

occurs via attack of hydroxide ion on the equatorial ligand, serves as a precedent, since only the hydroxo species is reactive (the aquo species is at least 140-fold less reactive).<sup>10</sup> In the case of the (2-hydroxyethyl)cobaloximes, the excess reactivity of the hydroxo species could be due to hyperconjugation, as shown in the resonance hybrid 6, since the hyperconjugated resonance contributor will clearly be less reactive toward the 1,2-hydride shift. As this hyperconjugative interaction also places negative charge on the metal atom, ionization of the axial water ligand would be expected to destabilize this resonance contributor, thus enhancing hydride shift reactivity. Indeed, the greater reactivity of the hydroxo species may indicate the importance of hyperconjugation in this system.

**Summary.** The kinetics of the alkali-induced decomposition of (2-hydroxyethyl)cobaloxime have been shown to be consistent with a simple scheme in which both the aquo and hydroxo species decompose, with the latter being about 20-fold more reactive. Despite the fact that the measured rate constants for base-catalyzed exchange of acetaldehyde methyl protons with solvent deuterons and those for the exchange of the methyl deuterons of per-deuterioacetaldehyde with solvent protons exceed the rate

constants for decomposition of HOCH<sub>2</sub>CH<sub>2</sub>Co(D<sub>2</sub>H<sub>2</sub>)OH<sub>2</sub> in <sup>2</sup>H<sub>2</sub>O and of HOC<sup>2</sup>H<sub>2</sub>C<sup>2</sup>H<sub>2</sub>Co(D<sub>2</sub>H<sub>2</sub>)OH<sub>2</sub> in H<sub>2</sub>O, respectively, under all conditions, it was nonetheless possible to determine the isotopic composition of the nascent acetaldehyde from both decomposition reactions. This was accomplished by quenching the decomposition reaction at various times and converting the product acetaldehyde to its oxime for isotopic analysis by MS. The results unequivocally show that the acetaldehyde formed obtains its third methyl proton (or deuterium) from starting material and not from solvent. This eliminates any mechanism which directly forms the enol of acetaldehyde and strongly suggests that acetaldehyde is formed from (2-hydroxyethyl)cobaloximes in aqueous base by a 1,2-hydride shift mechanism.

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## Tricarbon Carborane Chemistry. 1. Syntheses and Structural Characterizations of Monocage Iron, Manganese, and Nickel Metallatricarbaborane Complexes

Carole A. Plumb, Patrick J. Carroll, and Larry G. Sneddon\*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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Improvements in the route to the tricarbon carborane 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> (1) and its corresponding monoanion, 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup>, have enabled the syntheses of a series of monocage iron, manganese, and nickel tricarbonborane complexes that are analogues of the cyclopentadienyl complexes of these metals. Reaction of 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> with (η-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I gave two isomeric products, 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (2) and 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-4-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (3), while reaction of the anion with Mn(CO)<sub>5</sub>Br yielded 1-(CO)<sub>3</sub>Mn-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (4). Single-crystal X-ray structural determinations of 2 and 3 confirm that they are hybrid complexes in which an iron atom is sandwiched between cyclopentadienyl and tricarbon carborane ligands. The ferratricarbaborane cages in both 2 and 3 have closo-octadecahedral structures, consistent with their 24-skeletal-electron counts, with the iron atom in the six-coordinate position and two of the cage carbon atoms in four-coordinate positions adjacent to the iron. The two structures differ in the position of the exopolyhedral methyl group. In 2 the methyl group is bound to a four-coordinate carbon as in 1. In 3 the methyl group has rearranged to an adjacent five-coordinate cage carbon. The reaction of 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> with [(η-C<sub>5</sub>H<sub>5</sub>)NiCO]<sub>2</sub> yielded the compound 9-(η-C<sub>5</sub>H<sub>5</sub>)Ni-8-CH<sub>3</sub>-7,8,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (5), which is proposed, on the basis of its skeletal-electron count and the spectroscopic data, to have a sandwich structure in which the nickelatricarbaborane cage has an open-cage geometry based on an icosahedron missing one vertex.

### Introduction

Tricarbon carboranes have been a largely unexplored class of boron cage compounds. The first tricarbon carboranes, the C-methyl and C,C'-dimethyl derivatives of nido-2,3,4-C<sub>3</sub>B<sub>3</sub>H<sub>7</sub>, were isolated by Grimes<sup>1</sup> in 1966 from the reaction of B<sub>4</sub>H<sub>10</sub> and acetylene. Initial investigations<sup>2</sup>

of the metal chemistry of this cage system yielded the first tricarbonborane complexes, (η<sup>1</sup>-2,3,4-Me<sub>2</sub>C<sub>3</sub>B<sub>3</sub>H<sub>5</sub>)Mn(CO)<sub>5</sub> and (η<sup>5</sup>-2,3,4-Me<sub>2</sub>C<sub>3</sub>B<sub>3</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub>; however, the parent carborane could not be prepared on scales sufficient for more extensive chemical investigations. Recently Siebert<sup>3</sup>

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Table I. NMR Data<sup>a</sup>

compd	nucleus	$\delta$ (mult, $J$ (Hz), assign <sup>t</sup> )
1-( $\eta$ -C <sub>5</sub> H <sub>5</sub> )Fe-2-CH <sub>3</sub> -2,3,4-C <sub>3</sub> B <sub>7</sub> H <sub>9</sub> (2)	<sup>11</sup> B <sup>b</sup>	2.6 (d, 158, B9), 1.9 (d, 172, B8), -7.4 (d, 147, B5), -10.6 (d, 147, B6), -24.6 (d, 145, B11), -27.7 (d, 156, B10), -32.2 (d, 157, B7)
	<sup>11</sup> B- <sup>11</sup> B <sup>b</sup>	cross peaks: B9-B6, B8-B5, B5-B6, B9-B11, B8-B11, B5-B11, B6-B11, B10-B11, B9-B10, B8-B10, B7-B10, B9-B7
1-( $\eta$ -C <sub>5</sub> H <sub>5</sub> )Fe-4-CH <sub>3</sub> -2,3,4-C <sub>3</sub> B <sub>7</sub> H <sub>9</sub> (3)	<sup>1</sup> H <sup>c</sup>	6.60 (br s, C3H), 3.85 (s, Cp), 2.57 (s, CH <sub>3</sub> ), 0.71 (s br, C4H)
	<sup>11</sup> B <sup>b</sup>	4.6 (d, 155, B9), -0.9 (d, 166, B8), -9.7 (d, 150, B5), -11.1 (d, 153, B6), -23.1 (d, 144, B11), -23.5 (d, 163, B10), -29.4 (d, 159, B7)
1-(CO) <sub>3</sub> Mn-2-CH <sub>3</sub> -2,3,4-C <sub>3</sub> B <sub>7</sub> H <sub>9</sub> (4)	<sup>11</sup> B <sup>b</sup>	cross peaks: B9-B6, B8-B5, B5-B6, B9-B11, B8-B11, B5-B11, B6-B11, B10-B11, B9-B10, B8-B10, B7-B10, B9-B7
	<sup>1</sup> H <sup>c</sup>	6.89 (br s, C3H), 5.51 (br s, C2H), 3.83 (s, Cp), 0.89 (s, CH <sub>3</sub> )
9-( $\eta$ -C <sub>5</sub> H <sub>5</sub> )Ni-8-CH <sub>3</sub> -7,8,10-C <sub>3</sub> B <sub>7</sub> H <sub>9</sub> (5)	<sup>11</sup> B <sup>b</sup>	6.7 (d, 164, B9), 3.6 (d, 151, B8), 0.8 (d, 178, B5), -3.1 (d, 154, B6), -18.1 (d, 152, B11), -20.7 (d, 161, B10), -30.2 (d, 162, B7)
	<sup>1</sup> H <sup>c</sup>	6.58 (br s, C3H), 2.29 (s, CH <sub>3</sub> ), 1.53 (br s, C4H)
	<sup>13</sup> C <sup>d,e</sup>	217.45 (br s, CO), 107.63 (br s, C3), 80.79 (br s, C2), 56.74 (s, C5), 31.32 (s, CH <sub>3</sub> )
	<sup>11</sup> B <sup>b</sup>	8.7 (d, 151, B3), 3.1 (d, 151, B4, B6), -7.2 (d, 146, B11), -9.6 (d, 169, B5), -18.1 (d, 156, B2), -23.0 (d, 142, B1)
	<sup>1</sup> H <sup>c</sup>	4.59 (s, Cp), 2.48 (br s, CH), 1.57 (br s, CH), 1.05 (s, CH <sub>3</sub> )

