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Asymmetric 1,8/13,2,*x*-$M_2C_2B_{10}$ 14-vertex metallacarboranes by direct electrophilic insertion reactions; the VCD and BHD methods in critical analysis of cage C atom positions†‡§

Amelia McAnaw, Maria Elena Lopez, David Ellis, Georgina M. Rosair and Alan J. Welch*

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The isolation of six isomeric, low-symmetry, dicobaltacarboranes with bicapped hexagonal antiprismatic cage structures, always in low yield, is described from reactions in which 13-vertex cobaltacarborane anions and sources of cobalt-containing cations were present. The vertex-to-centroid distance (VCD) and boron–H distance (BHD) methods are used to locate the correct C atom positions in the cages, thus allowing the compounds to be identified as 1,13-Cp_2-1,13,2,10-*closo*-$Co_2C_2B_{10}H_{12}$ (**1**), 1,8-Cp_2-3-OEt-1,8,2,10-*closo*-$Co_2C_2B_{10}H_{11}$ (**2**), 1,13-Cp_2-1,13,2,9-*closo*-$Co_2C_2B_{10}H_{12}$ (**3**), 1,8-Cp_2-1,8,2,4-*closo*-$Co_2C_2B_{10}H_{12}$ (**4**), 1,13-Cp_2-1,13,2,4-*closo*-$Co_2C_2B_{10}H_{12}$ (**5**) and 1,8-Cp_2-1,8,2,5-*closo*-$Co_2C_2B_{10}H_{12}$ (**6**). It is shown that a common alternative method of cage C atom identification, using refined (as B) U_{eq} values, does not work well, at least in these cases. Having identified the correct isomeric forms of the six dicobaltacarboranes, their syntheses are tentatively rationalised in terms of the direct electrophilic insertion of a $\{CpCo^+\}$ fragment into $[CpCoC_2B_{10}]^-$ anions and it is demonstrated that compounds **1**, **4**, **5** and **6** can be successfully prepared by deliberately performing such reactions.

Introduction

Although there are now hundreds of 13-vertex MC_2B_{10} metallacarboranes whose origin can be traced to Hawthorne's original synthesis of 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$,[1] there are very few 14-vertex analogues.[2] The expected shape[3] of a *closo* 14-vertex heteroborane with 15 skeletal electron pairs is the bicapped hexagonal antiprism, shown together with its numbering scheme in Fig. 1a. It was Hawthorne, again, who prepared the first examples of 14-vertex metallacarboranes by reduction and subsequent metallation of 13-vertex MC_2B_{10} precursors.[4] Expansion of 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ afforded 1,14-Cp_2-1,14,2,10-*closo*-$Co_2C_2B_{10}H_{12}$, whose spectroscopically-presumed structure was recently confirmed crystallographically.[5] Similarly, reduction and metallation of 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ (*p*-cymene = η-$C_6H_4Me^iPr$-1,4) afforded both homo- and heterobimetallic $M_2C_2B_{10}$ species, again with 1,14,2,10-MC_2B_{10} architectures.[6] Hawthorne also expanded 4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ [4] and we recently established that the product here is the 1,14,2,9-*closo*-$Co_2C_2B_{10}$ isomer.[5] In an alternative approach, Grimes and co-workers reacted $[Me_4C_4B_8H_8]^{2-}$ with a source of $\{CpFe^+\}$ fragments to yield kinetic isomers of $(CpFe)_2Me_4C_4B_8H_8$ which had irregular (non bicapped hexagonal antiprismatic) cage structures. However, progressive isomerisation to thermodynamically-preferred regular structures was achieved by heating, affording 1,14,2,4,10,12- and 1,14,2,5,10,12-$Fe_2C_4B_8$ species.[7] Note that

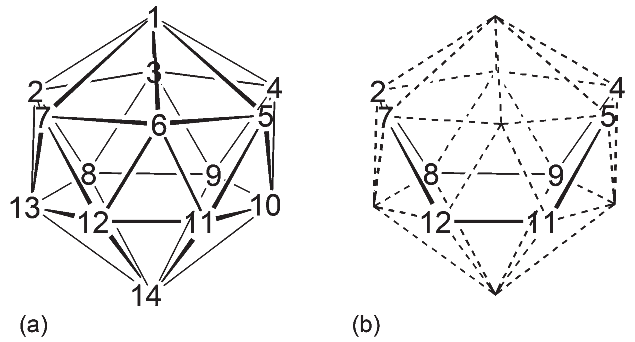

Fig. 1 (a) The bicapped hexagonal antiprism and vertex numbering scheme; (b) the eight vertices used in VCD calculations.

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK. E-mail: a.j.welch@hw.ac.uk; Fax: +44 (0)131 451 3180; Tel: +44 (0)131 451 3217

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§ Electronic supplementary information (ESI) available. CCDC 939752–939756 and 939818. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52101j in all the above examples of bicapped hexagonal antiprismatic $M_2C_2B_{10}$ metallacarboranes both metal atoms occupy degree-6 vertices (vertices 1 and 14 of Fig. 1a) in which they have maximum interaction with other cage atoms, consistent with the relatively diffuse nature of the frontier orbitals of transition metals compared to those of boron and especially carbon.[8]

14-vertex MC_2B_{11} species are also known. Reduction and subsequent metallation (with $\{(p\text{-cymene})Ru^{2+}\}$) of the 13-vertex tethered carborane 1,2-μ-$(CH_2)_3$-1,2-*closo*-$C_2B_{11}H_{11}$ afforded the first such species in two isomeric forms, 1,2,3-RuC_2B_{11} and 1,2,8-RuC_2B_{11},[9] whilst a 1,2,9-RuC_2B_{11} species was later prepared by reduction and metallation of a tether-free carborane.[10] Note that in these compounds the single metal atom is again located at a degree-6 vertex. The only known exceptions to this rule are two 8,2,3-NiC_2B_{11} compounds afforded by treatment of $[\mu\text{-}(CH_2)_3\text{-}C_2B_{11}H_{11}]^{2-}$ with $\{\text{nickel(chelating diphosphine)}^{2+}\}$ fragments.[11]

In the present study we report the synthesis and structural characterisation of six bicapped hexagonal antiprismatic $Co_2C_2B_{10}$ species in which one metal atom is in the degree-6 vertex 1 but, uniquely, the other is in a degree-5 site on the lower hexagonal belt (vertex 8 or 13, dependent on the C atom positions). We present evidence which suggests that these compounds are not formed by 2-e reduction and metallation of 13-vertex CoC_2B_{10} species (although in some cases they were first isolated from reactions in which this was the intention) rather that they may arise as the result of direct electrophilic attack by a metal fragment cation on a $[CoC_2B_{10}]^-$ monoanion. Crucial to rationalising their synthesis is the identification of the correct positions of the cage C atoms in the crystallographically-determined structures (in no cases do the C atoms carry *exo*-polyhedral substituents other than H) and for this we have used both the recently reported vertex-to-centroid distance (VCD) method[12] and a complementary approach, the boron–H distance (BHD) method which we first communicated in 2002[13] but for which we now provide more detail.

Results and discussion

Syntheses

Hawthorne's communication describing the original synthesis of the 14-vertex dicobaltacarborane 1,14-Cp_2-1,14,2,10-*closo*-$Co_2C_2B_{10}H_{12}$, by reduction and subsequent metallation ($Na[Cp]/CoCl_2$) of 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ followed by aerial oxidation ($Co^{II} \rightarrow Co^{III}$) noted "a mixture of products".[4] In repeating this experiment we found, by thin layer chromatography (TLC), evidence for at least eight products including the known compounds 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$,[14] 1,14-Cp_2-1,14,2,10-*closo*-$Co_2C_2B_{10}H_{12}$ [4] and 4,5-Cp_2-4,5,1,6-*closo*-$Co_2C_2B_9H_{11}$,[15] these compounds being identified by a combination of $^{11}B\{^1H\}$ and ^1H NMR spectroscopies. In addition we isolated in low yield a brown product **1** which by mass spectrometry appears to be $(CpCo)_2C_2B_{10}H_{12}$ but which, unlike 1,14-Cp_2-1,14,2,10-*closo*-$Co_2C_2B_{10}H_{12}$, is clearly asymmetric with two Cp resonances and two $C_{cage}H$ resonances in the ^1H NMR spectrum, and eight resonances, 1:2:2:1:1:1:1:1 from high frequency to low frequency, in the $^{11}B\{^1H\}$ spectrum.

