₅B₁₉Ru requires C 33.0, H 6.92. Found for 2: C 32.5, H 7.17%. ¹¹B{¹H} NMR [CDCl₃], δ 2.8 (1B), 0.5 (1B), -2.8 (2B), -3.9 (sh., 1B), -7.2 (2B), -8.8 (2B), -10.7 (4B), -12.6 (2B), -14.4 (1B), -17.2 (3B). ¹H NMR [CDCl₃], δ 6.11–5.96 (m, 4H, C₆H₄), 4.03 (s, 1H, CH_{cage}), 3.91 (s, 1H, CH_{cage}), 3.04 (app. septet, 1H, CH(CH₃)₂), 2.49 (s, 3H, CH₃), 1.37 (d, 3H, CH(CH₃)₂), 1.35 (d, 3H, CH(CH₃)₂). EIMS: envelope centred on *m/z* 510 (M⁺).

3: C₁₄H₃₅B₁₉Ru requires C 33.0, H 6.92. Found for 3: C 33.0, H 6.82%. ¹¹B{¹H} NMR [CDCl₃], δ -1.0 (2B), -2.8 (2B), -4.1 (1B), -4.9 (2B), -8.0 (1B), -10.1 (6B), -13.4 (2B), -16.2 (1B), -19.2 (1B), -20.4 (1B). ¹H NMR [CDCl₃], δ 5.94–5.84 (m, 4H, C₆H₄), 3.64 (s, 1H, CH_{cage}), 2.81 (app. septet, 1H, CH(CH₃)₂), 2.63 (s, 1H, CH_{cage}), 2.31 (s, 3H, CH₃), 1.30 (d, 3H, CH(CH₃)₂), 1.28 (d, 3H, CH(CH₃)₂). EIMS: envelope centred on *m/z* 510 (M⁺).

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 R_f = 0.51 identified as 3 (0.014 g, 58%) by ¹H and ¹¹B NMR spectroscopies.

[1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-3-Cp-3,1,2-*closo*-CoC₂B₉H₁₀] (4). [HNMe₃][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 added CpCo(CO)I₂ (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, R_f = 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*-C₂B₁₀H₁₁)-3-Cp-3,1,2-*closo*-CoC₂B₉H₁₀] (4). C₉H₂₆B₁₉Co requires C 27.1, H 6.57. Found for 4: C 26.5, H 6.67%. ¹¹B{¹H} NMR [CDCl₃], 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 [CDCl₃], δ 5.86 (s, 5H, C₅H₅), 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 ($R_f = 0.34$) identified as [8-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-2-Cp-2,1,8-*closo*-CoC₂B₉H₁₀] (5) was also observed and its identity confirmed *via* ¹H NMR spectroscopy.

[8-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-2-Cp-2,1,8-*closo*-CoC₂B₉H₁₀] (5). [HNMe₃][1] (0.20 g, 0.60 mmol) was deprotonated with *n*-BuLi (0.48 mL of 2.5 M solution, 1.20 mmol) as above and frozen at -196 °C. To this were added NaCp (0.89 mL of 2.0 M solution, 1.79 mmol) and CoCl₂ (0.28 g, 2.20 mmol) and the mixture stirred overnight at room temperature. Following aerial oxidation (0.5 h) and filtration through silica THF was replaced by DCM and the product again filtered, through Celite®. Following spot TLC** (DCM–petroleum ether, 50 : 50, $R_f = 0.69$) purification by column chromatography using the same eluent gave, on removal of solvent, a yellow powder (0.117 g, 49%), subsequently identified as [8-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-2-Cp-2,1,8-*closo*-CoC₂B₉H₁₀] (5). C₉H₂₆B₁₉Co requires C 27.1, H 6.57. Found for 6: C 27.1, H 6.75%. ¹¹B{¹H} NMR [CDCl₃], δ 1.7 (1B), 0.0 (2B), -0.9 (1B), -2.5 (1B), -3.8 (1B), -6.1 (2B), -9.9 (6B), -11.8 (1B), -13.2 (2B), -16.8 (1B), -17.7 (1B). ¹H NMR [CDCl₃], δ 5.50 (s, 5H, C₅H₅), 3.59 (s, 1H, CH_{cage}), 2.73 (s, 1H, CH_{cage}). EIMS: envelope centred on m/z 399 (M⁺).

**A trace amount of an orange spot ($R_f = 0.60$) identified as 4 was also observed and its identity confirmed *via* ¹H 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 ¹H and ¹¹B 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 ¹H and ¹¹B NMR spectroscopies.