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> 160 MHz. <sup>c</sup> 500 MHz. <sup>d</sup> 125.8 MHz. <sup>e</sup> Broad-band decoupled.

reported the characterization of a number of metal derivatives of the isomeric *nido*-2,3,5-R<sub>5</sub>C<sub>3</sub>B<sub>3</sub>H carborane cage, as well as the first synthetic routes to this carborane. Another three-carbon carborane, *closo*-C<sub>3</sub>B<sub>5</sub>H<sub>7</sub>, which was proposed to have one bare carbon atom, was prepared<sup>4</sup> in 1971 by the pyrolysis of *nido*- $\mu$ -H<sub>3</sub>Si- or 4-H<sub>3</sub>Si-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub>, but no further studies have been reported.

Stibr<sup>5</sup> and Kang<sup>6</sup> have separately reported the first synthetic routes to two different isomeric seven-boron tricarbon carboranes. Stibr showed that the thermolytic reaction of *arachno*-4,5-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> with 2-butyne gives a 15% yield of *nido*-5,6,10-(CH<sub>3</sub>)<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>, while Kang demonstrated that reaction of the *arachno*-4,6-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub><sup>-</sup> anion with acetonitrile followed by protonation yields *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub>. Although these synthetic routes were only recently developed, one seven-boron metallatricarbaborane complex, 1-[ $\eta$ -C<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>H]Ni-9,2,4-(CH<sub>3</sub>)<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>7</sub>, based on the 5,6,9-isomer has previously been isolated and structurally characterized as a minor product of the reaction of Ni atoms, 2-butyne, and *arachno*-4,5-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub>.<sup>7</sup>

Related to the polyhedral tricarbon carboranes are the diborole heterocycles R<sub>4</sub>C<sub>3</sub>B<sub>2</sub>H developed by Siebert.<sup>8</sup> The formal *archno*-R<sub>4</sub>C<sub>3</sub>B<sub>2</sub>H<sup>8-</sup> anion derived from these ring systems has been shown to exhibit a rich chemistry, yielding numerous metal complexes, including a range of multidecker sandwiches.

We report here improvements in the synthesis of *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> which now make this carborane the most accessible polyhedral tricarbon carborane cage system, thus enabling systematic investigations of its chemical properties. We also report in this, and the accompanying two papers,<sup>9,10</sup> some initial investigations of the metal chemistry of the tricarbon carborane anion 6-CH<sub>3</sub>-5,6,9-

C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> which illustrate that these types of tricarbon carboranes have a diverse organometallic chemistry with the resulting metallatricarbaboranes exhibiting properties complementary to both conventional dicarbon carborane and cyclopentadienylmetal complexes.

### Experimental Section

All experimental manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.<sup>11</sup>

**Materials.** 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> was obtained from Dexsil Corp., Hamden, CT. *arachno*-4,6-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> was prepared as previously reported.<sup>12</sup> ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I, Mn(CO)<sub>5</sub>Br, [ $\eta$ -C<sub>5</sub>H<sub>5</sub>]Ni(CO)<sub>2</sub>, and HCl/etherate solutions were purchased from Strem or Aldrich and used as received. Spectrochemical grade CH<sub>3</sub>CN, THF, Et<sub>2</sub>O, and CH<sub>2</sub>Cl<sub>2</sub> were purchased from Fisher or EM Science. Degassed THF and Et<sub>2</sub>O were stored over sodium-benzophenone ketyl until used. CH<sub>2</sub>Cl<sub>2</sub> was dried over P<sub>2</sub>O<sub>5</sub>, transferred onto activated 4-Å molecular sieves, and stored under vacuum until used. Anhydrous CH<sub>3</sub>CN was stored in vacuo on activated 4-Å molecular sieves. All other reagents were commercially obtained and used as received unless noted otherwise.

**Physical Measurements.** <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 equipped with the appropriate decoupling accessories. <sup>11</sup>B NMR spectra at 64.2 MHz, <sup>13</sup>C NMR spectra at 50.3 MHz, and <sup>1</sup>H NMR spectra at 200 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All <sup>11</sup>B chemical shifts were referenced to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.0 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% C<sub>6</sub>D<sub>6</sub> or CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>) and then referenced to (CH<sub>3</sub>)<sub>4</sub>Si (0.0 ppm). Two-dimensional COSY <sup>11</sup>B-<sup>11</sup>B experiments were performed at 160.5 MHz using the procedures described<sup>13</sup> previously. NMR data are summarized in Table I.

High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. A Hewlett-Packard 8452A diode array spectrophotometer was used to obtain ultraviolet-visible spectra. Cyclic voltammetric measurements were performed under argon gas in acetonitrile solvent using an HD Hokuto Denko Ltd HA-301 potentiostat-galvanostat in 5 × 10<sup>-4</sup> M (*n*-butyl)<sub>4</sub>NPF<sub>6</sub> electrolyte solutions referenced to SCE. Preparative thin-layer chromatography was conducted on 0.5-mm (20 × 20 cm) silica gel F-254 plates (Merck-5744).

