

# Metal–Metal Communication through Carborane Cages Supporting Electroactive $[\eta^5\text{-CpFe}(\text{CO})_2]$ Substituents

Timothy J. Wedge, Axel Herzog, Ramon Huertas, Mark W. Lee, Carolyn B. Knobler, and M. Frederick Hawthorne\*

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095

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A family of  $\eta^5\text{-CpFe}(\text{CO})_2$ -substituted *closo*-carboranes was synthesized and characterized, including cyclic voltammetry measurements. Like the previously reported bimetallic compound 1,12- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**8**), 1,10- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,10- $\text{C}_2\text{B}_8\text{H}_8$  (**9**) produces two dissimilar and irreversible one-electron oxidations within the same range, suggesting that it also exhibits through-cage electronic communication between iron centers. Structures determined by X-ray diffraction studies are reported for 1- $[\eta^5\text{-CpFe}(\text{PPh}_3)(\text{CO})]$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**5**), 1,12- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**8**), and 1,10- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,10- $\text{C}_2\text{B}_8\text{H}_8$  (**9**).

## Introduction

The *closo*-1,10- $\text{C}_2\text{B}_8\text{H}_{10}$  and *closo*-1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$  *p*-carboranes are highly symmetric cage cluster molecules that are also three-dimensionally aromatic. Their chemistry is firmly established, including well-described methods for achieving cage substitution at either the carbon or boron vertices.<sup>1</sup> The protons attached to the carboranyl carbon atoms can be easily removed by strong bases to provide nucleophilic carboranyl anions having the ability to react with electrophilic reagents. Wade et al. coupled the dianion of *p*- $\text{C}_2\text{B}_{10}\text{H}_{12}$  to aryl electron-donor and -acceptor moieties to study electronic transmission through the icosahedral carborane cage.<sup>2</sup> This was accomplished by monitoring the <sup>13</sup>C NMR chemical shifts and UV–vis spectra of a series of disubstituted 1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$ -1,12-ylene derivatives. This study established that the *p*-carborane cage has the ability to transmit electronic information from one carbon terminus to the other.

Expanding on Wade's findings and the fact that the use of similar metal-bonded carboranes for this purpose had not been previously described, Hawthorne et al. investigated a series of  $\eta^5\text{-CpFe}(\text{CO})_2$ -substituted *p*-carborane derivatives for evidence of electronic communication through the cage.<sup>3</sup> Although the syntheses of  $\eta^5\text{-CpFe}(\text{CO})_2$ -substituted icosahedral cages 1- $\text{CH}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ -2-yl<sup>4</sup> and 1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ -1-yl<sup>5</sup> as well as the smaller cage compound 1,10- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,10- $\text{C}_2\text{B}_8\text{H}_8$  (**9**)<sup>4</sup> were previously described, this chemistry had not

been extended to include 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$ . This was accomplished<sup>3</sup> through the synthesis of 1- $[\eta^5\text{-CpFe}(\text{CO})_2]$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**3**), 1- $[\eta^5\text{-CpFe}(\text{CO})_2]$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$ -12-yl<sup>2</sup>Hg (**6**), and 1,12- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**8**). Cyclic voltammetry measurements demonstrated single irreversible one-electron oxidations for the monometallic **3** and **6** but two irreversible one-electron oxidations for the bimetallic compound **8**. The UV–vis absorption spectra also provided strong evidence of electronic communication between the iron centers through the carborane cage. The extinction coefficient of the lowest energy peak of **5** was exactly double that of its parent compound **3**, while the extinction coefficient of coupled **8** was 6 times that of **3**.

Complementary to the Hawthorne findings, Low and co-workers found evidence for electronic communication through a *p*-carborane cage.<sup>6</sup> They investigated a 1,12- $[\text{Co}_2\text{C}_2(\text{SiMe}_3)(\text{CO})_4(\text{dppm})]_2$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$  system formed by the reaction of 1,12-bis((trimethylsilyl)ethynyl)-1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$  with  $[\text{Co}_2(\text{CO})_6(\text{dppm})]$ . The resulting product exhibited two reversible one-electron oxidations in a cyclic voltammogram trace. The fact that the oxidations were reversible demonstrated the stability of these complexes, in contrast to those studied by Hawthorne. This was excellent evidence for the ability of carborane cages to transmit electronic information and for the use of cyclic voltammetry to detect such phenomena.