Crystallography

Diffraction-quality crystals of salt [BTMA][1] and compounds 2, 3, 4 and 5 were afforded by slow diffusion of a CH₂Cl₂ 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 α 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 α X-radiation. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.³⁶ Structures were solved by direct methods (SHELXS³⁷ or OLEX2³⁸) and refined by full-matrix least-squares (SHELXL).³⁷

Cage C atoms not involved in the intercage link were identified by a combination of (i) the examination of refined (as B) isotropic thermal parameters, (ii) the lengths of cage connectivities, (iii) the *Vertex-Centroid Distance Method*³⁹ and (iv) the *Boron-H Distance Method*,⁴⁰ with all four methods affording excellent mutual agreement.

Table 4 Crystallographic data

	[BTMA][1]	2	3	4	5
Formula	C ₁₄ H ₃₈ B ₁₉ N	C ₁₄ H ₃₅ B ₁₉ Ru	C ₁₄ H ₃₅ B ₁₉ Ru	C ₉ H ₂₆ B ₁₉ Co	C ₉ H ₂₆ B ₁₉ Co
<i>M</i>	425.84	509.88	509.88	398.62	398.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	18.851(9)	11.5653(7)	10.9051(9)	6.7993(5)	12.6472(6)(4)
<i>b</i> /Å	10.072(4)	14.1222(9)	16.9528(14)	14.4533(10)	6.6422(3)
<i>c</i> /Å	13.477(6)	15.1116(10)	13.8437(11)	20.3575(14)	23.8175(10)
α (°)	90	90	90	89.609(3)	90
β (°)	97.068(13)	91.611(4)	105.039(4)	85.554(3)	95.642(2)
γ (°)	90	90	90	89.158(3)	90
<i>U</i> /Å ³	2540(2)	2467.2(3)	2471.7(4)	1994.3(2)	1991.10(16)
<i>Z</i> , <i>Z'</i>	4, 1	4, 1	4, 1	4, 2	4, 1
<i>F</i> (000)/ <i>e</i>	896	1032	1032	808	808
<i>D</i> _{calc} /Mg m ⁻³	1.114	1.373	1.370	1.328	1.330
μ (Mo-K α)/mm ⁻¹	0.052	0.640	0.639	0.853	0.855
θ _{max} (°)	20.84	27.47	33.53	27.48	29.57
Data measured	14 879	34 686	52 456	26 471	37 451
Unique data, <i>n</i>	2651	5604	9614	9102	5581
<i>R</i> _{int}	0.2172	0.0431	0.0388	0.0378	0.0368
<i>R</i> , <i>wR</i> ₂ (obs. data)	0.0867, 0.1912	0.0309, 0.0689	0.0288, 0.0639	0.0334, 0.0821	0.0325, 0.0732
<i>S</i>	1.005	1.029	1.031	1.070	1.086
Variables	308	373	374	649	325
<i>E</i> _{max} , <i>E</i> _{min} /e Å ⁻³	0.27, -0.26	0.68, -0.71	0.96, -1.37	0.66, -0.34	0.36, -0.24



The anion in [BTMA][1] is partially disordered. The C₂B₁₀ cage is fully ordered but the C₂B₉ 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 3 between atoms C2' and B3' (C₂B₁₀ cage), successfully modelled with vertex 2 being 0.446(19)C + 0.554(19)B, with complementary SOFs at vertex 3.

In [BTMA][1] it was not possible to locate the (disordered) bridging H atom associated with the open face of the *nido* cage and final refinement with constrained BH and C_{cage}H atoms (B–H = C_{cage}–H = 1.12 Å) afforded better agreement than that with these H atoms allowed to refine. In the BTMA cation the H atoms were constrained to C_{phenyl}–H = 0.95 Å, C_{secondary}–H = 0.99 Å, C_{methyl}–H = 0.98 Å. For all other structures BH and C_{cage}H atoms were allowed to refine positionally whilst other H atoms were constrained to idealised geometries; C_{aromatic}–H = 1.00 Å, C_{sp}–H = 1.00 Å, C_{tertiary}–H = 1.00 Å, C_{methyl}–H = 0.98 Å. All H displacement parameters, *U*_{iso}, were constrained to be 1.2 × *U*_{eq} (bound B or C) except Me H atoms [*U*_{iso}(H) = 1.5 × *U*_{eq} C(Me)]. Table 4 contains further experimental details.

