

# Synthesis and structural characterizations of new 12- and 13-vertex metallocarboranes based on supraicosahedral frameworks<sup>1</sup>

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## Abstract

Three new metallocarboranes, *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1**, *nido*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>, **2**, and *arachno*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>7</sub>H<sub>12</sub>, **3**, having cage structures derived from supraicosahedral frameworks, have been produced from metal-insertion reactions of the *arachno*-8-(NC)-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub><sup>-</sup> and *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>12</sub><sup>-</sup> anions. A structural determination of **1** showed it adopts a distorted *closo*-docosahedral geometry similar to those previously reported for isoelectronic 13-vertex metallocarboranes. Structural determinations of **2** and **3** showed that they both have open frameworks with that of **2** based on a docosahedron missing one vertex, and that of **3** based on a bicapped hexagonal antiprism missing two vertices. © 1998 Elsevier Science S.A.

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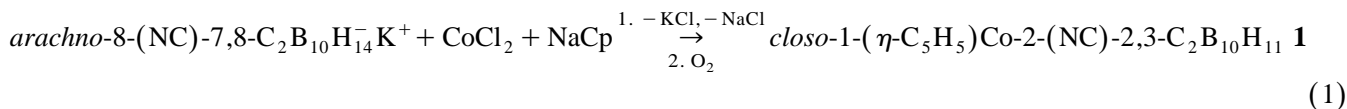
## 1. Introduction

Thanks in large part to the seminal contributions of Wade, the relationships between skeletal electron count and cluster geometry for subicosahedral cage clusters are now clearly established [1]. However, owing to the relatively few structurally characterized boron clusters based on supraicosahedral frameworks, the structural patterns in these larger cage systems are still being elucidated [2]. We previously reported the synthesis and characterization of two new isoelectronic and isostructural 12-vertex *arachno*-carboranes, *arachno*-8-(NC)-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub><sup>-</sup> and *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>13</sub> [3]. We have now found that the open frameworks of these two carboranes (Fig. 1) make them suitable starting materials for the construction of large-cage metallocarboranes. As an illustration, we report in this paper the synthesis and structural characterization of three new metallocarborane clusters having cage structures derived from supraicosahedral geometries.

## 2. Results and discussion

### 2.1. *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> **1**

The reaction of the *arachno*-8-(NC)-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub><sup>-</sup> anion with CoCl<sub>2</sub> and NaCp, followed by air oxidation, produced *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1** (Eq. (1)) which was isolated by TLC as an air-stable solid. Its composition was initially established by both high resolution mass spectrometry and elemental analysis.



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<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

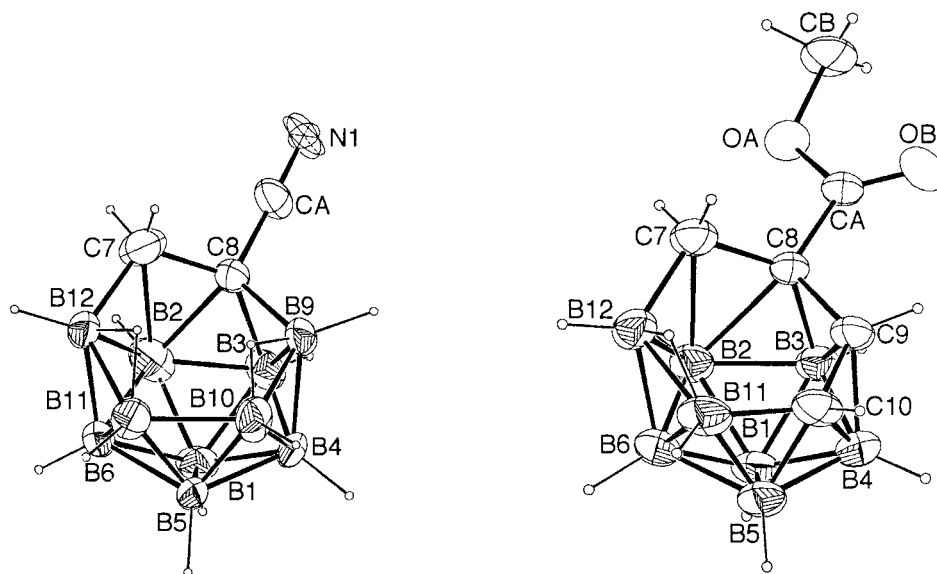


Fig. 1. X-ray-determined structures of *arachno*-8-NC-7,8- $C_2B_{10}H_{14}$  and *arachno*-8-( $CH_3OC(O)$ )-7,8,9,10- $C_4B_8H_{13}$ .

The spectroscopic data for **1** (Table 1) are consistent with its proposed formulation, with the  $^{11}B$  NMR spectrum at 160 MHz consisting of seven doublets of intensities 1:1:2:1:1:2:2. The  $^1H$  NMR spectrum contains a sharp Cp singlet (5.75 ppm) and a broad cage-CH resonance (5.56 ppm); the  $^{13}C\{^1H\}$  NMR spectrum contains resonances characteristic of the cyano- (122.35 ppm), cyclopentadienyl (93.98 ppm), cage-C3H (74.43 ppm), and cage-C2 (56.47 ppm) carbon atoms.

On the basis of the structural determinations of other 13-vertex, 28 skeletal electron count metallocarboranes, including *closo*-1-( $\eta$ - $C_5H_5$ )Co-7,9- $C_2B_{10}H_{12}$  [4], [*commo*-Ti-(Ti-1,6- $Me_2C_2Bi_{10}H_{10}$ )] $^{2-}$  [5], *closo*-4-dppe-4-Pd-1,6- $C_2B_{10}H_{12}$  [6], *closo*-4,4,4-H( $PPh_3$ ) $_2$ -2-OMe-4-Ir-1,6- $C_2B_{10}H_{11}$  [6], *closo*-1,1-( $PPh_3$ ) $_2$ -1-H-1,2,4-Rh $C_2B_{10}H_{12}$  [7], *closo*-1-Me-4-Et $_3P$ - $\mu_{4,6}$ -Co( $PEt_3$ ) $_2$ - $\mu$ -(H) $_2$ -4,1,2-Co $C_2B_{10}H_{10}$  [8] and many tungstadicarbaborane complexes [9], **1** would be expected to adopt a distorted 13-vertex dicosahedral cage geometry. As can be seen in the ORTEP drawing in