Similarly, when we repeated the polyhedral expansion of 4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ by reduction, metallation and oxidation,[4,5] we isolated not only the target species 1,14-Cp_2-1,14,2,9-*closo*-$Co_2C_2B_{10}H_{12}$ but also a small amount of a second brown compound, **3**. Compound **3** also appears to be $(CpCo)_2C_2B_{10}H_{12}$ by mass spectrometry but by NMR spectroscopy it is clearly different to **1** although it again appears asymmetric in the ^{11}B spectrum, with eight resonances, 1:1:1:1:1:2:2:1. Several of these, however, are unusually broad. Whilst there are two $C_{cage}H$ resonances in the ^1H spectrum there is only one cyclopentadienyl resonance, appearing as a broad unresolved singlet. We believe that this may be evidence for a functional process in **3** in solution which equivalences the two metal fragments whilst keeping distinct the two cage C atoms, and which occurs very near to room temperature. Further studies are currently underway.[16]

We initially isolated two further brown solids, compounds **4** and **5**, in trace amounts during the synthesis, first reported by Hawthorne,[1b] of 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ by the reduction and subsequent metallation then oxidation of 1,2-*closo*-$C_2B_{10}H_{12}$. Similarly, during the synthesis[17] of 4-Cp-4,1,10-*closo*-$CoC_2B_{10}H_{12}$ starting from 1,12-*closo*-$C_2B_{10}H_{12}$, yet another brown trace product, **6**, was observed. Like **1** and **3**, compounds **4–6** all appear by mass spectrometry to be $(CpCo)_2C_2B_{10}H_{12}$, but spectroscopically they are all different and clearly asymmetric. We therefore conclude that compounds **1**, **3**, **4**, **5** and **6** are all related as positional isomers. Table 1 summarises the ^1H and ^{11}B NMR chemical shifts for **1** and **3–6**. We have previously noted both the ^{11}B range and the weighted average ^{11}B chemical shift, $\langle\delta^{11}B\rangle$, for the compounds 1,14-Cp_2-1,14,2,10-*closo*-$Co_2C_2B_{10}H_{12}$ and 1,14-Cp_2-1,14,2,9-*closo*-$Co_2C_2B_{10}H_{12}$.[5] In moving from the 1,14,2,10- to 1,14,2,9- isomer the chemical shift range increases from *ca.* 13 ppm to *ca.* 24 ppm, but $\langle\delta^{11}B\rangle$ is fairly constant, −14.3 and −13.4 ppm, respectively. In compounds **1** and **3–6** the chemical shift ranges are much greater, *ca.* 35 to 48 ppm, with the weighted average shift moving significantly to high frequency, lying in the range −3.6 to −8.1 ppm. Clearly **1** and **3–6** are structurally quite different to both the 14,2,10- and 1,14,2,9-isomers.

Finally, a related brown compound, **2**, was isolated in trace amount from a complex mixture of products following an attempt to prepare a 14-vertex analogue of the 12- and 13-vertex cobaltacarborane sandwich compounds $[3,3'\text{-Co-}(1,2\text{-}closo\text{-}C_2B_9H_{11})_2]^-$,[18] $[3,3'\text{-Co-}(1,7\text{-}closo\text{-}C_2B_9H_{11})_2]^-$,[14] $[3,3'\text{-Co-}(1,12\text{-}closo\text{-}C_2B_9H_{11})_2]^-$,[19] $[4,4'\text{-Co-}(1,6\text{-}closo\text{-}C_2B_9H_{11})_2]^-$ [1b] and $[4,4'\text{-Co-}(1,10\text{-}closo\text{-}C_2B_9H_{11})_2]^-$ [20] part of which involved exposure of the reagents to EtOH. Although we never had sufficient amounts of **2** for NMR spectroscopy we were able to obtain a mass spectrum revealing a molecular ion consistent with the formula $(CpCo)_2C_2B_{10}H_{11}(OEt)$ and we were fortunate to grow a few single crystals of the compound.

Table 1 NMR spectroscopic chemical shifts in compounds **1** and **3–6**[a]

	^{1}H NMR				^{11}B NMR		
Compound	C_5H_5	C_5H_5	$C_{cage}H$	$C_{cage}H$	^{11}B pattern[b]	^{11}B range	$\langle\delta^{11}B\rangle$
1	5.29	4.89	3.10	2.57	1:2:2:1:1:1:1:1	13.9 to −28.2	−6.31
3	5.13(br)	5.13(br)	2.60	2.11	1:1:1:1:1:2:2:1	18.2 to −30.1	−3.62
4	5.46	5.07	3.80	2.89	1:1:2:1:1:1:1:1:1	7.0 to −27.7	−7.12
5	5.20	5.02	2.96	2.67	1:1:1:1:1:1:1:1:1:1	13.7 to −26.4	−6.64
6	5.21	5.04	2.71	2.25	1:2:1:1:1:1:1:1:1	8.4 to −28.3	−8.06

[a] Chemical shifts in ppm from $CDCl_3$ solutions at room temperature. [b] ^{11}B pattern from high frequency to low frequency.

Crystallographic studies – identification of the cage C atoms

Compounds **1–6** were studied by single-crystal X-ray diffraction. These studies establish that in all cases the heteroborane cage has a (distorted) bicapped hexagonal antiprismatic shape with one Co atom in a degree-6 (capping) site and the other at a degree-5 vertex in the hexagonal belt distant from the degree-6 metal. Consistent with empirical electron counting rules[3] (15 skeletal electron pairs for these 14-vertex *closo* clusters) and fully in agreement with the spectroscopic data described above, **1** and **3–6** are all formulated as $(CpCo)_2C_2B_{10}H_{12}$, whilst **2** is the compound $(CpCo)_2C_2B_{10}H_{11}(OEt)$. However, to establish the precise identities of compounds **1–6** it is essential that the positions of the cage C atoms are correctly identified, and for this we first made use of the vertex-to-centroid distance (VCD) method that we recently described.[12] Initially cage vertices were numbered according to Fig. 1a such that the Co atoms are at vertices 1 and 13. All other cage atoms were assumed to be B, and the structures were refined to convergence (including free refinement of cage H atoms). Using *OLEX2*[21] the cage centroid was calculated only from vertices 2,4,5,7,8,9,11 and 12, as shown in Fig. 1b. We omit the metal at vertex 1 and, for balance, the antipodal atom at vertex 14, to avoid compromising the centroid calculation. We also omit the metal at vertex 13 but, because the bicapped hexagonal antiprism does not contain a centre of inversion, we also omit vertex 10 (opposite 13 on the lower hexagonal belt) and, for balance, vertices 3 and 6 from the upper belt.

Table 2 lists the VCDs for compounds **1–6**. The shortest VCDs are those from vertex 14 but this is exceedingly unlikely to be the correct site of a cage C atom because the vertex is of degree-6.[8] These VCDs are artificially short because vertex 14 is pulled up towards the cage centroid simply by virtue of it capping a six atom face.[22] Notice that VCDs from the degree-6 Co atom at vertex 1 are consistently 0.3 Å shorter than those from the degree-5 Co atom at vertex 13 for the same reason. Ignoring, then, the VCDs from vertex 14, the two shortest VCDs are taken to be those from the cage C atoms, thus identifying the C atoms as being at vertices 2 & 10 (compound **1**), 2 & 11 (**2**), 2 & 9 (**3**), 2 & 6 (**4**), 2 & 4 (**5**) and 2 & 5 (**6**). In all cases except for compound **1** the two VCDs from the C atoms are at least 0.025 Å shorter than all VCDs from B atoms. However the situation is less clear in the case of **1** with VCDs from vertices 9 and 11 being close to that from vertex 2. Hence we have sought additional structural evidence for the cage C atom locations.

