13-VERTEX CARBACOBALTABORANES: SYNTHESIS AND MOLECULAR STRUCTURES OF THE 4,1,6-, 4,1,8- AND 4,1,12-ISOMERS OF $Cp^*CoC_2B_{10}H_{12}$

Anthony BURKE, Ruaraidh McINTOSH, David ELLIS, Georgina M. ROSAIR and Alan J. WELCH[1,*]

Department of Chemistry, Heriot–Watt University, Edinburgh EH14 4AS, U.K.; e-mail: [1] a.j.welch@hw.ac.uk

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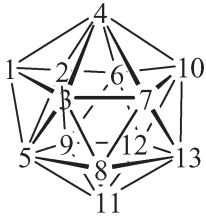
Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his many outstanding contributions to boron chemistry.

Attempted crystallographic studies of the known compounds 4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ and 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ were frustrated because of disorder which was impossible satisfactorily to model. Thus the family of Cp* compounds 4-Cp*-4,1,6-*closo*-$CoC_2B_{10}H_{12}$, 4-Cp*-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ and 4-Cp*-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ were prepared. The ^{11}B NMR spectroscopic properties of these compounds are closely similar to those of their Cp analogues. All three compounds were studied crystallographically. The 4,1,8- and 4,1,12-species are isomorphous and partially disordered, however the disorder was successfully modelled and structural analyses of 4,1,8- and 4,1,12-MC_2B_{10} compounds are reported for the first time. A new technique for distinguishing between cage C and B atoms in crystallographic study of (hetero)carboranes is reported. The 12-vertex compound 3-Cp*-3,1,2-*closo*-$CoC_2B_9H_{11}$ is formed as a minor co-product along with 4-Cp*-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ and is believed to result from partial degradation of the latter. The 12-vertex species has also been subjected to crystallographic analysis.
Keywords: Carboranes; Metallacarboranes; Supraicosahedral; Crystallography; X-Ray diffraction; Cobalt; Cyclopentadienyl ligands.

The development of (transition)metallacarborane chemistry over the last 35 years[1] has focussed heavily on icosahedral MC_2B_9 species, usually afforded by metallation of a nido C_2B_9 carborane dianion. The chemistry of sub-icosahedral metallacarboranes is less explored but is still appreciable[2]. In contrast, the field of supraicosahedral metallacarboranes is relatively poorly developed. There are only a few tens of examples of closed 13-vertex species, mainly of the MC_2B_{10} type[3] but occasionally of the $M_2C_2B_9$ type[4],

and only three examples of closed 14-vertex $M_2C_2B_{10}$ species[5], in the available literature.

13-Vertex closo metallacarboranes are based on the docosahedron (**I**). As predicted[6] for the (unknown) parent hydroborate $[B_{13}H_{13}]^{2-}$, this polyhedron has C_{2v} symmetry with the C_2 axis passing from the unique, 4-connected



(**I**)

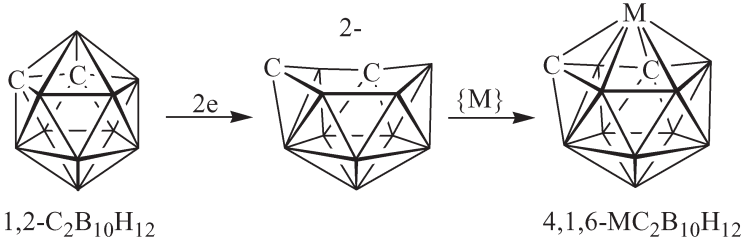
(with respect to the polyhedron) vertex 1 to the mid point of the 12–13 connectivity. Vertices 4 and 5 are both 6-connected. All structurally-characterised transition metal MC_2B_{10} species have the metal atom occupying the high-connected vertex 4 and one C atom occupying the low-connected vertex 1, consistent with their (relative to B) low and high electronegativities respectively. Assuming this, there are, however, no fewer than seven possible positions for the second C atom, giving rise to the following MC_2B_{10} isomers:

4,1,2-MC_2B_{10}	4,1,5-MC_2B_{10}	4,1,6-MC_2B_{10}	4,1,8-MC_2B_{10}
4,1,10-MC_2B_{10}	4,1,11-MC_2B_{10}	4,1,12-MC_2B_{10}	

To our knowledge there is only one reported example of a 4,1,2-MC_2B_{10} species, produced by direct insertion of a Co^0 nucleophile into 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ [7]. In contrast, when 13-vertex MC_2B_{10} species are produced by metallation of $[C_2B_{10}]^{2-}$ species the kinetic product is the 4,1,6-isomer, since 2e reduction of 1,2-*closo*-C_2B_{10} precursors immediately affords the carbon separated [7,9-*nido*-C_2B_{10}] dianion (Scheme 1). Thermolysis of 4,1,6-MC_2B_{10} metallacarboranes produces, successively, 4,1,8-MC_2B_{10} and 4,1,12-MC_2B_{10} isomers[3a,3b], but there are no current reports of 4,1,5-MC_2B_{10} (not surprising since this would involve a 6-connected C atom), 4,1,10- or 4,1,11-MC_2B_{10} metallacarboranes.