Calculations

All geometries were optimised without constraints using Gaussian 03, Revision D.01⁴¹ employing the BP86 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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References

- W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2014, **70**, 462.
- (a) J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1643; (b) T. E. Paxon, K. P. Callahan and M. F. Hawthorne, *Inorg. Chem.*, 1973, **12**, 708.
- X. Yang, W. Jiang, C. B. Knobler, M. D. Mortimer and M. F. Hawthorne, *Inorg. Chim. Acta*, 1995, **240**, 371.
- L. I. Zakharkin and A. I. Kovredov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1428.
- (a) X. Yang, W. Jiang, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1992, **114**, 9719; (b) J. Müller, K. Baše, T. F. Magnera and J. Michl, *J. Am. Chem. Soc.*, 1992, **114**, 9721.
- S. Ren and Z. Xie, *Organometallics*, 2008, **27**, 5167.
- (a) D. A. Owen and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 3194; (b) D. A. Owen and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1971, **93**, 873; (c) D. E. Harwell, J. McMillan, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1997, **36**, 5951.
- A. I. Yanovsky, N. G. Furmanova, Y. T. Struchkov, N. F. Shemyakin and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1523.
- M. F. Hawthorne, D. A. Owen and J. W. Wiggins, *Inorg. Chem.*, 1971, **10**, 1304.
- T. D. Getman, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1992, **31**, 101.
- T. D. Getman, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1990, **112**, 4594.
- (a) G. B. Dunks, R. J. Wiersema and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1972, 899; (b) G. B. Dunks, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1973, **95**, 3174.
- D. Ellis, D. McKay, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Angew. Chem., Int. Ed.*, 2010, **49**, 4943.
- D. Ellis, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2010, **46**, 7394.
- J. A. Doi, E. A. Mizusawa, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1984, **23**, 1482.
- J. A. Long, T. B. Marder, P. E. Behnken and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2979.
- P. E. Behnken, T. B. Marder, R. T. Baker, C. B. Knobler, M. R. Thompson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1985, **107**, 932.
- A B8–B9' linked species, [8-(9'-3'-Cp-3',1',2'-closo-CoC₂B₉H₁₀)-3-Cp-3,1,2-closo-CoC₂B₉H₁₀] has been reported but was prepared from the reaction between [3-Cp-3,1,2-closo-CoC₂B₉H₁₁] and S₈/AlCl₃, not from a bis(carborane); J. G. Planas, C. Viñas, F. Teixidor, M. E. Light and M. B. Hursthouse, *J. Organomet. Chem.*, 2006, **691**, 3472.
- J. Buchanan, E. J. M. Hamilton, D. Reed and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1990, 677.
- M. A. Fox, J. A. K. Howard, A. K. Hughes, J. M. Malget and D. S. Yufit, *J. Chem. Soc., Dalton Trans.*, 2001, 2263.
- M. F. Hawthorne, D. C. Young and P. A. Wegner, *J. Am. Chem. Soc.*, 1965, **87**, 1818.
- M. P. Garcia, M. Green, F. G. A. Stone, R. G. Somerville, A. J. Welch, C. E. Briant, D. N. Cox and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1985, 2343.
- C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, 1973, **12**, 606.
- A. Burke, R. McIntosh, D. Ellis, G. M. Rosair and A. J. Welch, *Collect. Czech. Chem. Commun.*, 2002, **67**, 991.
- W. Y. Man, S. Zlatogorsky, H. Tricas, D. Ellis, G. M. Rosair and A. J. Welch, *Angew. Chem., Int. Ed.*, 2014, **53**, 12222.



- 26 M. E. Lopez, M. J. Edie, D. Ellis, A. Horneber, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2007, 2243.
- 27 Since 1,1'-bis(*o*-carborane) is neutral overall and symmetric about the C1–C1' mid-point, the two halves individually must be neutral.
- 28 F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453. A free download of Mercury is available from the Cambridge Crystallographic Data Centre, <http://www.ccdc.cam.ac.uk/>.
- 29 D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.
- 30 e.g. (a) T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1972, **94**, 4882; (b) T. P. Hanusa and L. J. Todd, *Polyhedron*, 1985, **4**, 2063.
- 31 e.g. (a) D. Ellis, M. E. Lopez, R. McIntosh, G. M. Rosair, A. J. Welch and R. Quenardelle, *Chem. Commun.*, 2005, 1348; (b) S. Zlatogorsky, D. Ellis, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2007, 2178.
- 32 D. Mandal, G. Thiripuranathar, W. Y. Man, G. M. Rosair and A. J. Welch, work in progress.
- 33 M. A. Bennett, T.-N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 74.
- 34 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.
- 35 S. A. Frith and J. L. Spencer, *Inorg. Synth.*, 1990, **28**, 273.
- 36 Bruker AXS APEX2, version 2009-5, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- 37 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- 38 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
- 39 A. McAnaw, G. Scott, L. Elrick, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2013, **42**, 645.
- 40 A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2014, **43**, 5095.
- 41 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian Inc., Wallingford, CT, USA, 2004.
- 42 (a) H. L. Schmider and A. D. Becke, *J. Chem. Phys.*, 1998, **108**, 9624; (b) J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822.
- 43 (a) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (b) P. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- 44 (a) C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523; (b) C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154.
- 45 D. E. Smith and A. J. Welch, *Organometallics*, 1986, **5**, 760.
- 46 M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon and K. Wade, *Chem. Commun.*, 1996, 2285.