Presented here is a full account of a family of  $\eta^5\text{-CpFe}(\text{CO})_2$ -substituted *closo*-carboranes, expanding on those previously described and including the synthesis and cyclic voltammetry measurements of these derivatives. Structures from X-ray diffraction studies are presented for 1- $[\eta^5\text{-CpFe}(\text{PPh}_3)(\text{CO})]$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**5**), 1,12- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**8**), and 1,10- $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ -1,10- $\text{C}_2\text{B}_8\text{H}_8$  (**9**). Attempts to synthesize a more robust ferracarborane are also described.

\* To whom correspondence should be addressed. Tel.: +1-310-825-7378. Fax: +1-310-825-5490. E-mail: mfh@chem.ucla.edu.

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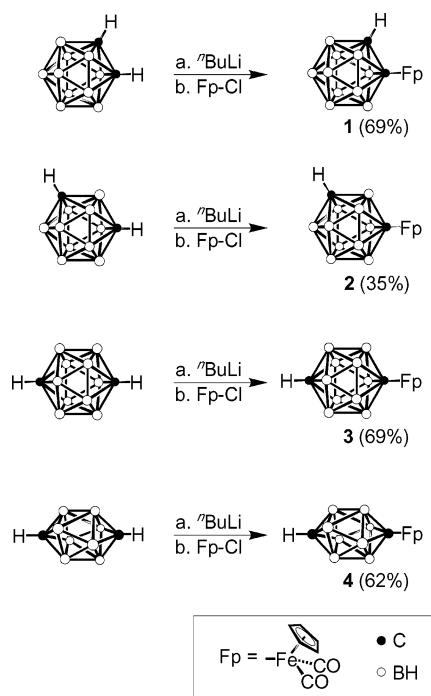
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## Scheme 1

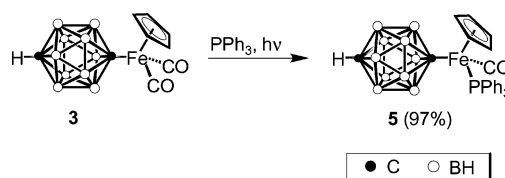


## Results and Discussion

**Synthesis.** The monoferracarborane compounds **1–4** were prepared in an analogous manner following preparative methods described for **3** (Scheme 1).<sup>3</sup> The desired products were independently synthesized by reacting the monolithio derivatives of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ , 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$ , 1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$ , and 1,10- $\text{C}_2\text{B}_8\text{H}_{10}$  with  $\eta^5\text{-Cp}^*\text{Fe}(\text{CO})_2\text{Cl}$  (Fp-Cl) in diethyl ether at room temperature. The reactions could be either subjected to an aqueous workup procedure or simply flashed through alumina with benzene to remove the lithium salts. The crude products were purified by flash chromatography through activated basic alumina (Aldrich, Brockmann I, ~150 mesh) with various ratios of petroleum ether and benzene as the eluting solvents. This purification method worked well, because the unreacted carboranes eluted first with pure petroleum ether and unreacted Fp-Cl adhered strongly to the stationary phase after the products were removed. The product-containing fraction could be easily seen on the column, since all four desired products are yellow. In each case, after the yellow fractions were collected and the solvent removed under vacuum, the yellow crystalline products were pure and required no further purification. The pure products were easily identified by their unique  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra, as well as by the use of other standard characterization techniques.

The four monoferracarborane compounds were found to be sensitive to light and oxygen. In solution, all compounds decomposed in less than 1 h, but as solids, they remained intact for longer periods of time. Even in the solid state, surface decomposition was observed (they became brown) if left in an oxygen-containing atmosphere. To maintain the ferracarboranes in a pure condition, they were stored in a glovebox under an argon atmosphere in brown glass bottles. Under these conditions the compounds were stable for extended periods of time.

## Scheme 2



Attempts were made to produce a more robust ferracarborane molecule. On the basis of similar chemistry described for alkynyl systems,<sup>7</sup> it was determined that a different iron complex should be investigated, i.e., one with bulkier ligands to protect the iron(II) center from oxidation. Thus, monolithio-*p*-carborane was reacted with  $\eta^5\text{-Cp}^*\text{Fe}(\text{CO})_2\text{Cl}$  (Fp\*-Cl)<sup>9</sup> in diethyl ether in an attempt to synthesize the Fp\* homologue of **3**. Unfortunately, even at elevated temperature, no reaction occurred. This is most likely due to the fact that the iron center with the large Cp\* ligand was too sterically encumbered to react with the bulky carborane anion.