Table 1  
NMR data for **1**, **2** and **3**

Compound <sup>a</sup>	Nucleus	$\delta$ , (multiplicity, $J$ (Hz), intensity or assignment)
<i>closo</i> -1-( $\eta$ - $C_5H_5$ )Co-2-(NC)-2,3- $C_2B_{10}H_{11}$ , <b>1</b>	$^{11}B^b$	20.8 (d, $J_{BH}$ = 188, 1), 19.5 (d, $J_{BH}$ = 171, 1), 13.4 (d, $J_{BH}$ = 149, 2), 9.5 (d, $J_{BH}$ = 166, 1), 8.2, (d, $J_{BH}$ = 138, 1), -5.5 (d, $J_{BH}$ = 153, 2), -7.2 (d, $J_{BH}$ = 150, 2)
	$^1H^c$	5.75 (s, Cp, 5H), 5.56 (s, CH)
	$^{13}C^d$	122.35 (CN), 93.98 (Cp), 74.43 (CH), 56.47 (C-CN)
<i>nido</i> -2-( $\eta$ - $C_5H_5$ )Fe-8-( $CH_3OC(O)$ )-6,7,8,9- $C_4B_7H_{11}$ , <b>2</b>	$^{11}B^e$	15.9 (d, $J_{BH}$ = 146, 1), 2.7 (d, $J_{BH}$ = 149, 1), -7.8 (d, $J_{BH}$ = 145, 1), -14.2 (d, $J_{BH}$ = 148, 1), -21.7 (d, $J_{BH}$ = 155, 1), -24.4 (d, $J_{BH}$ ~ 150, 1), -25.8 (d, $J_{BH}$ ~ 150, 1)
	$^1H\{^{11}B\}^f$	4.79 (s, Cp, 5), 4.20 (s, CH), 4.07 (s, Me), 3.22 (s, CH), 1.27 (s, CH), -6.04 ( $\mu$ -BHB)
	$^{11}B^b$	17.8 (d, $J_{BH}$ = 136, 1), 9.6 (d, $J_{BH}$ = 113, 1), 4.0 (d, $J_{BH}$ = 141, 1), -1.7 (d, $J_{BH}$ = 155, 1), -8.6 (d, $J_{BH}$ = 176, 1), -19.7 (d, $J_{BH}$ = 136, 1), -24.0 (d, $J_{BH}$ = 153, 1)
<i>arachno</i> -2- $\eta$ -( $C_5H_5$ )Co-8-( $CH_3OC(O)$ )-7,8,9,10- $C_4B_7H_{13}$ , <b>3</b>	$^1H\{^{11}B\}^e$	5.07 (s, Cp, 5), 4.42 (d of d, $J_{HH}$ = 13 and $J_{HH}$ = 7, 1), 3.67 (s, Me), 2.56 (s, CH), 1.67 (s, CH), 1.25 (s, CH), -3.81 (s, $\mu$ -BHB)

<sup>a</sup>  $CDCl_2$ .

<sup>b</sup> 160.1 MHz.

<sup>c</sup> 500.1 MHz.

<sup>d</sup> 125.1 MHz.

<sup>e</sup> 64.2 MHz.

<sup>f</sup> 200.1 MHz.

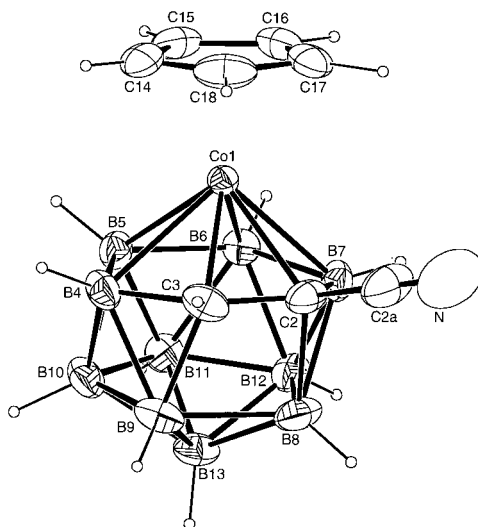


Fig. 2. ORTEP drawing of *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1**.

Fig. 2, a single crystal X-ray determination confirms this prediction. A regular dicosahedron would have all triangulated faces [2], but structural studies of the above 13-vertex *closo*-metallacarboranes have all found distorted cage-geometries containing either one or two quadrilateral faces located between the six-membered and five-membered rings. A similar quadrilateral distortion involving the C2–B8–B9–C3 atoms is observed in **1**. In Fig. 3 the distances and angles in the C2–B8–B9–C3 face are compared with those of the adjacent C2–B7–B12–B8 and B4–C3–B9–B10 faces and it is clear that the C2–B9 and C3–B8 distances are lengthened relative to normal B–C bonds. Because of this, the C2–C3–B9, C3–C2–B8, C3–B9–B8 and C2–B8–B9 angles are substantially larger than the ca. 60–70° angles normally found in triangulated faces (Table 2). Compound **1** is the cyano-substituted, adjacent-carbon isomer of the *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-7,9-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> compound previously reported by Hawthorne and coworkers [4,10]. The gross cage structures of the two compounds are similar; however, the latter compound has non-adjacent carbon atoms with two of the faces showing quadrilateral distortions.

Although, as noted above, metallacarborane complexes containing the non-adjacent carbon isomer of the C<sub>2</sub>B<sub>10</sub>H<sub>12</sub><sup>2-</sup> ligand are well known, only one adjacent-carbon complex *closo*-1-Me-4-Et<sub>3</sub>P- $\mu$ -<sub>4,6</sub>-Co(PEt<sub>3</sub>)<sub>2</sub>- $\mu$ -(H)<sub>2</sub>-4,1,2-Co<sub>2</sub>B<sub>10</sub>H<sub>10</sub> has been characterized [8]. As illustrated by the formation of **1**, reactions employing the *arachno*-8-R-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub><sup>-</sup> anions may now provide a new entry into this class of metallacarboranes.

## 2.2. *nido*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>, **2**

The ferratetetracarborane complex **2** was isolated from the reaction of the *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>12</sub><sup>-</sup> anion with ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I. Also produced in smaller amounts were the known [11] ferratricarboranes

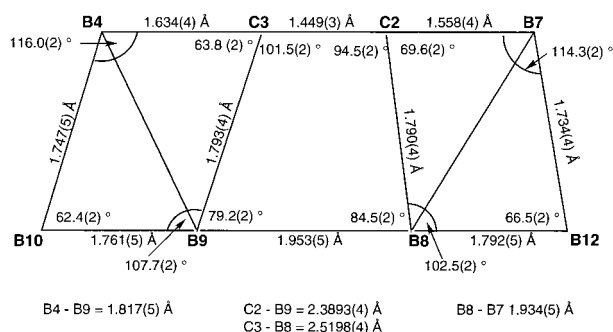


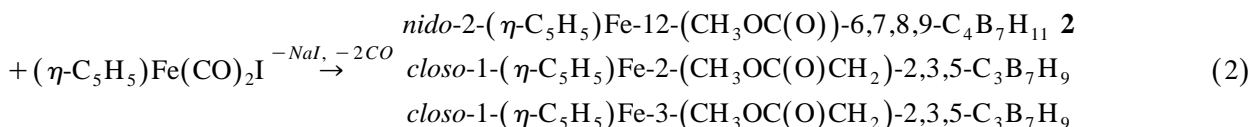
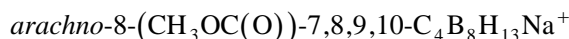
Fig. 3. Comparisons of facial bond lengths and angles in **1**.