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Analytical thin-layer chromatography was performed on 0.25 mm (5 × 10 cm) silica gel F-254 plates (Merck). Silica gel (230–400 mesh, Merck) was used for flash column chromatography. Elemental analyses were obtained from Galbraith Laboratories Inc., Knoxville, TN. The yields of all metallatricarbaborane products are calculated on the basis of starting metal reagent.

**Synthesis of Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> (Na<sup>+</sup>1<sup>-</sup>).** A modification of the published procedure<sup>6</sup> for the synthesis of Na<sup>+</sup>6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> was used. Freshly sublimed *arachno*-4,6-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> powder (1.0 mmol) and NaH (0.95 mmol) (prepared from a 60% dispersion washed free of mineral oil with pentane under an inert atmosphere) were added under an inert atmosphere to a 50-mL two-neck round-bottom flask, equipped with a stirbar, septum, and vacuum stopcock, and the flask was then evacuated. Degassed CH<sub>3</sub>CN (20 mL) was condensed into the flask and the reaction mixture warmed to room temperature with stirring until evolution of H<sub>2</sub> gas had ceased. At this point the reaction flask was connected to a reflux condenser under a N<sub>2</sub>(g) flush, and CH<sub>3</sub>CN was added via cannula until the reaction vessel was half full; then the reaction mixture was thoroughly flushed with N<sub>2</sub>(g) through the septum seal for 5 min. The mixture was brought to rolling reflux. After 12 h the reaction was observed to be complete by the <sup>11</sup>B NMR spectrum of the mixture. Reactions on a larger scale (10–15 mmol) were usually 95% complete in 3 days and complete after 4 days. After it was cooled, the reaction mixture was filtered under a N<sub>2</sub>(g) flow to remove solids. The solvent was removed from the filtrate in vacuo to leave a clear oily residue that was immediately dissolved in dry THF. The resulting clear solution could be kept in a refrigerator for 3–4 months without noticeable decomposition; however, storage in acetonitrile resulted in a color change to bright orange.

The molarity of stock anion solutions of Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> was determined by standardization relative to the total integral of the <sup>11</sup>B NMR spectrum of a B<sub>10</sub>H<sub>14</sub> sample of known concentration.

**Conversion of 6-CH<sub>3</sub>-5,6,8-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> to *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> (1).** A 1.0-mmol aliquot of 0.1 M Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> was syringed into a 25-mL round-bottom flask, equipped with a stirbar, containing 10 mL of THF, and the mixture was cooled to -10 °C in an ice-salt bath. A 1.0-mL aliquot of a 1 M solution of HCl in Et<sub>2</sub>O was added dropwise by syringe into the stirred reaction mixture, which then turned cloudy white. After 15 min at -10 °C the reaction mixture was warmed to room temperature, stirred for 5 min, and then fractionated in vacuo through -23 and -196 °C traps until all volatile materials were removed from the reaction flask. Refractionation of the contents of the -23 °C trap through a 0 °C trap removed any traces of *arachno*-4,6-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub>. *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> was isolated in 80% (0.80 mmol) yield in the -23 °C trap. Storage of the neutral carborane at room temperature resulted in decomposition to yellow solids.

**Synthesis of Ferratricarbaboranes 2 and 3.** A 2.56-mmol sample of (η-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I was loaded into a 100-mL three-necked round-bottom flask equipped with a stirbar, septum, and vacuum stopcock, and the flask was evacuated. THF (20 mL) was added by vacuum distillation. The mixture was warmed to room temperature and a 37-mL sample of 0.07 M Na<sup>+</sup>(6,5,9-CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> in THF solution added dropwise via syringe. The solution darkened to dark green and was then stirred at room temperature for 16 h. The reaction mixture was opened to the air and filtered and the dark filtrate evaporated to dryness. Preparative TLC (7:3 hexane-CH<sub>2</sub>Cl<sub>2</sub>) gave four bands. A red band (*R*<sub>f</sub> 0.87) yielded 8 mg (0.025 mmol, 1%) of *compro*-Fe-(1-Fe-5-CH<sub>3</sub>-2,3,5-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)(1-Fe-4-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>) (8; see the following paper for characterization). A deep blue band (*R*<sub>f</sub> 0.43) contained a mixture of 2 and 3. Also isolated were 3 mg (0.07 mmol) of 4,6-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> (*R*<sub>f</sub> 0.61) and 161 mg of unreacted CpFe(CO)<sub>2</sub>I (21%) (*R*<sub>f</sub> 0.28) as identified by comparison with authentic samples. Repeated fractional recrystallization of the material from the blue band resulted in the isolation of 166 mg (0.64 mmol, 26%) of 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (2) and 16 mg (0.06 mmol, 2%) of 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-4-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (3). For 2: dark blue; mp 206.5 °C; IR (KBr pellet, cm<sup>-1</sup>) 3012 (w), 2922 (w), 2640 (sh, w), 2598 (w), 2528 (s), 1554 (w), 1445 (sh, w), 1378 (w), 1130 (w), 1104 (m), 1060 (w), 1050 (sh, w), 1025 (w), 1010 (sh, w), 1002 (w), 965 (m), 855 (sh, w), 835 (m), 792 (w), 724 (w), 688 (w), 420 (w);

UV-vis (λ, nm (ε, L cm<sup>-1</sup> mol<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub>) 228 (2258), 260 (1494, sh). Anal. Calcd for C<sub>9</sub>H<sub>17</sub>B<sub>7</sub>Fe: C, 42.10; H, 6.67. Found: C, 41.51; H, 6.73. Exact mass measurement for <sup>12</sup>C<sub>9</sub><sup>1</sup>H<sub>17</sub><sup>11</sup>B<sub>7</sub><sup>56</sup>Fe: calcd, 258.1331; found, 258.1393. For 3: light blue; mp 200 °C; IR (KBr pellet, cm<sup>-1</sup>) 3112 (w), 3058 (w), 2960 (w), 2920 (w), 2574 (sh, s), 2538 (s), 2500 (sh, s), 2345 (w), 2340 (w), 1488 (w), 1422 (m), 1385 (w), 1362 (w), 1260 (w), 1168 (w), 1110 (m), 1116 (sh, m), 1054 (m), 1048 (m), 1012 (sh, m), 1008 (m), 948 (m), 858 (sh, w), 848 (s), 816 (sh, m), 790 (m), 724 (m), 688 (sh, w), 680 (w), 635 (w), 520 (m), 430 (s); UV-vis, (λ, nm (ε, L cm<sup>-1</sup> mol<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub>) 224 (3402), 258 (3206, sh). Exact mass measurement for <sup>12</sup>C<sub>9</sub><sup>1</sup>H<sub>17</sub><sup>11</sup>B<sub>7</sub><sup>56</sup>Fe: calcd, 258.1331; found, 258.1388.