In terms, therefore, of the synthesis and characterisation of new isomers and of detailed studies of the mechanisms of rearrangements between different isomers, the supraicosahedral carbametallaboranes offer considerable

scope for interesting new chemistry. In reviewing the field we were surprised to discover that there are no reports of structural studies of a homologous series of isomers of the 4,1,6-, 4,1,8- and 4,1,12-type. Indeed, there do not even appear to be reports of structural studies on isolated 4,1,8- or 4,1,12-MC_2B_{10} compounds. The first supraicosahedral metallacarborane was 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ [3a,3b] which has been structurally characterised[8], so initially we set out to study crystallographically its 4,1,8- and 4,1,12-analogues. Because of crystallographic disorder (described herein) this first objective proved impossible to achieve. Thus, we have prepared and structurally studied the 4,1,6-, 4,1,8- and 4,1,12-isomers of $Cp^*CoC_2B_{10}H_{12}$, and here present our results.



SCHEME 1

RESULTS AND DISCUSSION

Cyclopentadienyl Compounds

Reaction of $[C_2B_{10}H_{12}]^{2-}$ (produced by Na reduction of 1,2-*closo*-$C_2B_{10}H_{12}$) with $CpCo(CO)I_2$ in THF affords both 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ (**1**) and 4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ (**2**) as major and very minor co-products, respectively (Chart 1). Both compounds have previously been prepared (in yields somewhat better than we achieved) from reaction between $[C_2B_{10}H_{12}]^{2-}$, Cp^- and $CoCl_2$ followed by aerial oxidation[3b]. THF reflux of the reaction mixture yields **2** as major component, whilst heating to reflux a toluene solution of **1** affords some **2** but mainly 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ (**3**). These isomerisation conditions are similar to those reported by Hawthorne *et al.*[3b], except that they find that heating **1** to reflux in benzene affords only **3**. The **1** to **2** isomerisation is particularly facile, and a solution of **1** in $CDCl_3$ shows appreciable amounts of **2** present after only a few days at room temperature.

The ^{11}B NMR spectrum of **1** implies time-averaged C_s molecular symmetry, which Hawthorne has discussed in terms of a double diamond-square-

diamond (dsd) transformation[3b]. We have recently noted the same time-averaged symmetry in 4,1,6-*closo*-$SnC_2B_{10}H_{12}$ and confirmed by DFT calculations that the double dsd transformation is indeed the fluxional process operating[9]. In contrast, there is no molecular symmetry apparent from inspection of the ^{11}B NMR spectra of **2** and **3**, allowing the alternative 4,1,5-, 4,1,10- and 4,1,11-MC_2B_{10} architectures to confidently be ruled out. Weighted average ^{11}B chemical shifts, $\langle\delta(^{11}B)\rangle$[10], are +0.2, +3.6 and –1.4 for **1**, **2** and **3**, respectively.

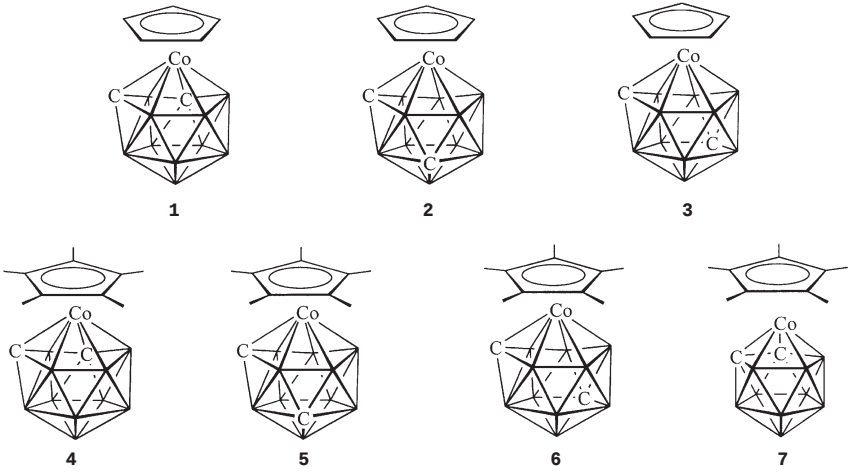


CHART 1

The kinetic isomer **1** has been studied crystallographically by Churchill and De Boer[8]. We attempted similarly to study compounds **2** and **3**. These are found to be isomorphous with each other but not further isomorphous with **1**, Table I lists crystal data for all three Cp compounds. Whilst **1** crystallises in general space (with no imposed symmetry) **2** and **3** crystallise with $Z = 4$ in the 8-fold space group $Cmc2_1$, requiring C_s molecular symmetry. Such molecular symmetry is, however, inconsistent with their anticipated (C_1) structures, necessitating disorder. However, since it is possible that the disorder could be limited to, *e.g.*, 1 : 1 disorder of C6 and B7 in the case of **2** and 1 : 1 disorder of C12 and B13 in the case of **3**, we decided to collect intensity data and to try to solve the structures.