In another effort to create a stable ferracarborane, **3** was photolyzed with triphenylphosphine in benzene to exchange the labile CO ligands with bulky triphenylphosphine groups (Scheme 2). This resulted in the formation of compound **5** as a racemic mixture of *R* and *S* enantiomers in nearly quantitative yield as a red crystalline solid. Again, the sterically crowded iron center influenced product formation and allowed only one CO to be exchanged for PPh<sub>3</sub>.

Compound **5** was slightly more stable than its parent **3**, which allowed for single crystals suitable for an X-ray diffraction study to be isolated by slow evaporation of a mixture of benzene and heptane in the presence of air. Although single crystals formed, a large fraction of the sample decomposed. A similar reaction was attempted whereby compound **8** (described below) was photolyzed with 1,2-bis(diphenylphosphino)ethane (DIPHOS) in benzene in an attempt to exchange both CO ligands on the iron centers with the bridged phosphines. This also failed to produce the desired compound, and thus further efforts to synthesize more stable ferracarboranes in this fashion were abandoned.

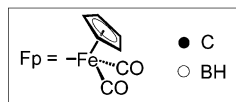
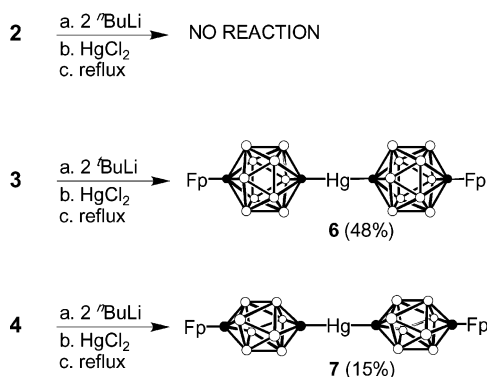
The diferracarboranyl mercury compounds **6** and **7** were synthesized by initial lithiation of their parent compounds **3** and **4**, respectively, followed by the addition of  $1/2$  equiv of mercury(II) dichloride in diethyl ether (Scheme 3). The reaction mixture was subjected to an aqueous workup procedure for product **6** but was flashed through alumina with benzene without water extraction for product **7**. The crude products were purified by flash chromatography through activated basic alumina (Aldrich, Brockmann I, ~150 mesh) with various ratios of petroleum ether and benzene as the eluting solvents. In both cases, unreacted ferracarborane starting material eluted first from the column. The yellow products were then removed from their respective columns with benzene. The mercury-linked products were isolated as yellow powders in low yields. The  $^{199}\text{Hg}\{^1\text{H}\}$  NMR spectra were indicative of product formation, and each

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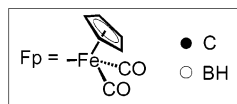
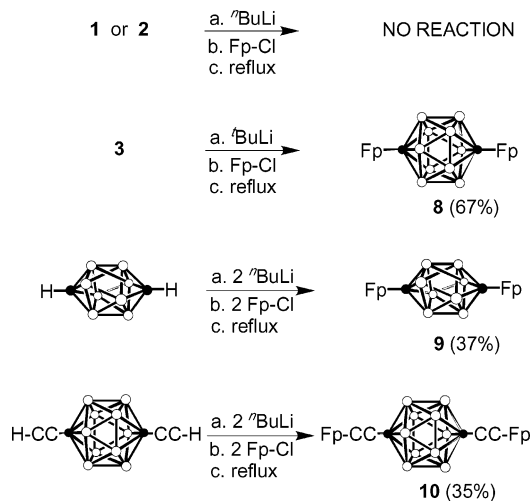
(8) Kaszynski, P.; Pakhornov, S.; Young, V. G. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1061.

(9) Fp\*-Cl was synthesized in a manner analogous to that for Fp-Cl.<sup>11</sup>

## Scheme 3



## Scheme 4



contained single resonances similar to those in known mercury(II) carboranyl compounds.<sup>10</sup>

Synthesis of a mercury-linked ferracarborane with the *m*-carborane parent **2** was attempted but failed. It is unclear whether the reaction failed because the formation of the *m*-ferracarborane anion did not occur or because of the reduced nucleophilicity of this anion toward an electrophilic center.