**Thermolysis of 2 and 3.** A 10-mg sample of 2 was sealed in vacuo in a length of 5-mm Pyrex tubing and placed in an oil bath at 240 °C for 10 h. Analysis of the product by <sup>11</sup>B NMR spectroscopy showed that ~90% of 2 had converted to 3. Recrystallization of the product from hexane yielded 6.7 mg (64%) of 3. Conversion did not take place at lower temperatures. A 10-mg sample of 2 heated at 320 °C for 1 h produced a purple material (*R*<sub>f</sub> 0.67 in 7:3 hexane-CH<sub>2</sub>Cl<sub>2</sub>). Both the <sup>11</sup>B and <sup>1</sup>H NMR spectra showed the presence of two products which were found to be inseparable by chromatographic methods or recrystallization. The product mixture exhibited a mass spectrum identical with those observed for 2 and 3. Exact mass measurement for <sup>12</sup>C<sub>9</sub><sup>1</sup>H<sub>17</sub><sup>11</sup>B<sub>7</sub><sup>56</sup>Fe: calcd, 258.1331; found, 258.1337. At lower temperatures no reaction was observed. At higher temperatures decomposition resulted. Heating 3 for 1 h at 320 °C was also found to produce a product mixture similar to that observed upon heating 2.

**Synthesis of 1-(CO)<sub>3</sub>Mn-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (4).** A 2.0-mmol sample of Mn(CO)<sub>5</sub>Br was loaded into a 100-mL three-neck round-bottom flask equipped with a stirbar, septum, and vacuum stopcock. The flask was then evacuated, and 20 mL of THF was added by vacuum distillation. Warming to room temperature generated a bright orange solution, to which a 20-mL aliquot of 0.10 M Na<sup>+</sup>(5,6,9-CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup>-THF solution was added dropwise via syringe. Within 30 min the solution darkened to a red color, and the solution was stirred for 8 h. The reaction mixture was next opened to the air and filtered and the resultant red-orange solution evaporated to dryness. The mixture was separated by preparative TLC (hexane) to give two bands. A bright yellow band (*R*<sub>f</sub> 0.94) yielded small amounts of Mn<sub>2</sub>(CO)<sub>10</sub> (probably formed by a competing reductive-coupling reaction of Mn(CO)<sub>5</sub>Br by comparison to an authentic sample). A bright red-orange band (*R*<sub>f</sub> 0.78) furnished 299 mg (1.09 mmol) of 4 (54% yield). Further purification was carried out by sublimation onto a 0 °C cold finger under vacuum. While the product remained stable for several hours in solution under vacuum at room temperature, it decomposed to white-tan solids overnight at 25 °C in solution exposed to air. For 4: orange-red; mp 97.5–98.5 °C; IR (KBr pellet, cm<sup>-1</sup>) 3020 (w), 2972 (w), 2925 (w), 2865 (w), 2560 (s), 2040 (vs), 2008 (sh), 1960 (vs), 1448 (m), 1384 (m), 1280 (w), 1135 (m), 1114 (m), 1123 (m), 968 (m), 870 (w), 734 (m), 645 (m). Anal. Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>3</sub>B<sub>7</sub>Mn: C, 30.60; H, 4.40. Found: C, 30.70; H, 4.57.

**Synthesis of 9-(η-C<sub>5</sub>H<sub>5</sub>)Ni-8-CH<sub>3</sub>-7,8,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (5).** A 0.56-mmol sample of [(η-C<sub>5</sub>H<sub>5</sub>)NiCO]<sub>2</sub> was loaded into a 100-mL three-neck round-bottom flask equipped with a stirbar, septum, and vacuum stopcock. The flask was evacuated and 20 mL of THF added by vacuum distillation. When the mixture was warmed to room temperature, a dark solution was obtained. A 6.2-mL aliquot of 0.18 M Na<sup>+</sup>(5,6,9-CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup>/THF solution was added dropwise via syringe. The solution darkened from red-brown to black, and the solution was then stirred for 24 h. The reaction mixture was next opened to the air and filtered and the dark solution evaporated to dryness. Preparative TLC of the mixture (7:3 hexane-CH<sub>2</sub>Cl<sub>2</sub>) gave three bands. A dark green band (*R*<sub>f</sub> 0.87) produced 62 mg (0.23 mmol) of 5 for a yield of 43%. The remaining bands were air-sensitive and could not be characterized. For 5: green; mp 142 °C; IR (KBr pellet, cm<sup>-1</sup>) 3120 (sh), 3102 (m), 3016 (w), 2970 (w), 2950 (w), 2978 (w), 2858 (w), 2590 (sh), 2550 (sh), 2535 (s), 2520 (sh), 1442 (m), 1405 (m), 1370 (m), 1350 (m), 1332 (w), 1260 (m), 1135 (m), 1112 (m), 1084 (m), 1050 (m), 1044 (sh), 1018 (w), 982 (m), 965 (m), 945 (w), 920 (w), 875 (vw), 845 (w), 835 (m), 808 (s), 740 (vw), 730 (vw), 718 (w), 695 (vw), 680 (vw), 662 (w), 640 (vw), 600 (w), 515 (vw). Anal. Calcd for C<sub>9</sub>H<sub>17</sub>B<sub>7</sub>Ni: C, 41.63; H, 6.56. Found: C, 41.65; H, 6.68. Exact

Table II. Data Collection and Structure Refinement Information

	2	3
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	25.961 (5)	8.098 (2)
<i>b</i> , Å	7.876 (1)	11.959 (3)
<i>c</i> , Å	13.913 (2)	13.956 (2)
$\beta$ , deg	118.20 (2)	106.53 (1)
<i>V</i> , Å <sup>3</sup>	2507 (2)	1295.7 (9)
<i>Z</i>	8	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.360	1.316
<i>F</i> (000)	1056	528
mol formula	FeC <sub>9</sub> H <sub>17</sub> B <sub>7</sub>	FeC <sub>9</sub> H <sub>17</sub> B <sub>7</sub>
mol wt	256.76	256.76
$\lambda$ , Å	Mo K $\alpha$ , 0.71073	Mo K $\alpha$ , 0.71073
$\mu$ , cm <sup>-1</sup>	11.65	11.27
transmissn (min, max)	69.9, 81.2	69.4, 99.9
$\theta$ range, deg	2–27.5	2–27.5
scan mode	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
$\pm h, \pm k, \pm l$ collected	$\pm 33, -10, 18$	10, 15, $\pm 18$
no. of measd intens	3212	3333
no. of unique intens	2880	2968
no. of $F_o^2 > 3\sigma(F_o^2)$	2367	1727
no. of variables	154	154
<i>R</i>	0.034	0.050
<i>R</i> <sub>w</sub>	0.052	0.060
GOF	1.707	1.648

mass measurement for <sup>12</sup>C<sub>9</sub><sup>1</sup>H<sub>17</sub><sup>11</sup>B<sub>7</sub><sup>64</sup>Ni: calcd, 260.1335; found 260.1375.