Unfortunately the crystallographic disorder in both **2** and **3** is more complicated than we had hoped it would be. Whilst the Cp ligand, the Co atom, and the 6 atom carborane ring to which the Co is bonded are all ordered, the lower pentagonal belt (defined by atoms 5, 8, 9, 12 and 13 in **I**) suffers severe disorder. Crystallographically, this can be modelled either in

terms of three off-mirror plane atoms each having an occupancy factor of 0.83, leading to reasonable U_{eq} values for all atoms involved (Fig. 1a), or in terms of five non-disordered atoms allowed to adopt unreasonable anisotropic displacement values (Fig. 1b). In both models, for both **2** and **3**,

TABLE I
Crystal data for compounds **1**[a], **2** and **3**

Parameter	**1**	**2**	**3**
Formula	$C_7H_{17}B_{10}Co$	$C_7H_{17}B_{10}Co$	$C_7H_{17}B_{10}Co$
M	268.24	268.24	268.24
T	293[b]	160	160
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pbc2_1$	$Cmc2_1$	$Cmc2_1$
a, Å	7.047(2)	7.232(2)	7.207(2)
b, Å	13.744(4)	16.176(4)	16.191(5)
c, Å	13.620(3)	10.963(3)	11.033(5)
V, Å^3	1 319.0(7)	1 282.5(6)	1 287.4(8)
Z	4	4	4
D_{calc}, Mg m^{-3}	1.351	1.389	1.384

[a] From ref.[8]; [b] assumed.

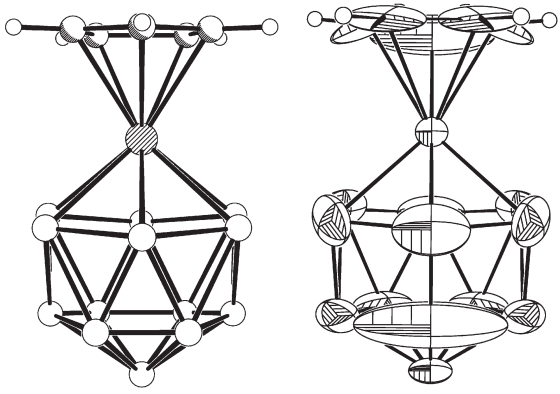


FIG. 1
Attempts to model the disorder in **2** and **3**. In a the lower belt of five cage atoms is modelled by 6 atoms each with an occupancy factor of 0.83. In b the five atoms are not disordered but clearly have unreasonable anisotropic thermal parameters

the resulting lack of precision meant that we could not identify the positions of the cage carbon atoms with any real confidence, and further refinement was abandoned.

Pentamethylcyclopentadienyl Compounds

Accordingly we switched attention to the analogous pentamethylcyclopentadienyl series. The red kinetic isomer 4-Cp*-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ (**4**) was obtained in *ca* 10% yield from the reaction between $[C_2B_{10}H_{12}]^{2-}$ and $Cp^*Co(CO)I_2$ in THF, and the yellow and red successive thermodynamic isomers, 4-Cp*-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ (**5**) and 4-Cp*-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ (**6**) were afforded by thermolysis of **4** in toluene. Again, pure solutions of the 4,1,6-isomer show evidence (^{11}B NMR) for rearrangement to the 4,1,8-isomer even at room temperature, but over a somewhat longer period for the Cp* compounds than the Cp compounds.

Not surprisingly the ^{11}B NMR spectra of the Cp* compounds closely resemble those of the respective Cp species. Thus the room temperature spectrum of **4** clearly reveals a molecule with time-averaged C_s symmetry, whilst no symmetry is apparent from inspection of the spectra of **5** and **6**. Calculated $\langle\delta(^{11}B)\rangle$ values are –1.3, +2.5 and –2.5, respectively, in the same relative order as noted for the Cp species. The ^{1}H NMR spectra of the Cp* compounds show two broad integral-1 peaks due to cage CH at δ 2.6–3.8 (one integral-2 peak for **4**) and the expected sharp integral-15 resonance at δ 1.7 due to the CH_3 groups of the Cp* ligands.

All three isomers of $Cp^*CoC_2B_{10}H_{12}$ were subjected to crystallographic study. The analysis of the kinetic isomer, **4**, was straightforward and a perspective view of the resulting molecule is shown in Fig. 2. Compounds **5** and **6** are isomorphous, and in both cases structural solution was non-standard. For **5** a ghost atom was located near the middle of the 3–7 connectivity, and satisfactory refinement was achieved by apportioning this ghost 15% of the occupancy of C1. For **6** there appeared to be 4 ghost atoms in the 1,2,6,9 region of the polyhedron. The best model for refinement involved 37% B occupancy of the ghost sites, with corresponding 63% occupancy of the major positions.