Table 2

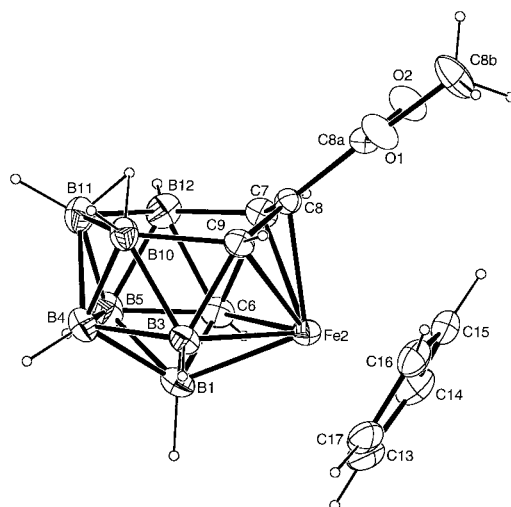
Selected bond distances (Å) for *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1**

Co1–B4	2.190(3)	B6–B11	1.764(4)	B11–B12	1.752(4)
Co1–B5	2.178(3)	B6–B12	1.780(4)	B11–B13	1.760(4)
Co1–B6	2.170(3)	B6–H6	1.062(25)	B11–H11	1.020(27)
Co1–B7	2.176(3)	B7–B8	1.934(5)	B12–B13	1.768(4)
Co1–C2	2.021(2)	B7–B12	1.734(4)	B12–H12	0.981(27)
Co1–C3	2.052(3)	B7–C2	1.588(4)	B13–H13	1.014(29)
Co1–C14	2.028(3)	B7–H7	0.893(29)	C2–C2a	1.461(4)
Co1–C15	2.031(3)	B8–B9	1.953(5)	C2–C3	1.449(3)
Co1–C16	2.055(3)	B8–B12	1.792(5)	C2a–N	1.129(5)
Co1–C17	2.079(3)	B8–B13	1.728(5)	C3–H3	1.045(27)
Co1–C18	2.063(3)	B8–C2	1.790(4)	C14–C15	1.414(5)
B4–B5	1.808(4)	B8–C3	2.390(4)	C14–C18	1.392(5)
B4–B9	1.817(5)	B8–H8	1.041(28)	C14–H14	0.763(31)
B4–B10	1.747(5)	B9–B10	1.761(5)	C15–C16	1.381(4)
B4–C3	1.634(4)	B9–B13	1.745(4)	C15–H15	0.869(34)
B4–H4	1.082(24)	B9–C2	2.520(4)	C16–C17	1.381(4)
B5–B6	1.777(4)	B9–C3	1.793(4)	C16–H16	1.089(32)
B5–B10	1.775(4)	B9–H9	1.041(28)	C17–C18	1.389(4)
B5–B11	1.773(4)	B10–B11	1.759(4)	C17–H17	1.025(33)
B5–H5	1.090(24)	B10–B13	1.764(4)	C18–H18	0.803(36)
B6–B7	1.776(4)	B10–H10	1.077(30)		

*closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-2-(CH<sub>3</sub>OC(O)CH<sub>2</sub>)-2,3,5-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> and *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-3-(CH<sub>3</sub>OC(O)CH<sub>2</sub>)-2,3,5-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>. Several other products gave mass spectral data indicating that they were isomers of **2**, but they were obtained in amounts insufficient for characterization.



The mass spectral and spectroscopic data for **2** confirm the loss of one boron during the formation of the complex. Thus, its <sup>11</sup>B NMR spectrum at 64.2 MHz consists of seven equal intensity doublet resonances. The <sup>1</sup>H NMR spectrum shows the expected sharp resonances for the Cp and Me protons, three broader resonances (4.20, 3.22 and 1.27 ppm) for the cage CH groups and a broad upfield singlet at a shift (–6.04 ppm) characteristic of a bridging hydrogen. Grimes and coworkers have previously reported [12] the synthesis of a tetramethyl-ferratetrecarbaborane of

Fig. 4. ORTEP drawing of *nido*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>, **2**.

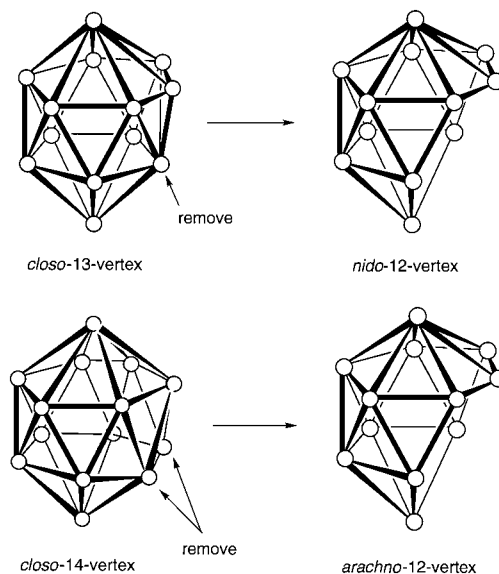


Fig. 5. Derivation of nido- and arachno-12-vertex structures from closo-13 and closo-14-vertex geometries.

composition *nido-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-1,7,8,9-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>7</sub>H<sub>8</sub>*; however, the <sup>11</sup>B NMR spectrum of this compound and **2** are substantially different, leading to the conclusion that **2** must have a different arrangement of the cage carbon atoms.

A single crystal X-ray structure determination of **2** showed that it adopts the *nido-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>* configuration pictured in Fig. 4. Grimes has demonstrated that 12-vertex, 28 skeletal-electron count clusters can adopt a variety of different cage geometries [13], but **2** adopts the commonly observed cage-structure that is based on a 13-vertex dicosahedron missing one six-coordinate vertex, as derived in Fig. 5. This structure is similar to those found for most isoelectronic 12-vertex cage systems, including *nido-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-1,7,8,9-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>7</sub>H<sub>8</sub>* [12], *nido-2,4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>-7,10,11,12-C<sub>4</sub>B<sub>6</sub>H<sub>10</sub>* [14], *nido-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-7,9,11,12-(CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>7</sub>H<sub>7</sub>* [15], and *nido-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-7-CH<sub>3</sub>-7,8,9,10,12-C<sub>5</sub>B<sub>6</sub>H<sub>10</sub>* [16,11]. The iron atom lies in a six-coordinate position bound to four-carbon and two-boron atoms. Five of the ring atoms form a plane with the C8 carbon atom distorted out of this plane 0.34 Å toward the iron atom. As a consequence, the Fe–C8 distance (1.976(3) Å) is shortened relative to Fe–C7 (2.241(4) Å), Fe–C6 (2.155(4) Å) and Fe–C9 (2.080(4) Å), as well as compared to the Fe–B1 and Fe–B3 distances (Table 3).