**Crystallographic Data for 2 and 3.** Single crystals of 2 and 3 were grown by slow evaporation in air of methylene chloride solutions. A suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

**Collection and Reduction of the Data.** Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo K $\alpha$  radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at regular intervals showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

**Solution and Refinement of the Structures.** All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package. The full-matrix least-squares refinement was phased on *F*, and the function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The weights (*w*) were taken as  $4F_o^2/(\sigma(F_o^2))^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections are those stored in the SDP package. Agreement factors are defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = (\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2)^{1/2}$ .

Three-dimensional Patterson syntheses gave the coordinates of the iron atoms in 2 and 3. Subsequent Fourier maps led to the locations of all other non-hydrogen atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all cage hydrogens. The positions of the remaining hydrogens were calculated. Hydrogen atoms were not refined but were included as constant contributions to the structure factors. The final refinements included numerical (2) or empirical (3) absorption corrections along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms (6 Å<sup>2</sup>). Final difference Fourier maps were featureless. Crystal and structure refinement data are summarized in Table II. Final positional parameters are given in Tables III and IV, and selected intramolecular bond distances are presented in the figure captions.

## Results and Discussion

The synthetic route to 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> reported by Kang<sup>6</sup> involved the reaction of acetonitrile with *arachno*-4,6-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub><sup>-</sup> in THF solution to produce Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup>. The original reaction procedure was un-

Table III. Refined Positional Parameters for 2

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> <sup>a</sup> , Å <sup>2</sup>
Fe1	0.38629 (1)	0.29472 (4)	0.37897 (2)	2.701 (6)
C2	0.33942 (8)	0.3680 (3)	0.4488 (2)	2.82 (4)
C3	0.42165 (9)	0.0738 (3)	0.4342 (2)	3.51 (5)
C4	0.3970 (1)	0.3294 (3)	0.5491 (2)	3.48 (5)
C2m	0.3082 (1)	0.5364 (4)	0.4316 (2)	4.72 (6)
Cp1	0.4265 (1)	0.2933 (4)	0.2803 (2)	5.50 (7)
Cp2	0.3670 (2)	0.2971 (4)	0.2180 (2)	5.98 (8)
Cp3	0.3456 (1)	0.4426 (5)	0.2429 (2)	6.55 (8)
Cp4	0.3963 (1)	0.5300 (4)	0.3266 (2)	7.48 (7)
Cp5	0.4440 (1)	0.4325 (5)	0.3456 (2)	6.26 (7)
B5	0.3098 (1)	0.1989 (3)	0.3938 (2)	3.08 (5)
B6	0.3546 (1)	0.0312 (3)	0.3822 (2)	3.42 (6)
B7	0.4455 (1)	0.1757 (4)	0.5435 (2)	3.57 (6)
B8	0.3316 (1)	0.2340 (4)	0.5352 (2)	3.62 (6)
B9	0.4071 (1)	-0.0255 (4)	0.5226 (2)	3.75 (6)
B10	0.3987 (1)	0.1296 (4)	0.6032 (2)	3.81 (6)
B11	0.3352 (1)	0.0314 (4)	0.4909 (2)	3.56 (6)

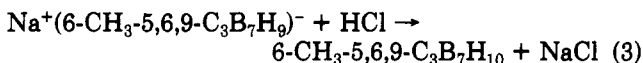
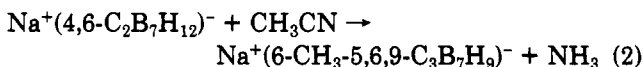
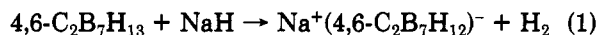
<sup>a</sup>  $B_{eq} = 1/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab(\cos \gamma) + \beta_{13}ac(\cos \beta) + \beta_{23}bc(\cos \alpha)]$ .

Table IV. Refined Positional Parameters for 3

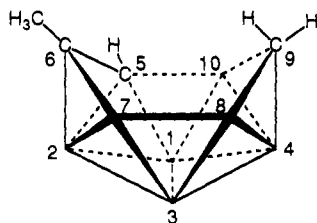
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> <sup>a</sup> , Å <sup>2</sup>
Fe1	0.05866 (7)	0.24433 (5)	0.38335 (4)	3.43 (1)
C2	0.2080 (5)	0.2420 (4)	0.2970 (3)	4.31 (9)
C3	-0.0125 (5)	0.3969 (4)	0.3990 (3)	4.25 (9)
C4	0.3023 (5)	0.3293 (3)	0.3682 (3)	3.88 (9)
C4m	0.4871 (6)	0.3067 (5)	0.4257 (4)	6.2 (1)
B5	0.0352 (7)	0.2855 (5)	0.2261 (4)	4.6 (1)
B6	-0.0922 (7)	0.3773 (4)	0.2834 (4)	4.5 (1)
B7	0.1901 (7)	0.4113 (4)	0.4320 (4)	4.2 (1)
B8	0.2377 (8)	0.3545 (5)	0.2360 (4)	5.2 (1)
B9	0.0487 (7)	0.4969 (5)	0.3337 (4)	5.1 (1)
B10	0.2491 (8)	0.4599 (5)	0.3241 (4)	5.1 (1)
B11	0.0582 (8)	0.4371 (5)	0.2224 (4)	5.4 (1)
Cp1	-0.0766 (6)	0.1877 (4)	0.4776 (4)	5.8 (1)
Cp2	-0.1372 (6)	0.1380 (4)	0.3875 (4)	5.6 (1)
Cp3	-0.0066 (7)	0.0793 (4)	0.3681 (4)	7.8 (1)
Cp4	0.1427 (7)	0.0944 (5)	0.4475 (5)	9.5 (2)
Cp5	0.0948 (7)	0.1623 (5)	0.5177 (4)	8.0 (1)

<sup>a</sup>  $B_{eq} = 1/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab(\cos \gamma) + \beta_{13}ac(\cos \beta) + \beta_{23}bc(\cos \alpha)]$ .

satisfactory, however, because of moderate and variable yields (30–50%) and long reaction times (up to 2 weeks):



A series of reactions was initiated to investigate the effects of conditions on reaction yield and efficiency. A procedure was developed that allows routine production of 10-mmol samples of Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> in yields of 80% or better after 4 days of reaction. There were a number of factors found to be critical to the reaction yields and rate. In the preparation of Na<sup>+</sup>(4,6-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub>)<sup>-</sup>, the amount of NaH must be less than 1 equiv relative to 4,6-C<sub>2</sub>B<sub>7</sub>H<sub>13</sub>. With larger amounts of NaH, a second species is produced that was found to both retard the rate of reaction and lower the yields. It was also found that Na<sup>+</sup>(4,6-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub>)<sup>-</sup> is best prepared directly in CH<sub>3</sub>CN, instead of THF, since this allows the reaction to be taken directly on to reflux, thereby eliminating several steps and the possibility of air exposure. Furthermore, the rate of reaction in acetonitrile was substantially increased, such that time for completion of, for example, a 10-mmol-scale reaction was shortened from 2 weeks to 4 days. Finally,