Thereafter we attempted to decide between positions 8 and 9 (**5**) and 12 and 13 (**6**) for the second cage C atom. In neither case was it possible to make this judgement on the basis of the usual criteria of U_{eq} values and/or interatomic distances (both atoms having been refined as B). Instead, we believe we have successfully identified the sites for C8 and C12, respectively, by allowing the H atoms bound to the two alternative sites (them-

selves treated as B) to refine freely, and comparing the B–H distances obtained. For **5** 9–H was 1.03 Å but 8–H (the alternative) was unrealistic at only 0.48 Å. Similarly, for **6** 13–H refined to 1.19 Å whilst 12–H dropped to only 0.53 Å. As far as we are aware this is a new method for distinguishing between C and B atoms in crystallographic studies of (hetero)carboranes. To validate the technique we refined C6 in (the well-behaved) **4** as B and allowed the H atom bound to it to refine. A very short 6–H distance of 0.19 Å resulted, supporting our approach.

Views of single molecules of **5** and **6** are presented in Figs 3 and 4, respectively, and Table II summarises the lengths of the cage connectivities in all three isomers of $Cp^*CoC_2B_{10}H_{12}$. In Table II the lengths of C–B connectivities (excluding those to C1) are italicised, and in 11/13 cases these are the shortest connectivities in their row, justifying the siting of C8 and C12 in the structural studies of **5** and **6**. Overall, the results in Table II are typical of the literature data on MC_2B_{10} compounds (although hitherto these are only available for 4,1,6-species[11]) in featuring short C1–B2 and C1–B3 distances and long B2–B5 and B3–B5 distances. At a superficial level these may be understood in terms of the electronegativities and connectivity numbers of the atoms involved: thus the longest 2–5 (**4**) and 3–5 (**5**) occur when B2 and B3, respectively, are adjacent to two cage C atoms.

A minor co-product in the synthesis of **4** was the yellow compound **7**. In the ^{1}H NMR spectrum were resonances at δ 2.9(br) and 1.8 in the ratio

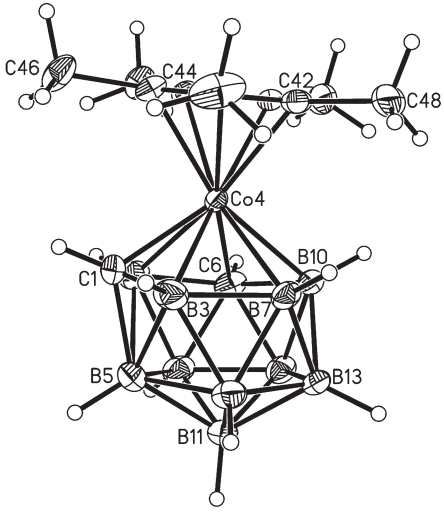


FIG. 2
Perspective view of **4**. Atoms are drawn as 50% probability ellipsoids except for H atoms

2 : 15. The ^{11}B NMR spectrum of **7** revealed resonances between 12 and –21 ppm in the 1 : 1 : 2 : 2 : 2 : 1 pattern of integrals (high frequency to low frequency) shown by Plešek and others[12] to be characteristic of an icosahedral 3,1,2-MC_2B_9 metallacarborane. The $\langle\delta(^{11}B)\rangle$ value of –5.1 is typical of a closo species[10]. Crystals were grown (with some difficulty) by solvent dif-

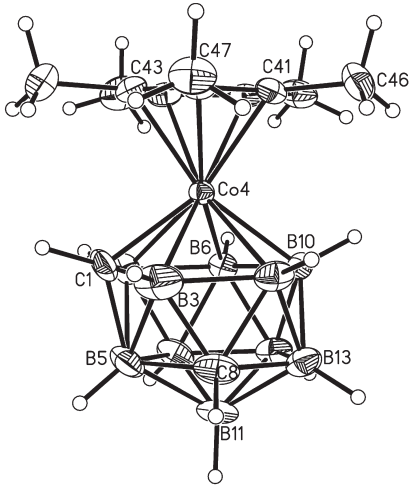


FIG. 3
Perspective view of **5**. Atoms are drawn as 50% probability ellipsoids except for H atoms

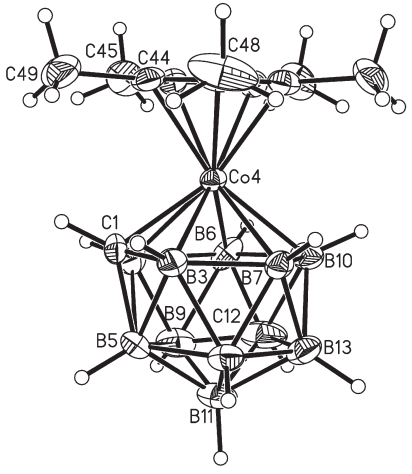


FIG. 4
Perspective view of **6**. Atoms are drawn as 50% probability ellipsoids except for H atoms