As in the starting *arachno-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>12</sub>*<sup>-</sup> anion, all four carbon atoms in **2** are adjacent and the formation of the complex may be envisioned to have occurred by a straightforward process involving initial iron

Table 3

Selected bond distances (Å) for *nido-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>*, **2**

Fe2–B1	2.119(5)	B3–C9	1.655(5)	B12–C7	1.586(6)
Fe2–B3	2.122(4)	B3–H3	1.054(40)	B12–H12	1.042(38)
Fe2–C6	2.155(4)	B4–B5	1.766(6)	C6–C7	1.692(5)
Fe2–C7	2.241(4)	B4–B10	1.750(6)	C6–H6	0.968(41)
Fe2–C8	1.976(3)	B4–B11	1.800(7)	C7–C8	1.435(5)
Fe2–C9	2.080(4)	B4–H4	1.037(37)	C7–H7	0.958(38)
Fe2–C13	2.065(5)	B5–B11	1.763(7)	C8–C9	1.440(4)
Fe2–C14	2.088(4)	B5–B12	1.733(6)	C8–C8a	1.491(5)
Fe2–C15	2.081(4)	B5–C6	1.660(6)	C9–H9	0.925(43)
Fe2–C16	2.043(5)	B5–H5	1.017(44)	C8a–O1	1.331(4)
Fe2–C17	2.046(4)	B10–B11	1.826(7)	C8a–O2	1.199(4)
B1–B3	1.747(6)	B10–C9	1.723(6)	C8b–O1	1.437(5)
B1–B4	1.812(7)	B10–H10	1.060(40)	C13–C14	1.409(5)
B1–B5	1.786(7)	B10–H1011	1.287(37)	C13–C17	1.409(6)
B1–C6	1.653(5)	B11–B12	1.800(6)	C14–C15	1.388(7)
B1–H1	1.115(43)	B11–H11	1.097(49)	C15–C16	1.408(5)
B3–B4	1.758(7)	B11–H1011	1.248(44)	C16–C17	1.395(6)
B3–B10	1.813(7)	B12–C6	1.717(6)		

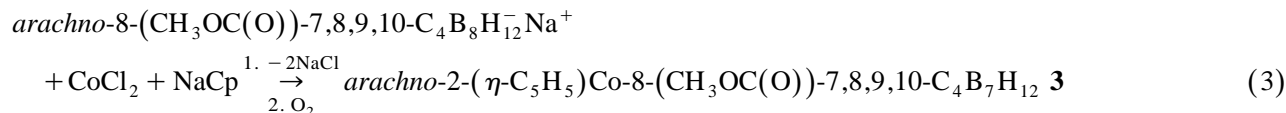
insertion onto the open face of the anion, followed by loss of one boron from the cluster to generate a new open face. Such a sequence would correctly predict the iron to be directly attached to all four carbon atoms, but have only three carbon atoms on the open face. The fourth carbon (C6) is located in a five-coordinate position in the belt below the open face. This also suggests **2** is a kinetic product, since cage-carbon atoms are known to strongly favor lower-coordinate positions on open faces [17]. Thus, **2** would be expected to rearrange under suitable conditions with migration of C6 to the open face and, indeed, **2** was found to readily isomerize at 190°C. The  $^{11}\text{B}$  NMR spectrum (Section 3) of the new isomer exhibits seven doublets, with six of these at chemical shifts quite close to the six resonances found in the spectrum of the isoelectronic ferrapentacarbaborane *nido*-2-( $\eta\text{-C}_5\text{H}_5$ )Fe-7- $\text{CH}_3$ -7,8,9,10,12- $\text{C}_5\text{B}_6\text{H}_{10}$  [11,16]. This observation strongly supports the predicted *nido*-2-( $\eta\text{-C}_5\text{H}_5$ )Fe-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,12- $\text{C}_4\text{B}_7\text{H}_{11}$  structure for the new isomer containing all four cage-carbon atoms on the open face. The  $R_f$  and color of this compound also match that of one of the minor products obtained during the synthesis of **2**.

The syntheses of metalla- $\text{Me}_4\text{C}_4\text{B}_7\text{H}_8$  clusters has previously been accomplished by reactions employing the tetracarbaborane  $\text{Me}_4\text{C}_4\text{B}_8\text{H}_8$  or its dianion  $\text{Me}_4\text{C}_4\text{B}_8\text{H}_8^{2-}$  [13], or by the oxidative fusion of smaller metallacarborane fragments [14]. The use of the readily available *arachno*-8-R-7,8,9,10- $\text{C}_4\text{B}_8\text{H}_{12}^-$  (R = CN,  $\text{CH}_3\text{OC}(\text{O})^-$  and  $\text{CH}_3\text{C}(\text{O})^-$ ) anions provides an alternative route to this class of cluster compounds, as well as allowing the production of new cage isomers.

Other characterized minor products of the reaction were the tricarbaborane complexes *closo*-1-( $\eta\text{-C}_5\text{H}_5$ )Fe-2-( $\text{CH}_3\text{OC}(\text{O})\text{CH}_2$ )-2,3,5- $\text{C}_3\text{B}_7\text{H}_9$  and *closo*-1-( $\eta\text{-C}_5\text{H}_5$ )Fe-3-( $\text{CH}_3\text{OC}(\text{O})\text{CH}_2$ )-2,3,5- $\text{C}_3\text{B}_7\text{H}_9$ , which were identified by comparison of their  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectra with those of authentic samples [16]. These complexes resulted from extrusion of the C8 carbon from the original tetracarbaborane *arachno*-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_8\text{H}_{12}^-$  framework by a process that must have involved cleavage of either the C8–C7 or C8–C9 bonds followed by hydrogen migration to C8 to produce the exopolyhedral  $-\text{CH}_2\text{C}(\text{O})\text{OCH}_3$  substituent.

### 2.3. *arachno*-2-( $\eta\text{-C}_5\text{H}_5$ )Co-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{12}$ , **3**

The reaction of *arachno*-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_8\text{H}_{12}^- \text{Na}^+$  with  $\text{CoCl}_2$  and  $\text{NaCp}$  produced *arachno*-2-( $\eta\text{-C}_5\text{H}_5$ )Co-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{12}$ , **3** (Eq. (3)). Three other metallacarborane products were observed by TLC, but they were isolated in insufficient amounts to allow characterization.



As was found for **2**, both the mass spectrum and the  $^{11}\text{B}$  NMR spectrum for **3**, which consisted of only seven doublet resonances of unit intensity, indicate the loss of one boron from the original *arachno*-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_8\text{H}_{12}^-$  anion framework during the formation of the complex. The  $^1\text{H}$  NMR spectrum also shows evidence of the presence of one additional hydrogen. Thus, in addition to the Cp, Me and bridge-hydrogen resonances, there are four CH resonances.

A single-crystal X-ray study confirmed the structure shown in the ORTEP drawing in Fig. 6 which is, in fact, quite similar to those found for the isoelectronic *arachno*-8-(NC)-7,8- $\text{C}_2\text{B}_{10}\text{H}_{14}^-$  and *arachno*-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10-

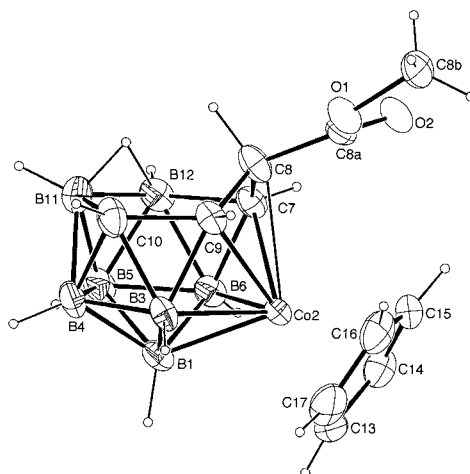


Fig. 6. ORTEP drawing of *arachno*-2-( $\eta\text{-C}_5\text{H}_5$ )Co-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{12}$ , **3**.