In 2002 we described an early alternative method of distinguishing between cage B and cage C atoms in (hetero)-carboranes, the B–H distance (BHD) method whereby we examined the vertex–H distances following refinement of all cage C or B atoms as B.[13] Under crystallographic refinement an H atom bonded to a vertex at which insufficient electron density

Table 2 Vertex-to-centroid distances (Å) in compounds **1–6**[a]

Vertex	**1**		**2**		**3**		**4**		**5**		**6**	
1	2.018(2)	Co1	2.020(3)	Co1	2.0047(7)	Co1	2.0304(18)	Co1	2.043(3)	Co1	2.0307(8)	Co1
2	$\underline{1.827(6)}$	C2	$\underline{1.774(9)}$	C2	$\underline{1.811(3)}$	C2	$\underline{1.820(5)}$	C2	$\underline{1.834(7)}$	C2	$\underline{1.8084(17)}$	C2
3	1.895(6)	B3	1.865(9)	B7	1.907(3)	B3	1.907(5)	B7	1.884(6)	B3	1.9005(19)	B7
4	1.935(7)	B4	1.916(10)	B6	1.941(2)	B4	1.931(6)	B6	$\underline{1.800(8)}$	C4	1.917(2)	B6
5	1.947(7)	B5	1.928(9)	B5	1.923(3)	B5	1.904(6)	B5	1.893(6)	B5	$\underline{1.797(3)}$	C5
6	1.908(7)	B6	1.904(9)	B4	1.894(2)	B6	$\underline{1.763(5)}$	C4	1.897(6)	B6	1.9021(18)	B4
7	1.917(6)	B7	1.940(9)	B3	1.905(2)	B7	1.896(5)	B3	1.883(8)	B7	1.9220(18)	B3
8	1.878(6)	B8	1.929(8)	B13	1.910(3)	B8	1.893(6)	B13	1.882(6)	B8	1.8809(18)	B13
9	1.829(7)	B9	1.870(10)	B12	$\underline{1.724(3)}$	C9	1.866(5)	B12	1.871(7)	B9	1.859(2)	B12
10	$\underline{1.758(8)}$	C10	1.876(10)	B11	1.880(3)	B10	1.882(5)	B11	1.892(6)	B10	1.900(2)	B11
11	1.830(7)	B11	$\underline{1.714(9)}$	C10	1.868(3)	B11	1.865(5)	B10	1.861(7)	B11	1.877(2)	B10
12	1.895(7)	B12	1.923(10)	B9	1.908(2)	B12	1.915(5)	B9	1.876(6)	B12	1.909(2)	B9
13	2.434(2)	Co13	2.375(4)	Co8	2.3792(10)	Co13	2.396(2)	Co8	2.372(2)	Co13	2.3723(8)	Co8
14	1.596(6)	B14	1.601(9)	B14	1.6016(18)	B14	1.591(5)	B14	1.589(5)	B14	1.5851(18)	B14

[a] Vertex numbers (left column) refer to the model before the C atoms were assigned; underlined entries identify C vertices; atom labels to the right of each entry are the final atom identifiers, shown in Fig. 2–7.

Table 3 Vertex–H distances (Å) in compounds **1–6**[a]

Vertex	**1**		**2**		**3**		**4**		**5**		**6**	
2	0.46(7)	0.99(6)	0.40(8)	0.86(7)	0.30(3)	0.95(2)	0.41(7)	0.95(5)	0.48(5)	0.97(5)	0.30(3)	0.99(2)
3	1.06(7)	1.05(5)	1.09(5)	1.04(5)	1.10(2)	1.09(2)	1.12(6)	1.04(5)	1.12(5)	1.14(5)	1.13(2)	1.11(2)
4	1.06(7)	1.05(7)	1.10(5)	1.18(7)	1.04(2)	1.04(2)	1.19(6)	1.09(5)	0.27(8)	1.04(5)	1.13(2)	1.11(2)
5	1.07(7)	1.08(6)	1.10(5)	1.10(6)	1.07(2)	1.06(2)	1.18(6)	1.19(5)	0.98(5)	1.18(5)	0.17(3)	1.03(2)
6	1.18(6)	1.19(6)	1.11(4)	1.14(6)	1.06(2)	1.05(2)	0.28(7)	0.96(5)	1.12(5)	1.09(5)	1.06(2)	1.06(2)
7	1.14(6)	1.13(5)	n/a	n/a	1.05(2)	1.09(2)	1.05(6)	1.09(5)	1.06(5)	1.04(5)	1.12(2)	1.12(2)
8	1.08(6)	1.08(6)	1.07(5)	0.92(6)	1.06(2)	1.06(2)	1.14(6)	1.15(5)	1.07(5)	1.04(5)	1.07(2)	1.07(2)
9	1.07(7)	1.04(7)	1.10(3)	1.07(6)	0.26(3)	0.99(2)	1.02(6)	0.90(5)	0.98(5)	1.08(5)	1.07(2)	1.08(2)
10	0.34(9)	0.86(8)	1.09(5)	1.02(7)	1.10(3)	1.10(2)	1.06(6)	1.13(5)	1.12(5)	1.18(5)	1.08(3)	1.07(2)
11	1.05(7)	1.05(7)	0.44(7)	0.89(7)	1.07(3)	1.06(2)	1.10(6)	1.10(5)	1.04(5)	1.01(5)	1.07(2)	1.08(2)
12	1.09(7)	1.09(7)	1.09(6)	1.09(6)	1.05(2)	1.07(2)	1.03(6)	1.05(5)	1.06(5)	1.06(5)	1.10(2)	1.12(2)
14	1.13(7)	1.13(7)	1.10(5)	1.10(6)	1.082(17)	1.09(2)	1.12(6)	1.12(5)	1.12(4)	1.10(4)	1.08(2)	1.08(2)

[a] For each structure the left hand entry is the vertex–H distance for the "all-B" model (where all non-metal vertices are assigned as B atoms); underlined entries identify C vertices. The right hand entry is the vertex–H distance following assignment of the cage C atoms.

Table 4 U_{eq} values (Å^2) for non-metal vertices refined as B in compounds **1–6**[a]

Vertex	**1**	**2**	**3**	**4**	**5**	**6**
2	0.0089(9)	0.014(2)	0.0095(4)	0.0076(8)	0.0119(11)	0.0096(3)
3	*0.0209(12)*	0.024(2)	0.0168(4)	0.0152(8)	*0.0240(13)*	*0.0166(3)*
4	0.0311(16)	0.035(2)	0.0182(4)	0.0162(9)	0.0275(15)	0.0206(3)
5	*0.0308(15)*	0.036(2)	0.0179(4)	0.0158(9)	0.0294(14)	0.0185(3)
6	*0.0237(13)*	0.029(2)	*0.0153(4)*	0.0110(9)	*0.0239(12)*	0.0192(3)
7	*0.0178(11)*	*0.021(2)*	*0.0135(4)*	0.0145(8)	*0.0186(13)*	*0.0151(3)*
8	*0.0163(10)*	0.027(2)	0.0175(4)	0.0143(8)	0.0278(13)	*0.0155(3)*
9	*0.0269(14)*	0.030(2)	0.0156(5)	0.0176(9)	0.0283(13)	0.0200(3)
10	0.0308(18)	0.040(2)	0.0216(5)	0.0172(9)	0.0316(12)	0.0241(4)
11	0.0340(17)	0.021(2)	0.0183(4)	0.0170(9)	0.0295(13)	0.0223(3)
12	*0.0231(12)*	0.030(2)	0.0158(4)	0.0149(8)	*0.0249(12)*	0.0188(3)
14	*0.0210(12)*	0.034(2)	0.0184(4)	0.0137(8)	*0.0181(7)*	*0.0169(3)*

[a] Vertex numbers (left column) refer to the model before the C atoms were assigned; underlined entries indicate C vertices identified by the VCD and BHD methods. *Italicised* entries show U_{eq} values for genuine B atoms that are ≤ those of atoms which are actually C.

has been specified will compensate by moving towards that vertex, affording an artificially short vertex–H bond. Thus short distances identify where in the cage the C atoms are. In Table 3 are the BHDs for compounds **1–6** calculated from such all-boron models (left hand entries). Whilst the true B–H distances are all around 1.1 Å, two distances in each structure are between 0.17(3) and 0.48(5) Å, and these identify *exactly the same* C atom positions as found by the VCD method in all compounds, including compound **1**. The right hand entries are the vertex–H distances once the cage C atoms have been identified as such and refinement completed; note that in all cases the artificially short "B"–H distances lengthen to sensible values when "B" is properly described as C. In some respects the BHD method might appear to be superior to the VCD method (at least in the case of compound **1**) but a drawback of the former is that it requires successful free crystallographic refinement of H atom positions, something which is not always practicable. Overall, we have always advocated a multi-modal approach to the problem of distinguishing cage B and cage C atoms in crystallographic studies of (hetero)carboranes, and for compounds **1–6** we can have complete confidence in the results from the VCD and the BHD methods since they are in perfect agreement with each other.