TABLE II
Cage connectivities (in Å) in compounds **4**, **5** and **6**

	Conectivity		
	4	**5**	**6**
1–2	1.523(4)	1.516(4)	1.489(13)
1–3	1.531(3)	1.491(5)	1.431(11)
1–4	2.016(2)	2.050(3)	2.094(6)
1–5	1.747(3)	1.675(4)	1.660(8)
2–4	2.175(2)	2.183(3)	2.220(8)
2–5	2.089(4)	1.967(4)	2.056(12)
2–6	*1.699(3)*	1.785(4)	1.834(14)
2–9	1.821(3)	1.775(4)	1.751(13)
3–4	2.228(2)	2.172(3)	2.169(5)
3–5	1.985(4)	2.014(5)	1.861(6)
3–7	1.807(3)	1.863(5)	1.778(6)
3–8	1.799(3)	*1.691(4)*	1.787(6)
4–6	2.160(2)	2.179(2)	2.114(7)
4–7	2.183(2)	2.149(3)	2.193(4)
4–10	2.120(2)	2.155(2)	2.148(5)
5–8	1.901(4)	*1.869(4)*	1.818(7)
5–9	1.902(4)	1.837(4)	1.946(12)
5–11	1.803(4)	1.787(4)	1.756(7)
6–9	*1.693(3)*	1.766(3)	1.868(15)
6–10	*1.699(3)*	1.777(3)	1.836(10)
6–12	*1.683(3)*	1.761(4)	*1.634(9)*
7–8	1.766(3)	*1.755(4)*	1.765(6)
7–10	1.784(3)	1.776(4)	1.784(6)
7–13	1.761(3)	1.759(4)	1.766(6)
8–11	1.750(3)	*1.717(4)*	1.751(6)
8–13	1.749(3)	*1.710(4)*	1.734(6)
9–11	1.744(3)	1.744(4)	1.680(10)
9–12	1.737(3)	1.749(4)	*1.579(14)*
10–12	1.796(3)	1.781(4)	*1.798(7)*
10–13	1.783(3)	1.789(3)	1.789(7)
11–12	1.790(3)	1.782(4)	*1.736(7)*
11–13	1.805(3)	1.778(4)	1.746(7)
12–13	1.765(3)	1.765(4)	*1.755(8)*

fusion between 40–60 petrol and a CH_2Cl_2 solution and were revealed to be the solvate $Cp^*CoC_2B_9H_{11}\cdot 1/2CH_2Cl_2$. The cobaltacarborane molecule is located on a crystallographic mirror plane passing through Co, C1, B10 and B12 (Fig. 5). The second cage carbon atom is disordered between the symmetry-related sites 2 and 4, which were refined as (50% C + 50% B). This judgement was made on the basis of the lengths of connectivities refining all non-Co cage atoms as B, yielding the following distances (in Å): 1–2 1.67, 1–6 1.72, 2–6 1.76, 2–7 1.76, all other >1.78.

Thus compound **7** is identified as 3-Cp*-3,1,2-*closo*-$CoC_2B_9H_{11}$. This compound appears not to have been previously reported. The Rh and Ir analogues are known, and both have been structurally characterised[13] but crystallise without solvent and are not isomorphous with **7**. The parent species 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ is also well-known[14] and crystallographically described[15]. It should be noted that this last compound was a minor product (1%) in the original synthesis of **1** [3a,3b] although we did not identify it in our work. Table III lists selected interatomic distances determined for (**I**). They are as expected.

The discovery of 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ as a co-product of **1** [3a,3b] and **7** as a co-product of **4** (this work) is most interesting. Recent studies in our group[16] have conclusively shown that the paramagnetic supraicosahedral molybdacarborane 1,6-Ph_2-4-(η^7-C_7H_7)-4,1,6-*closo*-$MoC_2B_{10}H_{10}$ undergoes

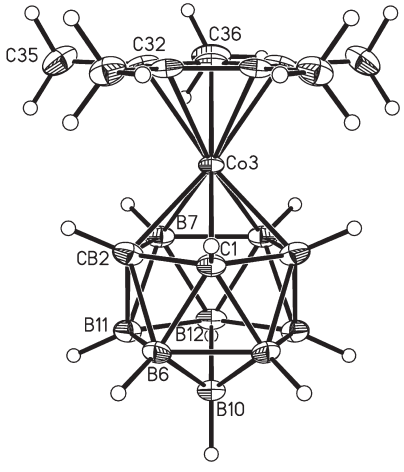
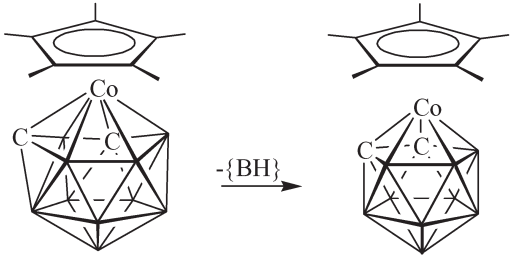