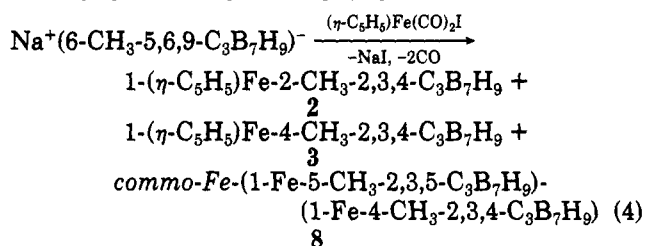
**Figure 1.** Proposed structure and numbering of 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> (1) (B-H hydrogens are not shown).

it was found that protonation of Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> using a stoichiometric amount of HCl/etherate in THF in -10 °C, instead of the anhydrous HCl used by Kang, gave greatly improved yields of *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> (>80%).

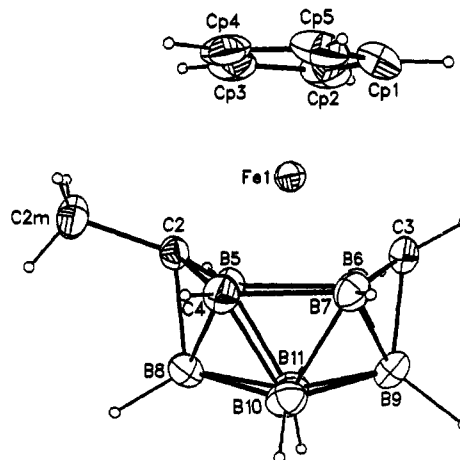
The proposed<sup>6</sup> structure of *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> is shown in Figure 1. Consistent with its 24-skeletal-electron count, the tricarbon carborane is proposed to have an open-cage structure based on an octadecahedron missing one vertex. The spectroscopic data indicate that, in the 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> anion, one of the hydrogens present at the 9-carbon is removed.

Only a few polyhedral metallatricarbaborane complexes have been reported; thus, the availability of 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> has now made the first systematic investigations of the syntheses and properties of these complexes possible. As a result of its charge and structure, the 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> ligand might be expected to exhibit metal coordination properties intermediate between those of the dicarbon carborane dianions, such as dicarbollide (C<sub>2</sub>B<sub>9</sub>H<sub>11</sub><sup>2-</sup>)<sup>14,15</sup> or C<sub>2</sub>B<sub>9</sub>H<sub>10</sub><sup>2-</sup><sup>15</sup> and the cyclopentadienyl ligand, C<sub>5</sub>H<sub>5</sub><sup>-</sup>. Thus, 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> has, like C<sub>5</sub>H<sub>5</sub><sup>-</sup>, a 1- charge, rather than the 2- charge of the *nido* dicarbon carborane anions. However, unlike C<sub>5</sub>H<sub>5</sub><sup>-</sup> (and C<sub>2</sub>B<sub>9</sub>H<sub>11</sub><sup>2-</sup>), the open face of 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> has an asymmetric, six-membered cyclohexane boatlike confirmation, similar to that found in C<sub>2</sub>B<sub>9</sub>H<sub>10</sub><sup>2-</sup>, in which the two carbon atoms in the 6- and 9-positions can interact with a metal more strongly than the remaining carbon and three borons on the face. To explore the metal-binding properties of 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup>, the syntheses of the monocage tricarbon carborane analogues of (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe, (η-C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>3</sub>, and (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni were initially investigated, as discussed in the following sections.

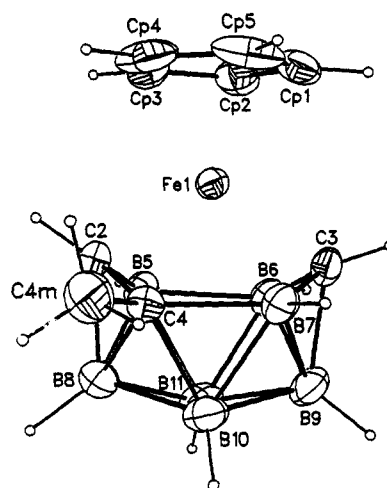
**Ferratricarbaboranes 2 and 3.** The reaction of (η-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I and Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> produced three metallatricarbaboranes with the major product being 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (2).



The two isomeric compounds 2 and 3 could not be separated by TLC methods but were separated by fractional recrystallization. The <sup>11</sup>B NMR spectra of both compounds are similar, consisting of seven doublet reso-



**Figure 2.** ORTEP drawing of the molecular structure of 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (2). Selected bond distances (Å): Fe-C2, 1.968 (2); Fe-C3, 1.947 (2); Fe-C4, 2.265 (3); Fe-B5, 2.222 (3); Fe-B6, 2.241 (3); Fe-B7, 2.270 (2); C2-C4, 1.517 (4); C2-B5, 1.547 (4); C4-B7, 1.775 (4); C3-B7, 1.565 (4); C3-B6, 1.574 (3); B5-B6, 1.816 (4); C2m-C2, 1.513 (3).



**Figure 3.** ORTEP drawing of the molecular structure of 1-(η-C<sub>5</sub>H<sub>5</sub>)Fe-4-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (3). Selected bond distances (Å): Fe-C2, 1.935 (5); Fe-C3, 1.944 (4); Fe-C4, 2.282 (4); Fe-B5, 2.204 (5); Fe-B6, 2.236 (5); Fe-B7, 2.274 (5); C2-C4, 1.492 (4); C2-B5, 1.555 (6); C4-B7, 1.745 (7); C3-B7, 1.582 (6); C3-B6, 1.577 (6); B5-B6, 1.838 (8); C4-C4m, 1.507 (6).

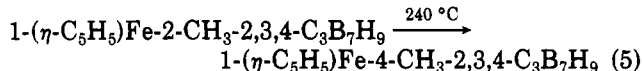
nances at comparable chemical shifts, and both compounds exhibit similar connectivities in their 2-D <sup>11</sup>B-<sup>11</sup>B NMR spectra. Likewise, one resonance in each spectrum, -32.2 ppm in 2 and -29.4 ppm in 3, is unusually sharp, suggestive of a boron (B7) situated between two carbons. These common features indicate that the boron frameworks in both isomers are similar. However, the <sup>1</sup>H NMR spectra of the two compounds exhibit significant differences. Both isomers have a low-field cage CH resonance at ~6.7 ppm and a cyclopentadienyl resonance at ~3.8 ppm, but the other cage CH resonance (0.70 ppm in 2 and 5.5 ppm in 3) and the methyl resonance (2.6 ppm in 2 and 0.88 ppm in 3) occur at very different chemical shifts, indicative of substitution at different cage-carbon positions.