In this respect it is instructive to examine critically a third often-used method of C/B discrimination, that of using the refined (as B atoms) U_{eq} values. The argument here is that if the model describes insufficient electron density at a vertex (*i.e.* the vertex is really C not B) crystallographic refinement will compensate by U_{eq} being significantly smaller. In Table 4 we list the U_{eq} values for vertices 2–12 and 14 in compounds **1–6**. Only in the case of compound **4** are the two smallest U_{eq} values correctly associated with the C atom positions. In compound **2** the U_{eq} of vertex 7 is as small as that of vertex 11, and in all the other structures there are at least two U_{eq}(B) smaller than one U_{eq}(C). We have previously noted[12] the potential of adjacent heavy atoms to artificially suppress U_{eq}(B) and we see several examples of this in Table 4 (note the consistently low values of U_{eq} for B atoms at vertex 7, the other vertex in addition to vertex 2 that is bound to both metal vertices). Overall, we would argue strongly against using U_{eq} values to identify cage C atoms in (hetero)carboranes.

Having identified the cage C atoms by both the VCD and BHD methods the cages were renumbered according to accepted convention,[2] and this numbering is shown as the final column of Table 2. Thus compounds **1–6** are correctly described as 1,13-Cp_2-1,13,2,10-*closo*-$Co_2C_2B_{10}H_{12}$ (**1**), 1,8-Cp_2-

3-OEt-1,8,2,10-*closo*-$Co_2C_2B_{10}H_{11}$ (**2**), 1,13-Cp_2-1,13,2,9-*closo*-$Co_2C_2B_{10}H_{12}$ (**3**), 1,8-Cp_2-1,8,2,4-*closo*-$Co_2C_2B_{10}H_{12}$ (**4**), 1,13-Cp_2-1,13,2,4-*closo*-$Co_2C_2B_{10}H_{12}$ (**5**) and 1,8-Cp_2-1,8,2,5-*closo*-$Co_2C_2B_{10}H_{12}$ (**6**).

Fig. 2–7 show perspective views of compounds **1–6**, respectively, and Table 5 lists the lengths of the connectivities in the cobaltacarborane cages. The Co1–vertex distances span the range 2.08–2.19 Å, similar to that (2.13–2.19 Å) in a series of 1,14,2,9- and 1,14,2,10-$MCoC_2B_{10}$ species (M = Ru or Co) we recently studied (five compounds and nine crystallographically independent Co atoms).[5] In contrast the Co–vertex distances from the degree-5 Co atom in **1–6** are more widely spread, spanning the range 1.96–2.28 Å. C–B and B–B distances involving only degree-5 atoms are in the ranges 1.64–1.72 and 1.71–1.81 Å which are perfectly normal.[12] However, distances to the degree-6 atom B14 are considerably longer, as expected, with B–B in the range 1.85–1.98 Å and three C–B distances of 1.844(11), 1.904(3) and 2.015(9) Å.

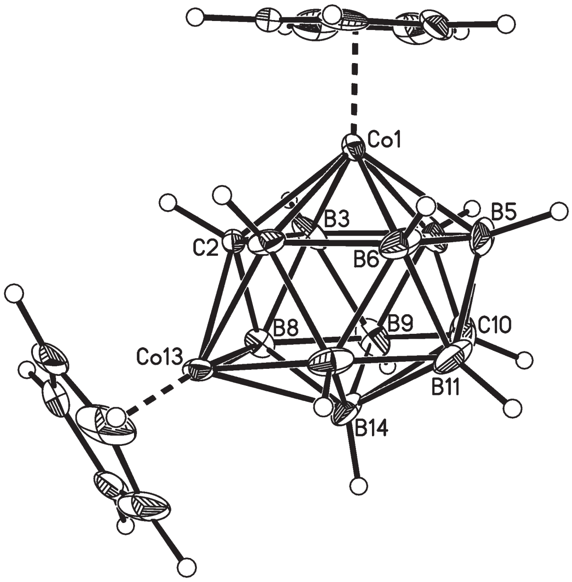

Fig. 2 Perspective view of compound **1**. Displacement ellipsoids are drawn at the 50% probability level except for hydrogen.

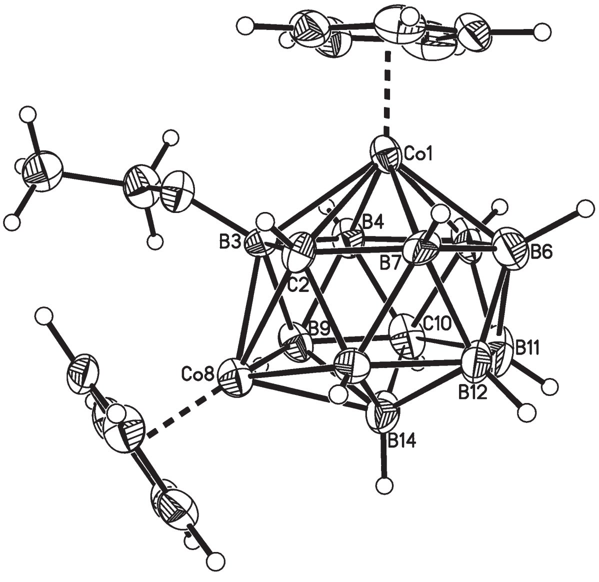

Fig. 3 Perspective view of compound **2**. Displacement ellipsoids as for **1**.

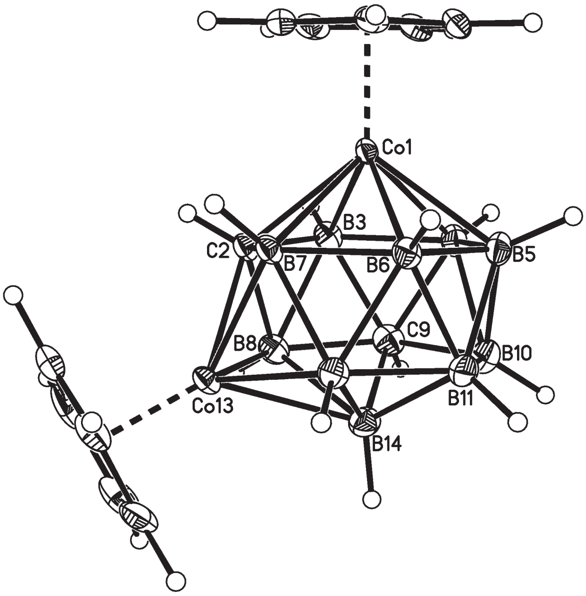

Fig. 4 Perspective view of compound **3**. Displacement ellipsoids as for **1**.

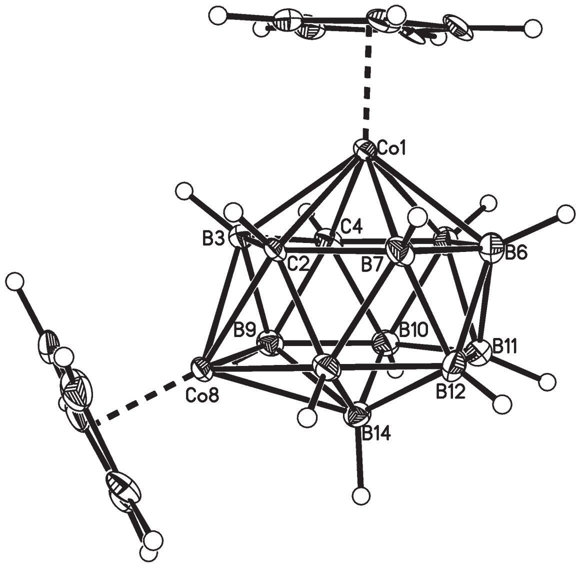

Fig. 5 Perspective view of compound **4**. Displacement ellipsoids as for **1**.

Mechanistic implications

It is rare to find transition metal atoms in degree-5 sites in bicapped hexagonal antiprismatic metallacarboranes. As already noted, the only currently known examples are the Ni atoms in two 8,1,2-NiC_2B_{11} species.[11] The Co8 and Co13 atoms

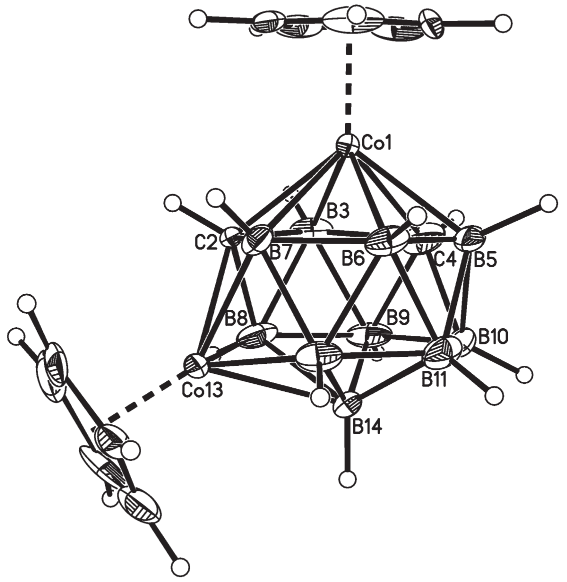

Fig. 6 Perspective view of compound **5**. Displacement ellipsoids as for **1**.