FIG. 5
Perspective view of **7**. Atoms are drawn as 50% probability ellipsoids except for H atoms. Only one of two possible orientations for the H atoms of the Me group attached to C36 shown for clarity

loss of a {BH} unit on chromatography on silica to afford 1,8-Ph_2-2-(η^7-C_7H_7)-2,1,8-*closo*-$MoC_2B_9H_9$. We suggest that **4** similarly loses {BH} in a process that results in the cage carbon atoms regaining their former adjacency (Scheme 2). It is not possible to achieve cage-C atom adjacency in the molybdenum system because the bulky Ph groups, together with the



4 **7**

SCHEME 2

TABLE III
Interatomic distances (in Å) in compound **7**

Atoms	Distance	Atoms	Distance
Co3–C31	2.048(4)	Co3–C32	2.065(3)
Co3–C33	2.073(3)	C31–C32	1.441(4)
C32–C33	1.429(4)	C33–C33[a]	1.440(6)
C31–C36	1.510(5)	C32–C35	1.495(5)
C33–C34	1.497(4)	C1–Co3	2.020(4)
C1–CB2	1.674(4)	C1–B6	1.715(4)
CB2–Co3	2.042(3)	CB2–B7	1.761(4)
CB2–B11	1.572(4)	CB2–B6	1.762(4)
B7–Co3	2.087(3)	B7–B7[a]	1.808(7)
B7–B12	1.799(5)	B7–B11	1.807(4)
B6–B6[a]	1.773(7)	B6–B11	1.780(5)
B6–B10	1.775(5)	B11–B12	1.787(4)
B11–B10	1.787(4)	B12–B10	1.783(6)
C10S–C11A	1.746(12)	C10S–C11B	1.773(12)

[a] Atom generated by reflection across crystallographically-imposed mirror plane.

C_7H_7 ligand on Mo, prevent a 3,1,2-MC_2B_9 architecture and give instead a C-isomerised species[17].

The facile partial degradation of 13-vertex heteroboranes into icosahedral derivatives has important implications for the future development of supraicosahedral chemistry. The mechanism by which this proceeds and the consequent development of strategies to prevent it are areas which are under current study in our laboratories.

EXPERIMENTAL

Synthesis – General

Experiments were performed under dry, oxygen-free N_2 using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. Solvents were freshly distilled over CaH_2 (CH_2Cl_2) or Na wire (THF, 60–80 petroleum ether) and were degassed (3 × freeze-pump-thaw cycles) before use, or were stored over 4 Å molecular sieves ($CDCl_3$). Preparative thin layer chromatography (TLC) employed 20 × 20 cm Kieselgel 60 F_{254} glass plates. IR spectra were recorded from CH_2Cl_2 solutions using either a Nicolet Impact 400 or a Perkin–Elmer Spectrum RX FT spectrophotometer. NMR spectra at 400.1 MHz (^{1}H), or 128.4 MHz (^{11}B) were recorded on a Bruker DPX400 spectrometer from $CDCl_3$ solutions at ambient temperature. Chemical shifts are given in ppm (δ-scale). Elemental analyses were determined by the departmental service. The starting materials $CpCo(CO)I_2$ and $Cp^*Co(CO)I_2$ were prepared by literature methods[18] or slight variants thereof. All other reagents and solvents were supplied commercially and were used as received.

4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ (**1**)

A solution of 1,2-*closo*-$C_2B_{10}H_{12}$ (0.506 g, 3.51 mmol) in THF was stirred overnight with sodium (0.178 g, 7.74 mmol). The resulting colourless solution of $Na_2[C_2B_{10}H_{12}]$ was then transferred by syringe to a second Schlenk tube containing $CpCo(CO)I_2$ (1.418 g, 3.49 mmol) partially dissolved in 50 ml THF at 0 °C. The reagents were stirred overnight at room temperature, resulting in a brown suspension which was filtered through Celite® and the filtrate reduced in volume. Initial column then preparative thin layer chromatography with a mixed eluent of CH_2Cl_2/40–60 petroleum ether (1 : 1) yielded red (major) and yellow (very minor) mobile bands. The major component (18% yield, not optimised) was recovered and identified as **1** by NMR spectroscopy. ^{11}B-{^{1}H} NMR: 17.79 (1 B), 4.84 (3 B), 0.18 (2 B), –3.19 (1 B), –7.36 (2 B), –12.68 (1 B), $\langle\delta(^{11}B)\rangle$ = +0.2.

4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ (**2**)

Yellow **2** is the minor co-product of the **1** reaction above. It was obtained as the major product by heating the reaction mixture (in THF) to reflux overnight followed by isolation involving both column and thin layer chromatography. ^{11}B-{^{1}H} NMR: 25.48 (1 B), 11.99 (1 B), 10.08 (1 B), 9.01 (1 B), 1.14 (1 B), –1.83 (2 B), –4.56 (2 B), –8.83 (1 B), $\langle\delta(^{11}B)\rangle$ = +3.6. Yellow blocks were grown by diffusion of 40–60 petroleum ether and a CH_2Cl_2 solution of **2**.