Table 4  
Selected bond distances (Å) for *arachno*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>7</sub>H<sub>12</sub>, **3**

Co2–B1	2.115(4)	B4–B11	1.802(6)	C8–H8	1.125(48)
Co2–B3	2.101(4)	B4–C10	1.705(6)	C9–C10	1.588(5)
Co2–B6	2.095(3)	B4–H4	1.092(34)	C9–H9	0.984(29)
Co2–C7	2.166(3)	B5–B6	1.769(6)	C10–H10	1.100(40)
Co2–C8	2.409(4)	B5–B11	1.815(7)	C8a–O1	1.327(4)
Co2–C9	2.176(3)	B5–B12	1.733(5)	C8a–O2	1.203(4)
Co2–C13	2.038(4)	B5–H5	1.075(37)	C8b–O1	1.451(4)
Co2–C14	2.049(4)	B6–B12	1.766(6)	C8b–H8b	0.924(30)
Co2–C15	2.085(4)	B6–C7	1.677(4)	C8b–H8b'	0.997(38)
Co2–C16	2.055(4)	B6–H6	1.084(32)	C8b–H8b''	0.988(38)
Co2–C17	2.035(4)	B11–B12	1.797(6)	C13–C14	1.381(5)
B1–B3	1.769(5)	B11–C10	1.674(6)	C13–C17	1.399(6)
B1–B4	1.763(6)	B11–H11	1.051(46)	C13–H13	0.944(40)
B1–B5	1.782(5)	B11–H1112	1.176(30)	C14–C15	1.385(5)
B1–B6	1.774(5)	B12–C7	1.639(5)	C14–H14	0.964(53)
B1–H1	1.088(29)	B12–H12	0.855(28)	C15–C16	1.362(5)
B3–B4	1.755(6)	B12–H1112	1.410(36)	C15–H15	0.938(39)
B3–C9	1.719(4)	C7–C8	1.491(4)	C16–C17	1.402(5)
B3–C10	1.757(5)	C7–H7	0.970(30)	C16–H16	0.777(37)
B3–H3	1.079(29)	C8–C9	1.501(4)	C17–H17	0.824(40)
B4–B5	1.749(6)	C8–C8a	1.511(4)		

C<sub>4</sub>B<sub>8</sub>H<sub>13</sub> clusters (Fig. 1), and for the cage fragment in [ $\sigma$ -( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co( $\eta$ <sup>4</sup>-C<sub>5</sub>H<sub>4</sub><sup>+</sup>)]-*arachno*-Me<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub><sup>-</sup> [18]. In contrast to **2**, in **3**, all four carbon atoms are located on the open face. Therefore, if **3** is formed by a process similar to that discussed above for **2**, involving the initial attack of the metal ion at the open face of the *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>12</sub><sup>-</sup> anion, then a carbon skeletal rearrangement must have occurred to allow migration of one carbon from a lower belt to the open face. Again, such a rearrangement is expected because of the strong preference of cage carbon atoms for low-coordinate cage-positions [17].

Based on a 30 skeletal electron count, **3** would be predicted to adopt an *arachno*-12-vertex structure based on a 14-vertex geometry missing two vertices. As shown in Fig. 5, the structure derived in this manner is similar to the normal structure found for *nido*-12-vertex clusters. The structure observed for **3** appears, in fact, to be grossly similar to that found for **2**, but upon detailed inspection there are several significant differences. Most importantly, the presence of the endo-hydrogen at the C8 carbon appears to have altered the bonding interactions of this carbon with the other cage atoms. Thus, Co–C8 is substantially longer (2.409(4) Å) than both the Fe–C8 length in **2** (1.976(3) Å) and the C6–C7 (2.166(3) Å) and Co–C9 (2.176(3) Å) lengths (Table 4). Also, unlike in **2**, in **3** the cobalt-bonded six-membered ring containing C8, B1–B3–C9–C8–C7–B6, is planar. As a result, C8 is much more displaced (0.80 Å) from the plane of the other atoms on the open face, C9–C10–B11–B12–C7, than was C8 in **2**. Thus, the dihedral angle between the C7–C8–C9 and C7–C9–C10–B11–B12 planes is only 114.1°, compared to the 141.7° in **2**. The angles at the C8 atom in **3** are also much closer to tetrahedral and the C9–C8 (1.501(4) Å) and C7–C8 (1.491(4) Å) lengths longer than those in **2** (C9–C8, 1.440(4) Å and C7–C8, 1.435(5) Å).

Structural studies [3,18] of the three isoelectronic clusters, *arachno*-8-(NC)-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub><sup>-</sup>, *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>12</sub><sup>-</sup> and [ $\sigma$ -( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co( $\eta$ <sup>4</sup>-C<sub>5</sub>H<sub>4</sub><sup>+</sup>)]-*arachno*-Me<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub><sup>-</sup> have also found in each case a unique three-coordinate carbon that exhibits similar bonding patterns to those of C8 in **3**. As previously discussed for these isoelectronic clusters, these structural features suggest an alternative interpretation of the structure of **3**. Thus, instead of considering **3** a 12-vertex *arachno*-tetracarborane cluster, the complex could be considered an 11-vertex *arachno*-tricarborane with an exopolyhedral methylene group bridging two cage-carbon atoms, i.e. *arachno*-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co- $\mu$ -((CH<sub>3</sub>OC(O))CH)-C<sub>3</sub>B<sub>7</sub>H<sub>11</sub>. Certainly, the bond distances and angles observed at C8 provide support for such a bridging methylene fragment. Thus, it appears that the major structural change that occurs between the *nido* and *arachno* configurations in these 12-vertex carborane and metallocarborane clusters is the conversion of one of the cage atoms to a more classical bridging-fragment.

### 3. Experimental section

All manipulations were carried out using standard inert atmosphere techniques [19].

### 3.1. Materials

*arachno*-8-(NC)-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub><sup>−</sup>K<sup>+</sup> and *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>13</sub> were prepared by the reported methods [3]. KH and NaH (35 wt.% dispersions in mineral oil), and Na lumps (stored in mineral oil) were rinsed with hexane prior to use. CoCl<sub>2</sub> was dried in vacuo at 120 °C and stored under an inert atmosphere until used. Proton sponge, sodium cyclopentadiene (NaCp) in THF and dicarbonylcyclopentadienyliodoiron(II) (( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I), were purchased from Aldrich and used as-received. Tetrahydrofuran was dried over Na–benzophenone and distilled prior to use under nitrogen. All other reagents and solvents were reagent grade unless otherwise noted.

### 3.2. Physical measurements

The <sup>11</sup>B NMR spectra at 160.5 MHz, <sup>13</sup>C NMR spectra at 125.7 MHz and <sup>1</sup>H NMR spectra at 500 MHz were obtained on a Bruker AM-500 spectrometer. <sup>11</sup>B NMR spectra at 64.2 MHz and <sup>1</sup>H NMR at 200 MHz were obtained on a Bruker AF-200 spectrometer. Both instruments were appropriately equipped with decoupling accessories. All <sup>11</sup>B chemical shifts are referenced to BF<sub>3</sub> · OEt<sub>2</sub> (0.00 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual protons from the lock solvent (99.5% CD<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, or CDCl<sub>3</sub>) and are referenced to (CH<sub>3</sub>)<sub>4</sub>Si (0.00 ppm). NMR data are presented in Table 1.

High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer using negative ionization techniques. Infrared spectra were obtained on a Perkin Elmer 1430 spectrophotometer.