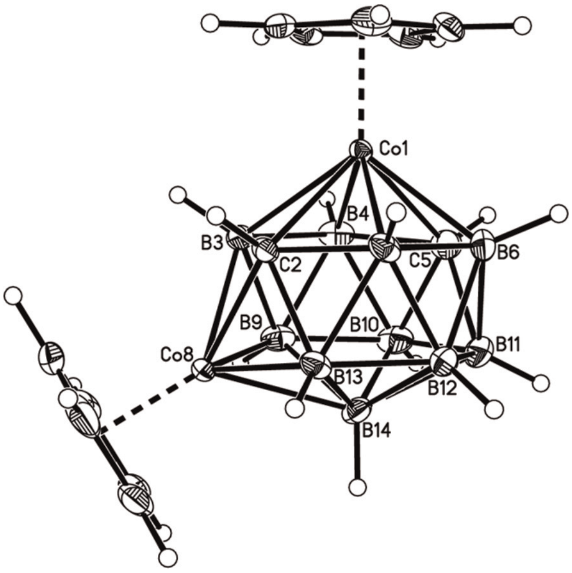

Fig. 7 Perspective view of compound **6**. Displacement ellipsoids as for **1**.

Table 5 Interatomic distances (Å) between the cage atoms of compounds **1–6** [a]

	1	**2**	**3**	**4**	**5**	**6**
1–2	**2.140(5)**	**2.138(7)**	**2.1210(16)**	**2.136(4)**	**2.127(5)**	**2.1403(13)**
1–3	**2.128(5)**	**2.199(7)**	**2.0842(19)**	**2.122(4)**	**2.125(5)**	**2.1569(16)**
1–4	**2.153(6)**	**2.127(8)**	**2.151(2)**	**2.114(4)**	**2.139(5)**	**2.1269(17)**
1–5	**2.153(6)**	**2.146(8)**	**2.1839(19)**	**2.161(4)**	**2.146(5)**	**2.1323(15)**
1–6	**2.148(6)**	**2.185(8)**	**2.1719(18)**	**2.175(4)**	**2.134(5)**	**2.1484(17)**
1–7	**2.153(5)**	**2.108(8)**	**2.1670(18)**	**2.153(5)**	**2.159(6)**	**2.1238(15)**
2–7	1.693(7)	1.693(9)	1.684(2)	1.677(6)	1.668(6)	1.677(2)
2–13	**2.031(4)**	1.719(10)	**2.0103(16)**	1.691(6)	**2.042(5)**	1.699(2)
2–8	1.715(7)	**2.063(7)**	1.704(3)	**2.023(4)**	1.712(8)	**2.0269(13)**
2–3	1.689(7)	1.663(10)	1.664(2)	1.691(6)	1.705(8)	1.678(2)
3–8	1.798(8)	**2.087(7)**	1.786(3)	**2.045(5)**	1.768(9)	2.0511(16)
3–9	1.784(9)	1.797(10)	1.698(3)	1.812(6)	1.771(8)	1.801(2)
3–4	1.752(9)	1.787(10)	1.796(3)	1.696(6)	1.692(9)	1.804(2)
4–9	1.768(9)	1.750(11)	1.708(3)	1.700(6)	1.704(9)	1.763(2)
4–10	1.665(11)	1.700(11)	1.762(3)	1.697(6)	1.686(7)	1.786(2)
4–5	1.803(10)	1.780(11)	1.742(3)	1.698(6)	1.685(7)	1.702(3)
5–10	1.692(8)	1.691(10)	1.767(3)	1.769(6)	1.760(8)	1.689(2)
5–11	1.755(11)	1.777(13)	1.773(3)	1.756(7)	1.733(9)	1.699(2)
5–6	1.760(10)	1.722(12)	1.786(3)	1.760(6)	1.742(9)	1.666(3)
6–11	1.805(9)	1.733(12)	1.774(3)	1.757(7)	1.779(8)	1.771(3)
6–12	1.778(9)	1.760(12)	1.760(3)	1.774(7)	1.767(9)	1.765(2)
6–7	1.776(9)	1.780(11)	1.793(3)	1.791(7)	1.769(9)	1.789(2)
7–12	1.793(8)	1.775(11)	1.793(3)	1.757(6)	1.782(9)	1.769(2)
7–13	**2.058(6)**	1.799(10)	**2.0585(18)**	1.762(6)	**2.051(7)**	1.781(2)
8–13	**1.992(5)**	**1.998(8)**	**1.9597(19)**	**2.003(4)**	**1.983(7)**	**1.9869(16)**
8–14	1.862(8)	**2.192(8)**	1.973(3)	**2.284(4)**	1.954(7)	**2.2412(16)**
8–9	1.730(8)	**2.005(8)**	1.653(3)	**2.008(5)**	1.727(9)	**2.0247(18)**
9–14	1.932(9)	1.979(12)	1.904(3)	1.925(6)	1.892(8)	1.947(2)
9–10	1.638(9)	1.671(10)	1.664(3)	1.721(7)	1.726(9)	1.741(3)
10–14	2.015(9)	1.844(11)	1.925(3)	1.883(7)	1.905(5)	1.883(2)
10–11	1.637(11)	1.646(11)	1.725(3)	1.728(7)	1.699(10)	1.718(3)
11–14	1.893(9)	1.890(12)	1.858(3)	1.931(6)	1.897(8)	1.913(2)
11–12	1.758(10)	1.714(12)	1.744(3)	1.735(7)	1.744(9)	1.719(3)
12–14	1.858(8)	1.903(11)	1.893(3)	1.921(6)	1.930(8)	1.937(3)
12–13	**2.029(6)**	1.747(11)	**2.0360(19)**	1.730(6)	**2.002(6)**	1.723(2)
13–14	**2.213(6)**	1.950(12)	**2.224(2)**	1.937(6)	**2.266(3)**	1.937(2)

[a] **Bold** entries, distances involving metal vertex; underlined entries, distances involving C vertex.

in compounds **1–6** represent further examples. We believe that the unexpected finding of these degree-5 Co atoms, coupled with the unambiguous location of the cage C atoms, allows comment on the possible mechanisms of formation of **1–6**.

Compounds **1** and **3** were both isolated from reactions in which 4,1,8- and 4,1,12-CoC_2B_{10} 13-vertex cobaltacarboranes were treated firstly with large excess of Na and then with Na[Cp] and $CoCl_2$. The sodium reduction would have been expected to open up the cobaltacarborane to generate a *nido* dianion with a 6-atom open face opposite the original metal atom which would then have been capitated by the second metal and, indeed, 1,14,2,9- and 1,14,2,10-$Co_2C_2B_{10}$ species, respectively, were formed in these reactions in significantly greater yields than were **1** and **3**. Nevertheless, it remains possible that **1** and **3** were produced *via* reduction to an alternative *nido* intermediate with a 5-atom open face which was subsequently capitated. However, compounds **2**, **4**, **5** and **6** were produced from reactions that did *not* involve 2-e reduction and subsequent metallation of a 13-vertex CoC_2B_{10} precursor and we have ultimately also produced **1** not *via* 2-e reduction/metallation. We believe that the formation of compounds **1–6** may be rationalised instead by *direct electrophilic insertion*, and that the isomeric forms of the products are readily understood in terms of this process.

Direct electrophilic insertion, a term coined by Kudinov and co-workers,[23] involves the polyhedral expansion of an anionic *closo* metallacarborane by its reaction with a cationic metal fragment. It is a complement to *direct nucleophilic insertion* of zerovalent metal fragments into neutral *closo* carboranes and metallacarboranes developed by Stone, Green and co-workers several decades ago,[24] with both approaches offering interesting alternatives to the traditional method of polyhedral expansion *via* the two-stage approach of 2-e reduction followed by metallation.