The structures of 2 and 3 were established by single-crystal X-ray determinations, as shown in the ORTEP drawings in Figures 2 and 3, respectively, and confirm that they are hybrid complexes in which an iron atom is sandwiched between cyclopentadienyl and tricarbon carborane ligands. The ferratricarbaborane cages in both compounds have gross closo-octadecahedral structures, consistent with their 24-skeletal-electron counts, with the

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iron atom in the six-coordinate position and two of the cage-carbon atoms in four-coordinate positions (C2 and C3) adjacent to the iron. The third cage carbon in both complexes is in a five-coordinate position (C4) that is connected to the iron and one (C2) of the four-coordinate carbons. Consistent with the conclusions drawn from their  $^1\text{H}$  NMR spectra, the two structures differ in the position of the exopolyhedral methyl group. In **2** the methyl group is bound to a four-coordinate carbon (C2) as in **1**. In **3** the methyl group has rearranged to the five-coordinate cage carbon (C4). The conversion of **2** to **3** was subsequently found to occur quantitatively at 240 °C:



At higher temperatures further carbon skeletal rearrangements were observed in both **2** and **3** that produced a mixture of isomeric products. Separation of these isomers was not achieved; however, on the basis of the isolation of the rearrangement product *commo-Fe*-(1-Fe-10-CH<sub>3</sub>-2,3,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sub>2</sub> (**9**), presented in the following paper,<sup>9</sup> one likely rearrangement product of **2** and **3** is 1-( $\eta\text{-C}_5\text{H}_5$ )Fe-10-CH<sub>3</sub>-2,3,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>. This isomer would allow the maximum separation of the cage carbons and the maximum separation of the third carbon from the iron atom, in agreement with well-known trends in metallacarborane cage migrations.<sup>16</sup> The possible mechanisms of these rearrangements, which were also observed in other metallatricarbaboranes reported in the following paper, are discussed in the final paper of this series.<sup>10</sup>

The Fe atom in both **2** and **3** is formally six-coordinate but is significantly closer to the two four-coordinate carbons. Thus, the Fe-C2 and Fe-C3 distances in **2** and **3** range from 1.935 (**5**) to 1.968 (**5**) Å, but the distances from iron to the other carbon C4 (2.265 (**3**) and 2.282 (**4**) Å, respectively) and the three ring borons (B5, B6, B7; average 2.241 Å) are significantly longer, supporting a stronger bonding interaction between the Fe and the C2 and C3 carbons. It is also significant that the Fe is nearly centered over the tricarbon carborane face. In the compound 1- $[\eta\text{-C}_4(\text{CH}_3)_4\text{H}]\text{Ni-9,2,4-(CH}_3)_3\text{-2,3,4-C}_3\text{B}_7\text{H}_7$ ,<sup>7</sup> the *commo-Fe*-(1-Fe-CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sub>2</sub> complexes reported in the following paper,<sup>9</sup> and many other 11-vertex dicarbon carborane<sup>17</sup> complexes which contain a carbon atom in the 4(5)-vertex cage position, significant cage distortions have been observed. These distortions involve elongated metal-C4(5) distances, resulting in an open four-membered polyhedral face (FeC2C4B7).

Mingos has pointed<sup>18</sup> out that the slip distortions observed in metallacarboranes and -boranes substituted by nonconical metal fragments, such as Pt(PPh<sub>3</sub>)<sub>2</sub>, may result

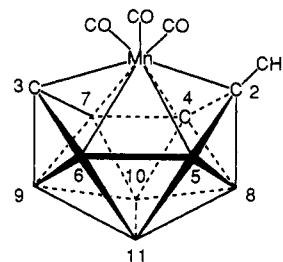


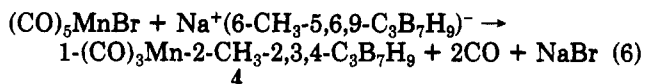
Figure 4. Proposed structure of 1-(CO)<sub>3</sub>Mn-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (**4**).

from the unequal bonding abilities of the metal orbitals involved in the cage bonding. On the basis of these arguments, we had proposed<sup>7</sup> that the presence of such distortions in 1- $[\eta\text{-C}_4(\text{CH}_3)_4\text{H}]\text{Ni-9,2,4-(CH}_3)_3\text{-2,3,4-C}_3\text{B}_7\text{H}_7$  arises because of the nonconical bonding nature of the cyclobutenyl ligand, and both the absence of such distortions in **2** and **3** (which contain the conical cyclopentadienyl ligand) and the presence of significant cage distortions in the *commo-Fe*-(1-Fe-CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sub>2</sub> complexes discussed in the following paper support this conclusion.

The C2-C4 distances in the two isomers (1.517 (**2**) and 1.492 (**5**) Å) are at the upper end of the range observed for carbon-carbon distances for adjacent carbons in analogous cage sites in 11-vertex metalladiboraboranes.<sup>17</sup> The remaining boron-boron and boron-carbon cage distances are within normal ranges. The Cp ring centroid to the Fe atom distance is equivalent in both isomers at 1.68 Å.

Cyclic voltammetry was conducted on the major product **2** in acetonitrile using Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. Compound **2** produced a reversible oxidation at 0.79 V, which is shifted ~0.4 V more positive than that of ferrocene (Fc). Studies<sup>19</sup> of substituted ferrocenes have previously shown that electron-withdrawing groups result in increased oxidation potentials (e.g. Fc at 0.40 V but FcCN at 0.715 V), while electron-releasing groups give decreased oxidation potentials (e.g. Me<sub>2</sub>Fc at 0.30 V). Thus, the 2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> ligand would appear to be strongly electron withdrawing compared to an unsubstituted cyclopentadienyl ligand and similar in properties to, for example, the phosphoferrocenes (*E* = 0.78 V).<sup>19b</sup>

1-(CO)<sub>3</sub>Mn-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (**4**). Reaction of (CO)<sub>5</sub>MnBr and Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> at 25 °C produced a single metallatricarbaborane, **4**.



The product was isolated in reasonable yield (~50%) as a volatile bright orange noncrystalline solid that was found to be both heat-sensitive and mildly air-sensitive in solution. The composition of **4** was established by elemental analysis, but the parent ion could not be observed in its mass spectra using either CI or FAB techniques. Only fragment envelopes were observed at *m/e* 137 (CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>+</sup>) and *m/e* 329 ((CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sub>2</sub>Mn<sup>+</sup>).