4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ (**3**)

Orange **3** (major component) and **2** (minor) were obtained by heating a toluene solution of **1** to reflux for 36 h followed by isolation by TLC. ^{11}B-{^1H} NMR: 11.27 (1 B), 8.81 (1 B), 6.51 (1 B), 5.34 (1 B), –0.64 (1 B), –4.55 (1 B), –6.18 (1 B), –9.37 (1 B), –11.95 (1 B), –13.35 (1 B), $\langle\delta(^{11}B)\rangle$ = –1.4. Red-orange blocks of relatively poor habit were grown by diffusion of equal volumes of 40–60 petroleum ether and a CH_2Cl_2 solution of the compound.

4-Cp*-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ (**4**) and 3-Cp*-3,1,2-*closo*-$CoC_2B_9H_{11}$ (**7**)

A solution of 1,2-*closo*-$C_2B_{10}H_{12}$ (0.207 g, 1.44 mmol) in THF (40 ml) was stirred overnight with sodium (0.073 g, 3.18 mmol). The resulting colourless solution of $Na_2[C_2B_{10}H_{12}]$ was then transferred by syringe to a second Schlenk tube containing Cp*Co(CO)I_2 (0.690 g, 1.44 mmol) partially dissolved in 40 ml THF at 0 °C. An intense bright green solution immediately formed, giving way to a brown colouration following overnight stirring and aerial exposure. The mixture was filtered through Celite® and the filtrate reduced in volume. Preparative TLC with a mixed eluent of CH_2Cl_2/40–60 petroleum ether (1 : 1) yielded mobile yellow (minor, R_F 0.69) and red (major, R_F 0.63) bands subsequently collected.

Major component, **4**. 10% yield (not optimised). For $C_{12}H_{27}B_{10}Co$ calculated: 42.6% C, 8.04% H; found: 42.2% C, 8.05% H. IR, ν_{max}: 2 540 cm^{-1}. ^1H NMR: 3.6 (br s, 2 H, cage CH); 1.70 (s, 15 H, CH_3). ^{11}B-{^1H} NMR: 17.41 (1 B), 5.16 (2 B), –0.03 (1 B), –1.81 (2 B), –3.14 (1 B), –9.53 (2 B), –14.37 (1 B), $\langle\delta(^{11}B)\rangle$ = –1.3. Red blocks were grown by diffusion of 40–60 petroleum ether and a CH_2Cl_2 solution of the compound.

Minor component, **7**. 2% yield. For $C_{12}H_{26}B_9Co$ calculated: 44.1% C, 8.02% H; found: 44.4% C, 8.26% H. IR, ν_{max}: 2 541 cm^{-1}. ^1H NMR: 2.9 (br s, 2 H, cage CH); 1.83 (s, 15 H, CH_3). ^{11}B-{^1H} NMR: 12.10 (1 B), 1.08 (1 B), –0.81 (2 B), –3.60 (2 B), –14.87 (2 B), –20.12 (1 B), $\langle\delta(^{11}B)\rangle$ = –5.1. Yellow block crystals were grown with difficulty by diffusion of 40–60 petroleum ether and a CH_2Cl_2 solution of the compound.

4-Cp*-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ (**5**) and 4-Cp*-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ (**6**)

A toluene solution of **4** was heated to reflux for 30 h. After cooling to room temperature toluene was removed *in vacuo* and the products dissolved in the minimum amount of THF and filtered. Preparative TLC using a mixed eluent of CH_2Cl_2/40–60 petroleum ether (1 : 1) yielded mobile red (major, R_F 0.60) and yellow (minor, R_F 0.55) bands subsequently shown to be **6** and **5**, respectively.

Compound **5**. IR, ν_{max}: 2 528 cm^{-1}. ^1H NMR: 2.6 (br s, 1 H, cage CH); 3.8 (br s, 1 H, cage CH); 1.72 (s, 15 H, CH_3). ^{11}B-{^1H} NMR: 25.59 (1 B), 12.31 (1 B), 10.05 (2 B), 0.61 (1 B), –3.94 (1 B), –6.28 (2 B), –7.19 (1 B), –10.28 (1 B), $\langle\delta(^{11}B)\rangle$ = +2.5. Yellow block crystals were grown by diffusion of 40–60 petroleum ether and a CH_2Cl_2 solution of the compound.

Compound **6**. IR, ν_{max}: 2 531 cm^{-1}. ^1H NMR: 3.1 (br s, 1 H, cage CH); 3.8 (br s, 1 H, cage CH); 1.70 (s, 15 H, CH_3). ^{11}B-{^1H} NMR: 11.38 (1 B), 8.37 (1 B), 6.27 (2 B), –0.18 (1 B), –8.50 (2 B), –11.55 (1 B), –13.65 (1 B), –15.20 (1 B), $\langle\delta(^{11}B)\rangle$ = –2.5. Red-orange blocks were grown by diffusion of 40–60 petroleum ether and a CH_2Cl_2 solution.