We illustrate the possibility of direct electrophilic insertion as the mechanism by which the present compounds are afforded with respect to compounds **4** and **5**. We first isolated **4** and **5** as trace co-products in the synthesis of 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$. This neutral Co^{III} species is prepared by reaction between $[7,9$-*nido*-$C_2B_{10}H_{12}]^{2-}$, Na[Cp] and $CoCl_2$. The initial product of the reaction is the anionic Co^{II} species [4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}]^-$, subsequently oxidised to the final product by O_2.[1] However, Na[Cp] and $CoCl_2$ (together a source of the $\{CoCp^+\}$ fragment) are used in excess in these reactions,[1] so it is possible to envisage reaction between [4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}]^-$ and $\{CoCp^+\}$ to afford $(CpCo)_2C_2B_{10}H_{12}$ products by direct electrophilic insertion. Fig. 8 shows the docosahedral shape and numbering system of 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ and we presume that essentially the same shape is preserved in the anion.

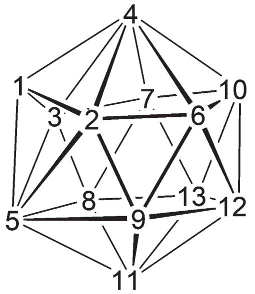

Fig. 8 The docosahedron and numbering scheme.

Docosahedral 4,1,*x*-MC_2B_{10} metallacarboranes (x = 6, 8, 10, 11, 12) are known for a wide variety of metal types[25] and structural determinations consistently shown long connectivities to the degree-6 atom B5, particularly the B2–B5, B3–B5, B/C8–B5 and B9–B5 connectivities.[25b–f,26] It is therefore reasonable to imagine attack by the $\{CoCp^+\}$ fragment on both the forward (B2B5B9) and back (B3B5B8) triangles of [4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}]^-$ with the new metal fragment breaking the presumably relatively weak B2–B5[27] and B9–B5 connectivities and bonding to the 1-2-9-11-5 open face so created, or breaking the B3–B5 and B8–B5 connectivities and bonding to the 1-3-8-11-5 face. The result of the former insertion is compound **4**, and the result of the latter insertion is compound **5**. The process of forming **4** from [4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}]^-$ is perhaps best illustrated in the form of a Schlegel diagram, Fig. 9. In this the

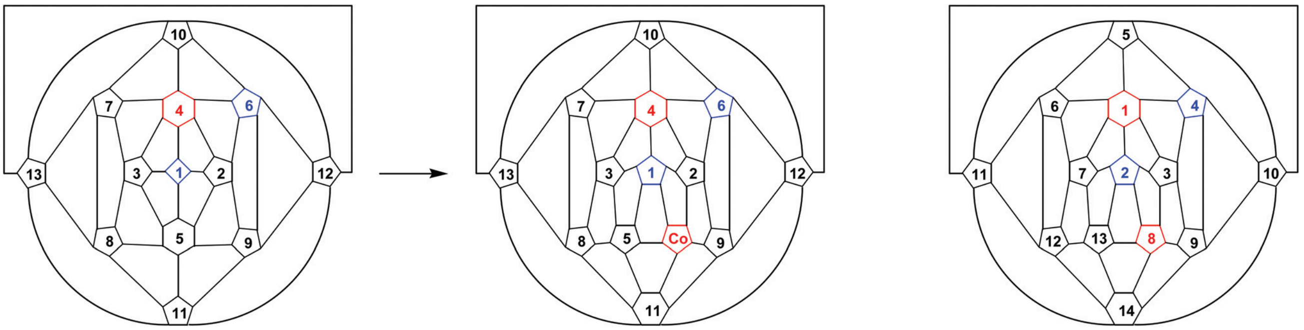

Fig. 9 Schlegel diagrams showing schematically the transformation from a 4,1,6-MC_2B_{10} docosahedron (left) to a bicapped hexagonal antiprism (centre) by the direct insertion of a new vertex (labelled Co) into the 1-2-9-11-5 face. Squares, pentagons and hexagons are used to represent degree-4, degree-5 and degree-6 vertices, respectively. To help follow the process atom numbering is maintained between left and centre diagrams, but on the right the product is renumbered according to convention, and is shown to be a 1,8,2,4-$MCoC_2B_{10}$ bicapped hexagonal antiprism (*i.e.* compound **4**).

metal atoms are shown in red and the cage C atoms in blue, and squares, pentagons and hexagons are used to denote degree-4, -5 and -6 vertices, respectively. The process of breaking the B2–B5 and B9–B5 connectivities and inserting the new {CoCp$^+$} fragment into the pentagonal face so created has the effect of increasing the degrees of vertices 1 and 11 by one unit and decreasing the degree of vertex 5 by one unit. The degrees of vertices 2 and 9 remain constant. The product, when labelled according to convention,[2] would be 1,8-Cp_2-1,8,2,4-*closo*-$Co_2C_2B_{10}H_{12}$, *i.e.* compound **4**.

In an attempt to support the possibility of direct electrophilic insertion, 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ was reduced with strictly one mole of electrons (sodium naphthalenide) and treated with Na[Cp] and $CoCl_2$. Compounds **4** and 1,8-Cp_2-1,8,2,6-*closo*-$Co_2C_2B_{10}H_{12}$, **5**, were isolated (albeit in very low yields) following work-up.

Direct electrophilic attack of {CoCp$^+$} on [4-Cp-4,1,10-*closo*-$CoC_2B_{10}H_{12}$]$^-$ would be expected to afford only one product, 1,8-Cp_2-1,8,2,5-*closo*-$Co_2C_2B_{10}H_{12}$, **6**, because of the C_s symmetry of the precursor (the 1-2-9-11-5 and 1-3-8-11-5 pentagons are equivalent). Compound **6** was first isolated during the synthesis of 4-Cp-4,1,10-*closo*-$CoC_2B_{10}H_{12}$,[17] but again can be deliberately prepared by 1-e reduction of 4-Cp-4,1,10-*closo*-$CoC_2B_{10}H_{12}$ followed by treatment with Na[Cp]/$CoCl_2$. Similarly, 1,13-Cp_2-1,13,2,10-*closo*-$Co_2C_2B_{10}H_{12}$, **1**, can be deliberately prepared by 1-e reduction and subsequent metallation of 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$, a result which is fully consistent with its formation by direct electrophilic insertion into the 1-3-8-11-5 pentagonal face of the 4,1,12-CoC_2B_{10} precursor. Insertion into the 1-2-9-11-5 pentagon might also be expected to occur but we have not yet isolated the product of such an insertion, 1,8-Cp_2-1,8,2,10-*closo*-$Co_2C_2B_{10}H_{12}$, from reduction and metallation of 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$. However, a derivative of this "missing" product, 1,8-Cp_2-3-OEt-1,8,2,10-*closo*-$Co_2C_2B_{10}H_{11}$, compound **2**, was isolated in low yield from a reaction in which 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ was reduced, treated with $CoCl_2$, and subjected to [K(18-crown-6)]Br in EtOH. The EtOH is clearly the source of the ethoxide substituent on B3 and we presume that the addition Cp ligand on Co8 was scavenged from another molecule of cobaltacarborane. Notwithstanding these complications it is possible that compound **2** was also formed by a direct electrophilic insertion reaction.

Similarly, direct electrophilic insertion of {CoCp$^+$} into [4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$]$^-$ might be expected to lead to two products. Attack on the 1-2-9-11-5 pentagon of the 13-vertex precursor would result in a 1,13,2,9-$Co_2C_2B_{10}$ 14-vertex species, and indeed 1,13-Cp_2-1,13,2,9-*closo*-$Co_2C_2B_{10}H_{12}$, **3**, was recovered as a minor co-product during the attempted 2-e reduction then metallation of 4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$. Alternatively attack on the 1-3-8-11-5 pentagon would lead to 1,8-Cp_2-1,8,2,9-*closo*-$Co_2C_2B_{10}H_{12}$, but this has not so far been isolated.

In Table 6 we summarise the expected products from direct electrophilic insertion of an {M$'^+$} fragment into anionic 13-vertex metallacarboranes [4,1,*x*-MC_2B_{10}]$^-$ and list the examples of such insertions that are described herein. Although one example of a 4,1,11-MC_2B_{10} metallacarborane is known[26e] we do not expect that direct electrophilic insertion into the anionic form of this will be very likely since the "product" would have a 1,8,2,14-MM′C_2B_{10} architecture with a cage C atom in the very unfavoured[8] degree-6 vertex 14.