Analytical TLC was performed on 0.25 mm (2 × 4 cm<sup>2</sup>) silica gel F-254 plates (Merck). Preparative thin layer chromatography was conducted on 0.50 mm (20 × 20 cm<sup>2</sup>) silica gel F-254 plates (Merck 5744). Flash column chromatography was performed using silica gel (230–400 mesh, Merck) and the indicated solvents.

### 3.3. Synthesis of *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1**

A two-neck round bottom flask equipped with stirbar, septum and nitrogen inlet was charged with 0.93 g (7.0 mmol) of CoCl<sub>2</sub> and ca. 10 ml of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was maintained at 0 °C while a 5 ml aliquot (12.5 mmol)

Table 5

Data collection and structural refinement information for *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1**, *nido*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>, **2**, and *arachno*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>7</sub>H<sub>12</sub>, **3**

Formula	CoC <sub>8</sub> B <sub>10</sub> H <sub>16</sub> N	FeB <sub>7</sub> C <sub>11</sub> H <sub>19</sub> O <sub>2</sub>	CoB <sub>7</sub> C <sub>11</sub> H <sub>20</sub> O <sub>2</sub>
Formula weight	293.27	313.60	318.89
Crystal class	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	4	4	4
Cell constants			
<i>a</i> (Å)	7.557(1)	9.805(1)	7.489(2)
<i>b</i> (Å)	13.070(2)	9.545(1)	14.067(4)
<i>c</i> (Å)	14.682(3)	16.212(2)	14.469(2)
$\beta$ (deg)	98.57(1)	106.64(1)	102.97(1)
<i>V</i> (Å <sup>3</sup> )	1433.9(7)	1453.6(6)	1485.4(1)
$\mu$ (cm <sup>−1</sup> )	11.69	10.26	11.44
Trans. (min, max)	91.97, 99.94	79.34, 99.87	90.30, 99.92
Crystal size (mm <sup>3</sup> )	0.09 × 0.20 × 0.45	0.08 × 0.08 × 0.54	0.10 × 0.12 × 0.32
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	1.358	1.433	1.426
<i>F</i> (000)	592	644	656
Radiation (Mo K $\alpha$ ) (Å)	0.71073	0.71073	0.71073
$\theta$ range (deg)	2.0–27.5	2.0–27.5	2.0–27.5
Scan mode	$\omega$ –2 $\theta$	$\omega$ –2 $\theta$	$\omega$ –2 $\theta$
<i>h, k, l</i> collected	+9, −16, $\pm$ 19	+12, +12, $\pm$ 21	$\pm$ 9, +18, +18
No. reflections measured	3685	3742	3675
No. unique reflections	3284	3336	3398
No. reflections used ( <i>F</i> <sup>2</sup> > 3.0 $\sigma$ )	2488	2042	2295
Data/parameter ratio	10.2	9.2	8.5
<i>R</i> <sub>1</sub>	0.032	0.042	0.036
<i>R</i> <sub>2</sub>	0.041	0.050	0.044
GOF	1.303	1.325	1.237

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|; R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}.$$



of 2.5 M NaCp–THF, followed by a 17 ml aliquot (6.97 mmol) of a 0.41 M THF solution of *arachno*-8-(NC)-7,8-C<sub>2</sub>B<sub>10</sub>H<sub>14</sub>K<sup>+</sup> were added dropwise via syringe. Following reaction for 16 h under nitrogen, the flask was opened and 1 l of dry air bubbled through the solution. The solution was filtered through a  $\frac{1}{2}$ " plug of silica gel, then the solvent vacuum evaporated from the filtrate to give a dark oil that was separated by preparative TLC (CH<sub>2</sub>Cl<sub>2</sub>) to give as the major product 0.62 g (2.1 mmol, 30%) of *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**1**), R<sub>f</sub> = 0.42, red-orange, m.p. 225 °C, IR (KBr pellet) 3120(m), 3000(w), 2910(w), 2500(vs), 2200(vw), 1410(s), 1380(w), 1260(s), 1090(w), 1050(sh), 1020(m), 980(w), 850(s), 800(s) cm<sup>-1</sup>; HRMS: calcd., 295.1545; found, 295.1495. Anal. Calcd. for C<sub>8</sub>H<sub>16</sub>B<sub>10</sub>CoN; C, 32.77; H, 5.50; B, 36.86; N, 4.78. Found: C, 32.64; H, 5.36; B, 36.18; N, 4.59.

### 3.4. Synthesis of *nido*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>, **2**

A two-neck flask fitted with stirbar, septum and nitrogen inlet was charged with a 0.73 g (2.4 mmol) sample of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I and 30 ml of CH<sub>2</sub>Cl<sub>2</sub>. The anion of *arachno*-8-(CH<sub>3</sub>OC(O))-7,8,9,10-C<sub>4</sub>B<sub>8</sub>H<sub>13</sub> (0.49 g, 2.4 mmol) was made by reaction with excess NaH in THF (15 ml). When gas evolution ceased, the anion–THF solution was cannulated into the flask containing the ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I–CH<sub>2</sub>Cl<sub>2</sub> solution. The reaction mixture was stirred for 16 h at room temperature under a positive pressure of nitrogen. The dark solution was air oxidized and filtered through a  $\frac{1}{2}$ " plug of silica gel, washed with enough CH<sub>2</sub>Cl<sub>2</sub> until the washings were colorless, and the resultant dark brown solution was evaporated to dryness. The crude yield of metallacarboranes was ca. 50% (0.31 g). The residue was further purified by preparative TLC using 100% CH<sub>2</sub>Cl<sub>2</sub> to give 0.095 g (0.30 mmol, 12.5% yield) of *nido*-2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-8-(CH<sub>3</sub>OC(O))-6,7,8,9-C<sub>4</sub>B<sub>7</sub>H<sub>11</sub>, **2**, purple, R<sub>f</sub> = 0.36, m.p. 122 °C, IR (NaCl plates, CCl<sub>4</sub>) 3050(vw), 2910(s), 2900(s), 2810(m), 2520(vs), 1730(vs), 1490(sh), 1430(s), 1320(w), 1280(s), 1170(m), 1120(w), 1080(w),

Table 6

Refined positional parameters and isotropic thermal parameters for *closo*-1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co-2-(NC)-2,3-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, **1**