Crystallography

Single crystals of all compounds were studied at 160 ± 1 K on a Bruker P4 diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71069 Å) using ω scans. Standard reflections were re-measured every 100 data and crystal decay corrected. Data were

TABLE IV
Crystallographic data for compounds **4**, **5**, **6** and **7**[a]

Parameter	**4**	**5**	**6**	**7**
Formula	$C_{12}H_{27}B_{10}Co$	$C_{12}H_{27}B_{10}Co$	$C_{12}H_{27}B_{10}Co$	$C_{12}H_{26}B_9Co{\cdot}1/2CH_2Cl_2$
M	338.37	338.37	338.37	369.01
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2/m$
a, Å	8.2221(7)	12.444(2)	12.610(7)	16.368(12)
b, Å	14.9887(10)	10.1812(11)	10.063(3)	9.198(7)
c, Å	14.5566(11)	14.478(2)	14.464(5)	14.419(11)
β, °	99.8538(8)	109.240(13)	108.68(3)	119.15(3)
U, Å^3	1 767.5 (2)	1 731.8(4)	1 738.7(12)	1 896
Z	4	4	4	4
D_{calc}, Mg m^{-3}	1.272	1.298	1.293	1.293
μ(MoKα), mm^{-1}	0.958	0.977	0.973	1.036
$\theta_{data\ collection}$, °	1.97–25.00	2.49–25.00	2.51–25.02	2.50–25.01
Data measured	4 135	3 918	3 897	2 204
Unique data	3 123	3 041	3 035	1 761
R_{int}	0.0251	0.0286	0.0508	0.0475
Data $I > 2\sigma(I)$	3 102	2 861	2 893	1 634
R (all data)	0.0352	0.0350	0.0591	0.0490
wR_2 (all data)	0.0872	0.0878	0.1562	0.1273
a, *b*	0.0334, 1.44	0.0375, 1.38	0.0850, 3.21	0.0714, 4.91
S (all data)	1.006	1.040	1.092	1.103
Variables	244	249	261	127
E_{max}, e Å^{-3}	0.280	0.406	0.900	0.894
E_{min}, e Å^{-3}	–0.309	–0.517	–0.676	–0.921

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$ (where $w^{-1} = [\sigma_c^2(F_o)^2 + (aP)^2 + bP]$ and $P = [0.333\max\{F_o, 0\} + 0.667(F_o)^2]$), $S = \Sigma[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where *n* is the number of data and *p* the number of parameters).

corrected for absorption by psi scans. Structures were solved by direct and difference Fourier methods and refined[19] by full-matrix least-squares against F^2. Compounds **2** and **3** are isomorphous and disordered. Although *R* values of *ca* 0.04 could be achieved it proved impossible to model the disorder in a chemically-sensible way (see above) and refinement was not completed. Table I summarises comparative crystal data for **1**, **2** and **3**. Solution and refinement of the structures of **4** and **7** were fairly straightforward. In the case of **4** it was necessary to decide between vertices 6 and 7 for the position of the 5-connected (w.r.t. the polyhedron) cage carbon atom, but this was unambiguously done on the basis of interatomic distances having refined both as boron. In the case of compound **7** there was clear 50 : 50 B : C disorder in the symmetry-related vertices 2 and 4 which was easily modelled. Compound **7** crystallises with 1/2 CH_2Cl_2 of solvation, the C and Cl atoms sitting on a crystallographic mirror plane close to a 2-fold rotation axis about which they are disordered in two intersecting "V's". H atoms of the solvate were not included in the final model. Compounds **5** and **6** are isomorphous. Satisfactory solutions for both required a model containing fractionally-occupied ghost atoms (1 in the case of **5**; 4 in the case of **6**) without which anisotropic refinement of cage atoms was unrealistic. Thereafter the problem became one of deciding the location of the 5-connected cage C atom. For **5** this could be at positions 8 or 9, and for **6** at positions 12 or 13. In both cases a clear decision could not be made by either analysis of U_{eq} values of the respective atoms (having been refined as B) or on interatomic distances, and we used instead the technique of comparing vertex–H distances as described above (see Results and Discussion). Refinement was completed with all non-hydrogen atoms assigned anisotropic displacement parameters. For **5** and **6** cage H atoms were restrained to B–H distances of 1.10(2) Å and C–H distances of 1.15(2) Å. For **4** only the former restraint was applied. In the case of compound **7** B–H and C–H were set at 1.12 Å. All cage H atoms were assigned displacement parameters set at 1.2 times that of the U_{eq} of their bound atom. Methyl H atoms were set in calculated (riding) positions with displacement parameters calculated as 1.5 the bound carbon atom U_{eq}. Table IV contains details of the crystallographic studies of compounds **4**, **5**, **6** and **7**. CCDC 183672, CCDC 183673, CCDC 183674 and CCDC 183671 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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