Table 6 Expected products from direct electrophilic insertion of {M$'^+$} into 13-vertex precursors [4,1,*x*-MC_2B_{10}]$^-$

13-Vertex precursor	14-Vertex product	Example
[4,1,6-MC_2B_{10}]$^-$	1,8,2,4-MM′C_2B_{10}	4
	1,13,2,4-MM′C_2B_{10}	5
[4,1,8-MC_2B_{10}]$^-$	1,8,2,9-MM′C_2B_{10}	—
	1,13,2,9-MM′C_2B_{10}	3
[4,1,10-MC_2B_{10}]$^-$	1,8,2,5-MM′C_2B_{10}	6
[4,1,12-MC_2B_{10}]$^-$	1,8,2,10-MM′C_2B_{10}	2
	1,13,2,10-MM′C_2B_{10}	1
[4,1,11-MC_2B_{10}]$^-$	1,8,2,14-MM′C_2B_{10}	Unlikely (see text)

Conclusions

A series of six asymmetric, 14-vertex, $(CpCo)_2C_2B_{10}$ dicobaltacarboranes with bicapped hexagonal antiprismatic cage structures in which one metal atom is at the capping vertex 1 and the other is at a degree-5 vertex (8 or 13) in the distant hexagonal belt, have been isolated. The VCD and BHD methods have been used to distinguish between cage B and cage C atoms in the crystallographically-determined structures, both leading to the same clear conclusions and thus allowing the identities of these species to be established unambiguously.[28] The isomeric forms of the six compounds have been tentatively rationalised in terms of direct electrophilic insertion of a {CoCp$^+$} fragment cation into a [$CpCoC_2B_{10}$]$^-$ monoanion.

Experimental

Synthesis

Experiments were performed under dry, oxygen free N_2, 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 (CH_2Cl_2; CaH_2 : 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 F_{254} glass plates. NMR spectra at 400.1 MHz (^1H) and 128.4 MHz (^{11}B) or 300.1 MHz (^1H) and 96.3 MHz (^{11}B) were recorded on Bruker AVIII-400 or AVIII-300 spectrometers, respectively, from $CDCl_3$ solutions at room temperature. Electron ionisation mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. The starting materials 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$,[1b] 4-Cp-4,1,10-*closo*-$CoC_2B_{10}H_{12}$ [17] and 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ [1b,17] were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially. Low yields of all the compounds isolated precluded elemental analyses.

1,13-Cp$_2$-1,13,2,10-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (1). A solution of 4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{12}$ (0.24 g, 0.84 mmol) in THF (30 mL) was stirred overnight with sodium (0.23 g, 10 mmol) and naphthalene (0.05 g, catalytic). The resultant solution was transferred *via* cannula to a second Schlenk tube, cooled to 0 °C, to which was then added Na[Cp] (3 mL of a 1 M solution, 3 mmol) and CoCl$_2$ (0.45 g, 3.5 mmol). The reaction mixture was allowed to warm to room temperature, stirred overnight, and then aerially oxidised for 1 h and filtered through silica eluting with CH$_2$Cl$_2$. The brown filtrate was concentrated *in vacuo* and purified by TLC using a 3 : 2 CH$_2$Cl$_2$: 40–60 petroleum ether eluent. A complex mixture of at least nine mobile bands were observed including, in order of elution, the following compounds; 4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{12}$ (starting material), 1,13-Cp$_2$-1,13,2,10-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (R_f 0.68, brown, 0.012 g, 3.6%, **1**), 3-Cp-3,1,2-*closo*-CoC$_2$B$_9$H$_{11}$ (identified spectroscopically[14]), 1,14-Cp$_2$-1,14,2,10-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (identified spectroscopically[4]) and 4,5-Cp$_2$-4,5,1,6-*closo*-Co$_2$C$_2$B$_9$H$_{11}$ (identified spectroscopically[15]). For **1**: ^{1}H NMR: δ 5.29 (s, 5H, C$_5$*H*$_5$), 4.89 (s, 5H, C$_5$*H*$_5$), 3.10 (br s, 1H, C$_{cage}$*H*), 2.57 (br s, 1H, C$_{cage}$*H*). ^{11}B{^{1}H} NMR: δ 13.9 (1B), 5.2 (2B), −2.1 (2B), −5.7 (1B), −6.7 (1B), −15.8 (1B), −26.8 (1B), −28.2 (1B). EIMS: envelopes centred on *m*/*z* 392 (M$^+$), 329 (M$^+$ − Cp).

1,8-Cp$_2$-3-OEt-1,8,2,10-*closo*-Co$_2$C$_2$B$_{10}$H$_{11}$ (2). A solution of 4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{12}$ (0.50 g, 1.75 mmol) in THF (50 mL) was stirred overnight with sodium (0.25 g, 10.9 mmol) and naphthalene (*ca.* 0.015 g, catalytic). The resultant solution was transferred *via* cannula to a second Schlenk tube containing a frozen solution of CoCl$_2$ (0.12 g, 0.93 mmol) in THF. The mixture was allowed to warm to room temperature and stirred overnight, followed by aerial oxidation and filtration through Celite®. The solvent was changed to EtOH (20 mL) and to the solution was added a solution of [K(18-crown-6)]Br (*ca.* 1 mmol) in EtOH (10 mL). Following concentration the oily brown residue was subjected to TLC (3 : 2 CH$_2$Cl$_2$: 40–60 petroleum ether). A complex mixture of six mobile bands was observed including 4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{12}$ (R_f 0.86, starting material), 1,13-Cp$_2$-1,13,2,10-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (R_f 0.75, identified spectroscopically, **1**), 2-OEt-4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{11}$ (R_f 0.39, identified crystallographically[29]) and 1,8-Cp$_2$-3-OEt-1,8,2,10-*closo*-Co$_2$C$_2$B$_{10}$H$_{11}$ (R_f 0.21, brown, 0.006 g, *ca.* 1%, **2**). For **2**: EIMS: envelope centred on *m*/*z* 437 (M$^+$).

1,13-Cp$_2$-1,13,2,9-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (3). Compound **3** was isolated as a minor co-product (R_f 0.50, brown, 0.015 g, 2%) during the synthesis of 1,14-Cp$_2$-1,14,2,9-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ *via* reduction and metallation of 4-Cp-4,1,8-*closo*-CoC$_2$B$_{10}$H$_{12}$.[4,5] For **3**: ^{1}H NMR: δ 5.13 (br s, 10H, C$_5$*H*$_5$), 2.60 (br s, 1H, C$_{cage}$*H*), 2.11 (br s, 1H, C$_{cage}$*H*). ^{11}B{^{1}H} NMR: δ 18.2 (br, 1B), 8.8 (br, 1B), 6.6 (br, 1B), 2.8 (br, 1B), −2.5 (1B), −5.1 (br, 2B), −14.9 (2B), −30.1 (1B). EIMS: envelope centred on *m*/*z* 392 (M$^+$).

1,8-Cp$_2$-1,8,2,4-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (4) and 1,13-Cp$_2$-1,13,2,4-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (5). Compounds **4** and **5** were first isolated in trace amounts as very minor co-products in the synthesis of Hawthorne's compound[1b] 4-Cp-4,1,6-*closo*-CoC$_2$B$_{10}$H$_{12}$ in our laboratory. We have subsequently prepared these compounds deliberately by direct electrophilic insertion as follows: a THF (20 mL) solution of Na[C$_{10}$H$_{10}$] (1.12 mmol) was prepared by reduction of naphthalene (0.143 g, 1.12 mmol) with sodium metal (0.129 g, 5.59 mmol, excess) and transferred *via* filter stick to a frozen solution of 4-Cp-4,1,6-*closo*-CoC$_2$B$_{10}$H$_{12}$ (0.30 g, 1.12 mmol) in THF (10 mL). On warming to room temperature a deep red solution was produced. Na[Cp] (2.9 mL of a 2 M solution, 5.8 mmol) and CoCl$_2$ (0.93 g, 7.2 mmol) were added at 0 °C and the reaction mixture stirred overnight at room temperature. The resulting brown suspension was filtered through silica, concentrated and purified by initial column chromatography on silica then TLC (4 : 1 CH$_2$Cl$_2$: 40–60 petroleum ether) to afford 1,13-Cp$_2$-1,13,2,4-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (R_f 0.65, **5**) and 1,8-Cp$_2$-1,8,2,4-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (R_f 0.58, **4**) as brown solids (on removal of solvent) in low yields (*ca.* 2 mg, 0.5%). For **4**: ^{1}H NMR: δ 5.46 (s, 5H, C$_5$*H*$_5$), 5.07 (s, 5H, C$_5$*H*$_5$), 3.80 (br s, 1H, C$_{cage}$*H*), 2.89 (br s, 1H, C$_{cage}$*H*). ^{11}B{^{1}H} NMR: δ 7.0 (1B), 3.6 (1B), 2.0 (2B), −4.2 (1B), −5.5 (1B), −10.2 (1B), −18.3 (1B), −19.9 (1B), −27.7 (1B). EIMS: envelopes centred on *m*/*z* 392 (M$^+$), 268 (M$^+$ − CpCo). For **5**: ^{1}H NMR: δ 5.20 (s, 5H, C$_5$*H*$_5$), 5.02 (s, 5H, C$_5$*H*$_5$), 2.96 (br s, 1H, C$_{cage}$*H*), 2.67 (br s, 1H, C$_{cage}$*H*). ^{11}B{^{1}H} NMR: δ 13.7 (1B), 11.5 (1B), 2.0 (1B), −0.7 (1B), −5.3 (1B), −8.2 (1B), −13.8 (1B), −18.0 (1B), −21.2 (1B), −26.4 (1B). EIMS: envelopes centred on *m*/*z* 392 (M$^+$), 268 (M$^+$ − CpCo).