Atom	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Co1	0.97622(4)	0.76705(2)	0.77060(2)	2.353(5)
B4	1.2568(4)	0.7561(2)	0.7501(2)	3.55(6)
B5	1.1516(4)	0.6351(2)	0.7683(2)	3.27(5)
B6	0.9341(4)	0.6185(2)	0.7050(2)	3.07(5)
B7	0.8465(4)	0.7222(2)	0.6341(2)	3.57(5)
B8	1.0264(5)	0.7467(3)	0.5557(2)	4.69(7)
B9	1.2642(4)	0.7628(3)	0.6272(2)	4.31(6)
B10	1.3062(4)	0.6477(3)	0.6890(2)	4.02(6)
B11	1.1213(4)	0.5654(2)	0.6635(2)	3.47(6)
B12	0.9519(4)	0.6226(2)	0.5855(2)	3.57(6)
B13	1.1791(4)	0.6481(2)	0.5781(2)	3.79(6)
C2	0.9553(4)	0.8266(2)	0.6424(2)	3.93(5)
C2a	0.8526(5)	0.9183(3)	0.6122(2)	6.36(8)
C3	1.1344(3)	0.8433(2)	0.6908(2)	3.85(5)
N	0.7731(5)	0.9887(3)	0.5874(2)	10.5(1)
C14	1.0346(4)	0.8092(3)	0.9047(2)	5.68(7)
C15	0.9252(4)	0.7209(2)	0.8962(2)	4.69(6)
C16	0.7657(4)	0.7477(2)	0.8429(2)	4.43(6)
C17	0.7733(4)	0.8494(2)	0.8184(2)	4.65(6)
C18	0.9395(5)	0.8880(2)	0.8560(2)	5.45(7)
H3	1.180(3)	0.919(2)	0.699(2)	4.6(6)*
H4	1.357(3)	0.793(2)	0.800(2)	4.2(6)*
H5	1.196(3)	0.599(2)	0.835(2)	4.0(6)*
H6	0.833(3)	0.574(2)	0.729(2)	3.6(6)*
H7	0.729(4)	0.731(2)	0.615(2)	5.5(7)*
H8	0.992(4)	0.786(2)	0.494(2)	4.7(6)*
H9	1.360(3)	0.808(2)	0.602(2)	4.7(6)*
H10	1.439(4)	0.616(2)	0.700(2)	6.4(8)*
H11	1.139(3)	0.488(2)	0.661(2)	4.0(6)*
H12	0.874(4)	0.578(2)	0.543(2)	5.4(7)*
H13	1.239(4)	0.626(2)	0.524(2)	5.6(7)*
H14	1.131(4)	0.805(3)	0.929(2)	7.6(9)*
H15	0.942(4)	0.660(3)	0.919(2)	6.9(8)*
H16	0.650(4)	0.700(3)	0.818(2)	7.2(9)*
H17	0.677(5)	0.887(3)	0.774(2)	8(1)*
H18	0.977(5)	0.943(3)	0.843(2)	8(1)*

Starred atoms were refined isotropically.  $B_{\text{eq}} = 4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha)$ .

1070(w), 1020(w), 980(w), 920(w), 840(m), 820(w), 730(m)  $\text{cm}^{-1}$ ; HRMS calcd. for  $\text{C}_{11}\text{H}_{19}\text{B}_7\text{FeO}_2$ , (M – H) 316.1386. Found 316.1385.

Several other products were also produced in smaller amounts, including the tricarbaboranyl complexes *closo*-1-( $\eta$ - $\text{C}_5\text{H}_5$ )Fe-2-( $\text{CH}_3\text{OC}(\text{O})\text{CH}_2$ )-2,3,5- $\text{C}_3\text{B}_7\text{H}_9$ , blue,  $R_f = 0.34$ , 0.031 g (0.10 mmol, 4.3% yield; m.p. 119 °C) and *closo*-1-( $\eta$ - $\text{C}_5\text{H}_5$ )Fe-3-( $\text{CH}_3\text{OC}(\text{O})\text{CH}_2$ )-2,3,5- $\text{C}_3\text{B}_7\text{H}_9$ , blue,  $R_f = 0.30$ , 0.076 g (0.24 mmol, 10% yield; m.p. 133 °C) which were identified by comparison of their spectroscopic data with those of authentic samples.

The mass spectra of other minor products indicated they were isomers of **2**, but were obtained in insufficient amounts to allow characterization. Thermolysis of an approximate 10 mg sample of **2** in an evacuated Pyrex tube for 1 h at 190 °C led to about 15% conversion to an isomeric compound having a color and  $R_f$  value matching those of one of the side products, blue,  $R_f = 0.32$  ( $\text{CH}_2\text{Cl}_2$ ), m.p. 109 °C;  $^{11}\text{B}$  (64.2 MHz); 13.2 (d,  $J_{\text{BH}} = 119$ ), –0.59 (d,  $J_{\text{BH}} = 131$ ), –8.9 (d,  $J_{\text{BH}} = 152$ ), –18.7 (d,  $J_{\text{BH}} = 112$ ), –23.5 (d,  $J_{\text{BH}} = 129$ ), –25.4 (d,  $J_{\text{BH}} = 125$ ), –27.3 (d,  $J_{\text{BH}} = 131$ );  $^1\text{H}$  (200 MHz) 4.65 (s, Cp, 5), 3.92 (s, Me, 3), –6.16 ( $\mu$ -BHB).

### 3.5. Synthesis of *arachno*-2-( $\eta$ - $\text{C}_5\text{H}_5$ )Co-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{12}$ , **3**

The *arachno*-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{13}$  (0.50 g, 2.40 mmol) was converted to its anion by reaction with excess NaH in THF. When gas evolution ceased, about 30 min, the solution was cannulated into a two-neck flask,

Table 7

Refined positional parameters and isotropic thermal parameters for *nido*-2-( $\eta$ - $\text{C}_5\text{H}_5$ )Fe-8-( $\text{CH}_3\text{OC}(\text{O})$ )-6,7,8,9- $\text{C}_4\text{B}_7\text{H}_{11}$ , **2**

Atom	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Fe2	0.19350(5)	0.47738(5)	0.35670(3)	2.352(8)
B1	0.1965(5)	0.3312(5)	0.2589(3)	3.18(9)
B3	0.1188(4)	0.4921(4)	0.2205(3)	2.69(8)
B4	0.2149(5)	0.4048(5)	0.1596(3)	3.3(1)
B5	0.3584(5)	0.3136(5)	0.2301(3)	3.6(1)
B10	0.2391(5)	0.5858(5)	0.1736(3)	2.92(9)
B11	0.3934(5)	0.4725(5)	0.1846(3)	3.41(9)
B12	0.4843(5)	0.4254(5)	0.2940(3)	3.31(9)
C6	0.3547(4)	0.3462(4)	0.3300(2)	2.93(8)
C7	0.4216(4)	0.5077(4)	0.3599(2)	2.75(7)
C8	0.3268(3)	0.6256(4)	0.3440(2)	2.26(6)
C9	0.2058(4)	0.6320(4)	0.2687(2)	2.51(7)
C8a	0.3630(4)	0.7450(4)	0.4058(2)	2.64(7)
C8b	0.2917(5)	0.9693(5)	0.4385(3)	4.8(1)
C13	0.0803(4)	0.3412(5)	0.4112(3)	3.92(9)
C14	0.1966(4)	0.3946(5)	0.4764(3)	4.10(9)
C15	0.1834(4)	0.5393(5)	0.4779(2)	3.95(9)
C16	0.0591(4)	0.5771(5)	0.4133(3)	3.78(8)
C17	–0.0052(4)	0.4553(5)	0.3724(3)	3.89(9)
O1	0.2712(3)	0.8503(3)	0.3819(2)	3.49(6)
O2	0.4622(3)	0.7460(3)	0.4694(2)	3.82(6)
H1	0.133(4)	0.234(5)	0.257(2)	5.0*
H3	0.010(4)	0.513(4)	0.191(3)	5.0*
H4	0.161(4)	0.361(5)	0.101(2)	5.0*
H5	0.395(4)	0.220(5)	0.216(2)	5.0*
H6	0.387(4)	0.276(5)	0.374(2)	5.0*
H7	0.485(4)	0.506(4)	0.417(3)	5.0*
H9	0.146(4)	0.709(5)	0.265(2)	5.0*
H10	0.203(4)	0.657(5)	0.122(2)	5.0*
H11	0.444(4)	0.483(4)	0.133(3)	5.0*
H12	0.588(4)	0.387(4)	0.318(3)	5.0*
H1011	0.375(4)	0.594(5)	0.208(2)	5.0*
H8b	0.2065	1.0155	0.4316	5*
H8b'	0.3793	1.0189	0.4551	5*
H8b''	0.3078	0.9299	0.5022	5*
H13	0.0620	0.2429	0.3943	5*
H14	0.2735	0.3397	0.5136	5*
H15	0.2494	0.6027	0.5159	5*
H16	0.0243	0.6716	0.3996	5*
H17	–0.0913	0.4506	0.3248	5*