A compound of this composition would be a 24-skeletal-electron, 11-vertex cluster system and should adopt a closo-octadecahedral structure similar to those exhibited by **2** and **3**. A number of different arrangements for the C<sub>3</sub>B<sub>7</sub> framework, as well as the exopolyhedral methyl

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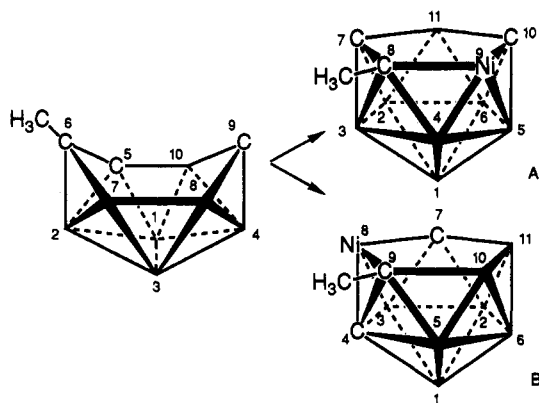
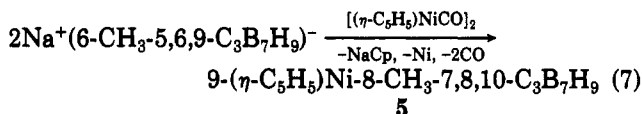


Figure 5. Possible structures for 9-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni-8-CH<sub>3</sub>-7,8,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (5).

group, are possible; however, the similarity of the <sup>11</sup>B, <sup>1</sup>H, and <sup>13</sup>C NMR spectra of 4 with those of 2, 1-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe-2-CH<sub>3</sub>-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>, support the structure shown in Figure 4. In particular, the <sup>1</sup>H NMR spectrum of 2, like that of 4, shows one cage CH resonance near 6.6 ppm and the other at a much higher field (1.53 ppm). Likewise, the methyl resonances of both compounds appear near 2.5 ppm.

The CO stretching absorptions in the IR spectrum of 4 are at higher energies (2040, 2008, and 1960 cm<sup>-1</sup>) than those in (CO)<sub>3</sub>Mn(2-Me-2,3,4-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>) (2035 and 1956 cm<sup>-1</sup>)<sup>2</sup> and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>3</sub> (2023 and 1939 cm<sup>-1</sup>).<sup>20</sup> These data suggest that 4 has the least metal to CO back-bonding interaction, consistent with CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> being the most electron withdrawing of these ligands. This conclusion is also consistent with the electrochemical investigations of 2 discussed above.

9-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni-8-CH<sub>3</sub>-7,8,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (5). The reaction of [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)NiCO]<sub>2</sub> with 2 equiv of Na<sup>+</sup>(6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sup>-</sup> gave multiple products, of which only the major product 5 could be characterized.<sup>21</sup>



Unlike the (CO)<sub>3</sub>Mn and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe fragments, a ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni fragment is a three-skeletal-electron donor. Thus, 5 would be an example of a 26-skeletal-electron nido (*n* + 2) cluster and should have a structure based on an icosahedron missing one vertex. In principle, as shown in Figure 5, two such structures are possible, since the ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni fragment could attack the 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> fragment from either the C5-B10 or the B7-B8 side.

Insertion at the B7-B8 edge results in all three carbons and the ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni unit being on the open face of the

complex (A). Insertion along the C5-C10 edge would give complex B, in which the C5 carbon would be off the open five-membered face. A structural determination of the compound *commo*-Pt-(*nido*-1-Pt-2-CH<sub>3</sub>-2,3,5-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sub>2</sub>, prepared from the reaction of PtCl<sub>2</sub> and 2-CH<sub>3</sub>-2,3,5-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup>, demonstrated<sup>22</sup> that the two cages of that complex adopt the A configuration. The similarity of the <sup>11</sup>B and <sup>1</sup>H NMR spectra of 5 and *commo*-Pt-(*nido*-1-Pt-2-CH<sub>3</sub>-2,3,5-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub>)<sub>2</sub> strongly suggests that 5 adopts the A structure.

It is also significant that even though the nickel atoms in the complexes 9-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni-8-CH<sub>3</sub>-7,8,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> (5), *commo*-Ni-(1-Ni-2,3-Me<sub>2</sub>-4,6-Et<sub>2</sub>-2,3,5-C<sub>3</sub>B<sub>2</sub>H)<sub>2</sub>, and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni each have formal 20-electron counts, the complexes adopt different electronic and geometric structures. Thus, *commo*-Ni-(1-Ni-2,3-Me<sub>2</sub>-4,6-Et<sub>2</sub>-2,3,5-C<sub>3</sub>B<sub>2</sub>H)<sub>2</sub> and nickelocene are paramagnetic, with two unpaired electrons in their degenerate e<sub>g</sub> antibonding orbitals, but 5 is diamagnetic. This difference is reasonable, however, since, due to the lower tricarbon carborane symmetry, the HOMO orbitals of 5 would not be expected to be degenerate and, therefore, electron pairing should occur to produce a diamagnetic compound. Each of the 1-Ni-2,3,5-R<sub>4</sub>C<sub>3</sub>B<sub>2</sub>H cage units in *commo*-Ni-(1-Ni-2,3-Me<sub>2</sub>-4,6-Et<sub>2</sub>-2,3,5-C<sub>3</sub>B<sub>2</sub>H)<sub>2</sub> have, like the Ni-9-CH<sub>3</sub>-7,9,10-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub> cage in 5, a nido skeletal-electron count, but they adopt close-pentagonal cage structures<sup>3</sup> instead of the predicted open-cage geometries. Triple-decker complexes, such as *commo*-Ni-(1-Ni-2,3-Me<sub>2</sub>-4,6-Et<sub>2</sub>-2,3,5-C<sub>3</sub>B<sub>2</sub>H)<sub>2</sub>, have been shown to be unique, however, in their abilities to accommodate different numbers of skeletal-electron counts without undergoing cage-opening distortions.<sup>23</sup>

In summary, it is clear from the results presented above that the polyhedral tricarbon carboranes may prove to be versatile transition-metal ligands and, further, that the resulting complexes, although analogues of both the known metalla dicarbon carboranes and metallocenes, may have unique or enhanced properties. In the following paper, the organometallic chemistry of the 6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> anion is further expanded to include the syntheses and structural characterizations of a new series of ferra and cobalta bis(tricarbaborane) analogues of ferrocene and cobaltocene.

**Acknowledgment.** We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also thank Professor Sang Kang for his comments concerning the synthesis of MeC<sub>3</sub>B<sub>7</sub>H<sub>10</sub> and Mr. Gabriel Asturias for assistance with the electrochemical measurements.

**Supplementary Material Available:** Tables of hydrogen atom positional parameters, anisotropic temperature factors, bond distances, and bond angles for 2 and 3 (12 pages); tables of structure factors (20 pages). Ordering information is given on any current masthead page.

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(21) Hawthorne has previously used a similar reaction between [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)NiCO]<sub>2</sub> and a borane anion to prepare ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)NiB<sub>11</sub>H<sub>11</sub>. See: Sullivan, B. P.; Leyden, R. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1975, 97, 455-456.

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