1,8-Cp$_2$-1,8,2,5-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (6). Similarly, compound **6** was first isolated in trace amount during the synthesis of 4-Cp-4,1,10-*closo*-CoC$_2$B$_{10}$H$_{12}$,[17] and again we have subsequently prepared it deliberately: In a similar manner to that described above, 4-Cp-4,1,10-*closo*-CoC$_2$B$_{10}$H$_{12}$ (0.30 g, 1.12 mmol) in THF (10 mL) was reduced with Na[C$_{10}$H$_{10}$] (1.12 mmol) in THF (20 mL) then treated with Na[Cp] (2.9 mL of a 2 M solution, 5.8 mmol) and CoCl$_2$ (0.93 g, 7.2 mmol) at 0 °C. On work-up as before the brown product 1,8-Cp$_2$-1,8,2,5-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ (**6**) was isolated following final TLC (3 : 2 CH$_2$Cl$_2$: 40–60 petroleum ether, R_f 0.51) in low yield (*ca.* 10 mg, 2%). ^{1}H NMR: δ 5.21 (s, 5H, C$_5$*H*$_5$), 5.04 (s, 5H, C$_5$*H*$_5$), 2.71 (br s, 1H, C$_{cage}$*H*), 2.25 (br s, 1H, C$_{cage}$*H*). ^{11}B{^{1}H} NMR: δ 8.4 (1B), 3.0 (2B), −0.7 (1B), −2.4 (1B), −9.9 (1B), −14.8 (1B), −17.7 (1B), −21.2 (1B), −28.3 (1B). EIMS: envelopes centred on *m*/*z* 392 (M$^+$), 268 (M$^+$ − CpCo).

Deliberate synthesis of 1. Similarly, 4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{12}$ (0.30 g, 1.12 mmol) in THF (10 mL) was reduced with Na[C$_{10}$H$_{10}$] (1.12 mmol) in THF (20 mL) then treated with Na[Cp] (2.9 mL of a 2 M solution, 5.8 mmol) and CoCl$_2$ (0.93 g, 7.2 mmol) at 0 °C. On work-up as above the brown product **1** was isolated following final TLC (3 : 2 CH$_2$Cl$_2$: 40–60 petroleum ether, R_f 0.51) in low yield (*ca.* 5 mg, 1%) and identified spectroscopically.

Crystallography

Diffraction-quality crystals of compounds **1–6** were grown by slow diffusion of a CH$_2$Cl$_2$ solution of the appropriate compound and 40–60 petroleum ether at −30 °C. Intensity data

Table 7 Crystallographic data

	1	2	3	4	5	6
Formula	$C_{12}H_{22}B_{10}Co_2$	$C_{14}H_{26}B_{10}Co_2O$	$C_{12}H_{22}B_{10}Co_2$	$C_{12}H_{22}B_{10}Co_2 \cdot CH_2Cl_2$	$C_{12}H_{22}B_{10}Co_2$	$C_{12}H_{22}B_{10}Co_2$
M	392.26	436.31	392.26	477.18	392.26	392.26
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$Pbca$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1$	$Pbca$
a/Å	14.9436(12)	10.813(4)	7.4419(4)	7.6842(8)	7.7083(6)	14.8157(18)
b/Å	13.3925(10)	13.146(6)	10.1756(6)	11.0372(11)	11.3413(9)	13.3179(18)
c/Å	16.7499(13)	13.159(5)	12.2035(7)	11.7319(12)	9.9968(8)	16.818(2)
α (°)			90.288(3)	93.130(5)		
β (°)		96.620(16)	103.174(3)	95.145(5)	109.900(4)	
γ (°)			111.022(3)	98.582(5)		
U/Å^3	3352.2(5)	1858.1(13)	836.07(8)	977.56(17)	821.76(11)	3318.4(8)
Z	8	4	2	2	2	8
F(000)/e	1584	888	396	480	396	1584
D_{calc}/Mg m^{-3}	1.554	1.560	1.558	1.621	1.585	1.570
μ(Mo-K$_\alpha$)/mm^{-1}	1.966	1.786	1.971	1.965	2.005	1.986
θ_{max} (°)	28.26	23.25	29.97	31.29	30.98	35.17
Data measured	93 508	20 203	16 116	31 755	16 215	98 827
Unique data	4134	2651	4740	6087	4694	7274
R_{int}	0.0959	0.1138	0.0280	0.0847	0.0337	0.0424
R, wR_2 (obs. data)	0.0611, 0.1447	0.0450, 0.0898	0.0291, 0.0669	0.0392, 0.1029	0.0469, 0.1026	0.0323, 0.0791
S	1.351	0.988	1.020	1.192	1.029	1.024
Variables	253	278	254	281	254	253
Flack parameter					0.21(3)	
E_{max}, E_{min}/e Å^{-3}	0.637, −0.857	0.480, −0.514	0.558, −0.475	1.211, −0.856	1.122, −1.202	0.906, −1.190

were collected on a Bruker X8 APEX2 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. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.[30] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97).[31]

Cage vertices were numbered as in Fig. 1a with the two Co atoms at positions 1 and 13. Initially all non-metal cage vertices were treated a B atoms. An ethoxide group as identified attached to vertex 7 in compound **2**. With free (positional) refinement of cage H atoms all six structures were refined to convergence and the structures analysed by the VCD and BHD methods to locate the cage C atoms, as described in Results and discussion. Once this was done it was necessary to renumber some of the structures to concur with accepted convention.[2] Finally, all structures were refined to full convergence.

The refinements of structures **3**, **4** and **5** were as two component twins, whilst all other structures were refined conventionally. Non-cage H atoms were set in idealised positions and allowed to ride on their bound C atom, with C–H = 1.00 Å (Cp), 0.99 Å (CH_2) or 0.98 Å (CH_2). 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 7 contains further experimental details. Compound **2** has an OEt group bound to one B atom and compound **4** co-crystallises with one molecule of CH_2Cl_2 solvent, but **1**, **3**, **5** and **6** only differ in having the cage C atoms in different cage vertices. In that respect it is perhaps surprising that only two of these compounds, **1** and **6**, are crystallographically isomorphous. Intermolecular contacts of possible significance are listed in the ESI,§ but in essence all six compounds crystallise as individual molecules.

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27 Supporting evidence for the relative weakness of B2–B5 in 4,1,6-MC_2B_{10} species is the well-known double diamond-square-diamond process (involving breaking this connectivity) which accounts for the functionality of these species in solution at room temperature. See ref. 1, 25*d*, 26*b*, *c*, *f*, *h*.

28 One referee commented on the relatively imprecise original structural determination of compound **6** and concluded "for this structure we cannot distinguish between B and C in the [metalla]carborane cage". In response we recollected crystallographic data from a second crystal of better quality (all data in the paper relating to compound **6** are from this second determination). However, it is apparent from analysis of the VCD, BHD and U_{eq} data that exactly the same conclusions regarding C atom positions in compound 6 are reached using both the relatively imprecise and the relatively precise data. See ESI§ for full details.

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