Starred atoms were not refined.  $B_{\text{eq}} = 4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha)$ .

fitted with a stirbar, nitrogen inlet and septum, containing 0.31 g (2.4 mmol) of  $\text{CoCl}_2$  suspended in 30 ml  $\text{CH}_2\text{Cl}_2$ . To this solution was added 1.5 ml (3.0 mmol) of 2 M  $\text{Na}^+\text{Cp}$  in THF. The solution was then stirred for 20 h at room temperature. The very dark solution was air oxidized and filtered through a  $\frac{1}{2}$ " plug of silica gel and separated by TLC to give 0.045 g (0.14 mmol), 5.9% of *arachno*-2-( $\eta$ - $\text{C}_5\text{H}_5$ )Co-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{12}$ , **3**,  $R_f = 0.73$ , purple; m.p. 150 °C; IR (NaCl plates,  $\text{CCl}_4$ ) 2930(sh), 2910(s), 2820(m), 2520(s), 1735(sh), 1710(s), 1430(w), 1420(w), 1260(m), 1240(m), 850(m)  $\text{cm}^{-1}$ ; HRMS calcd. for  $\text{C}_{11}\text{H}_{20}\text{B}_7\text{O}_2\text{Co}$  (M) 320.1447; found 320.1488. Also isolated in amounts insufficient for complete characterization were three other metallacarborane products,  $R_f = 0.70$ , 0.75 and 0.77 ( $\text{CH}_2\text{Cl}_2$ ) which, according to their mass spectra, could be isomers of **3**.

### 3.6. Crystallographic data for compounds **1**, **2** and **3**

Single crystals of **1**, **2** and **3** were grown by slow evaporation of  $\text{CH}_2\text{Cl}_2$ –heptane solutions under  $\text{N}_2$ . Suitably sized crystals were mounted and transferred to the diffractometer. Table 5 summarizes the data collection and structural refinement information for **1**, **2** and **3**.

Table 8  
Refined positional parameters for *arachno*-2-( $\eta$ - $\text{C}_5\text{H}_5$ )Co-8-( $\text{CH}_3\text{OC}(\text{O})$ )-7,8,9,10- $\text{C}_4\text{B}_7\text{H}_{12}$ , **3**

Atom	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Co2	0.02153(5)	0.21140(3)	0.21711(2)	2.568(6)
B1	−0.1599(5)	0.3282(3)	0.1861(3)	3.51(7)
B3	−0.2509(4)	0.2260(3)	0.2301(3)	3.55(7)
B4	−0.3137(5)	0.3397(3)	0.2615(3)	4.37(8)
B5	−0.1271(6)	0.4173(3)	0.2759(3)	4.37(9)
B6	0.0636(5)	0.3553(2)	0.2526(3)	3.36(7)
B11	−0.1820(7)	0.3629(3)	0.3798(3)	5.4(1)
B12	0.0495(5)	0.3838(3)	0.3696(3)	3.75(8)
C7	0.1489(4)	0.2858(2)	0.3462(2)	3.33(6)
C8	0.0746(4)	0.2013(2)	0.3873(3)	3.97(7)
C9	−0.1147(4)	0.1786(2)	0.3312(2)	3.31(6)
C10	−0.2628(4)	0.2541(3)	0.3469(3)	4.54(7)
C8a	0.2066(4)	0.1189(2)	0.4102(2)	3.16(6)
C8b	0.2355(5)	−0.0394(2)	0.4657(3)	4.85(8)
C13	0.0457(6)	0.2012(3)	0.0800(2)	5.30(8)
C14	0.2181(5)	0.2013(3)	0.1393(3)	4.74(8)
C15	0.2318(5)	0.1220(3)	0.1972(2)	4.62(8)
C16	0.0685(6)	0.0751(2)	0.1772(3)	5.36(9)
C17	−0.0508(5)	0.1230(3)	0.1035(3)	6.09(9)
O1	0.1205(3)	0.0402(1)	0.4259(2)	4.15(5)
O2	0.3703(3)	0.1252(2)	0.4216(2)	4.24(5)
H1	−0.209(4)	0.352(2)	0.113(2)	4.2(7)*
H3	−0.346(4)	0.177(2)	0.188(2)	4.6(8)*
H4	−0.458(5)	0.359(3)	0.242(2)	6.0(9)*
H5	−0.151(5)	0.492(3)	0.262(2)	5.5(8)*
H6	0.168(4)	0.393(2)	0.226(2)	4.1(7)*
H7	0.281(4)	0.289(2)	0.358(2)	4.0(7)*
H8	0.040(6)	0.219(3)	0.457(3)	9(1)*
H9	−0.154(4)	0.112(2)	0.330(2)	4.1(7)*
H10	−0.384(5)	0.223(2)	0.366(3)	6(1)*
H11	−0.243(6)	0.408(3)	0.421(3)	8(1)*
H12	0.117(4)	0.428(2)	0.400(2)	4.1(7)*
H1112	−0.045(4)	0.340(2)	0.432(2)	5.0(8)*
H8b	0.293(4)	−0.023(2)	0.527(2)	4.6(8)*
H8b'	0.155(5)	−0.093(3)	0.476(3)	6(1)*
H8b''	0.327(5)	−0.055(2)	0.428(2)	5.6(9)*
H13	0.008(6)	0.249(3)	0.034(3)	8(1)*
H14	0.308(7)	0.251(4)	0.142(3)	11(1)*
H15	0.341(6)	0.109(3)	0.241(3)	8(1)*
H16	0.046(5)	0.031(3)	0.205(3)	6(1)*
H17	−0.158(6)	0.113(3)	0.076(3)	9(1)*

Starred atoms were refined isotropically.  $B_{\text{eq}} = 4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha)$ .

### 3.6.1. Collection and reduction of the data

For **1**, **2** and **3** the X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated MoK $\alpha$  radiation. Three standard reflections measured every 3500 s of X-ray exposure showed no intensity decay over the course of data collection. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied.

### 3.6.2. Solution and refinement of the structure

The structures of **1**, **2** and **3** were solved by standard heavy atom Patterson techniques followed by weighted Fourier syntheses. Refinement was by full-matrix least squares techniques based on  $F$  to minimize the quantity  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2(F)$ . Non-hydrogen atoms were refined anisotropically. For **1** and **3**, hydrogen atoms were refined isotropically. For **2**, hydrogen atoms were included as constant contributions to the structure factors and were not refined (Tables 6–8). The tables of thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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