Direct synthesis of the diferracarborane compound **8** was attempted by room-temperature reaction of the dilithio-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> reagent with 2 equiv of Fp-Cl. This produced only the monosubstituted product **3**. Ultimately, the preparation of **8** was achieved using a preparation similar to that for **6** described above. The precursor, **3**, was lithiated with *tert*-butyllithium in diethyl ether followed by the addition of 1 equiv of Fp-Cl with heating at reflux for 20 h (Scheme 4). The reaction does not proceed at room temperature. Unreacted **3** was removed by flash chromatography through

**Table 1. Cyclic Voltammetry Measurements (V) for [η<sup>5</sup>-CpFe(CO)<sub>2</sub>]-Substituted Compounds (Oxidation Potentials vs Ag/AgCl Reference Electrode)**

compd	acetonitrile	methylene chloride
[η <sup>5</sup> -CpFe(CO) <sub>2</sub> ]Cl	1.29	1.27
<b>1</b>	1.68	1.66
<b>2</b>	1.58	1.59
<b>3</b>	1.54	1.58
<b>4</b>	1.48	1.54
<b>6</b>	1.49	1.55
<b>7</b>	1.41	1.48
<b>8</b>	1.44; 1.58	1.47; 1.65
<b>9</b>	1.34; 1.54	1.38; 1.57
<b>10</b>	1.45	1.41

activated basic alumina (Aldrich, Brockmann I, ~150 mesh) with petroleum ether/benzene (2:1) as the eluant. Although the yellow product did not elute from the column with this solvent mixture, it could be removed from the column with benzene, leaving any unreacted Fp-Cl behind. The product was isolated as yellow crystals in 67% yield. The same method was employed in an attempt to obtain the diferracarborane analogues of **1** and **2**, but neither reaction succeeded and only starting material was recovered. In contrast to the above results, compounds **9** and **10** could be synthesized directly from their non-Fp-substituted parent compounds, albeit in low yields.

**Cyclic Voltammetry.** Oxidation potentials for this family of [η<sup>5</sup>-CpFe(CO)<sub>2</sub>]-substituted compounds were obtained in both acetonitrile and methylene chloride solution. These data are presented in Table 1 and indicate no significant difference between the potentials obtained using these two solvents. For simplicity, the discussion is based upon the electrochemical data obtained in acetonitrile solution.

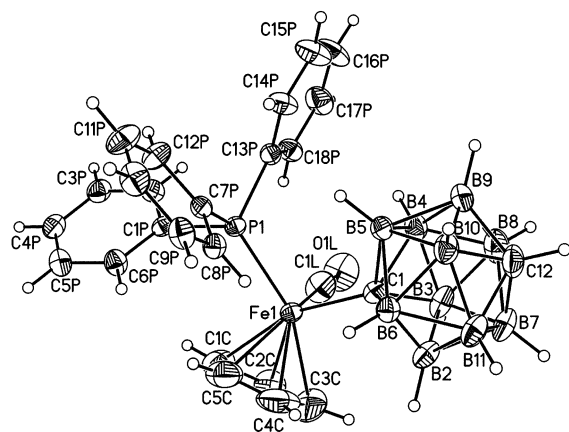
The monosubstituted compounds **1–4** each exhibit one irreversible single-electron oxidation potential. The potentials for the icosahedral cage molecules decrease as the carborane cage is varied from ortho to meta to para. The [η<sup>5</sup>-CpFe(CO)<sub>2</sub>]-substituted 1,10-C<sub>2</sub>B<sub>8</sub>-cage molecule **4** has a lower oxidation potential than its 1,12-C<sub>2</sub>B<sub>10</sub>-cage analogue **3**. The bimetallic systems consisting of two [η<sup>5</sup>-CpFe(CO)<sub>2</sub>]-substituted carborane cages connected by a mercury atom, **6** and **7**, each have only one irreversible oxidation potential (1.49 and 1.41 V, respectively, in CH<sub>3</sub>CN). These values are similar to those of their monometallic parent compounds **3** (1.54 V) and **4** (1.48 V).

There is evidence for electronic communication between the metal centers in the carborane-bridged compounds **8** and **9**. If there were no communication, both metals would be oxidized at the same potential, much like the mercury-linked compounds **6** and **7**, but if electronic communication exists, the second oxidation potential would be significantly different from that of the first oxidation. Both bimetallic species with one bridging carborane cage, **8** and **9**, show two irreversible oxidation potentials, 1.44 and 1.58 V for **8** and 1.34 and 1.54 V for **9**. These results demonstrate that the two metal centers exhibit electronic communication across a single carborane cage. Interestingly, compound **10**, which is also a bis-substituted system, has only one oxidation potential (1.45 V). This is most likely due to the poor p-orbital overlap between the ethynyl modules and the p-orbital of the carboranyl carbons.<sup>8</sup>

(10) For a review of carborane-mercury compounds, see: Wedge, T. J., Hawthorne, M. F. *Coord. Chem. Rev.* **2003**, *240*, 111.

Table 2. Crystal Data and Structure Refinement Details for Compounds 5, 8, and 9

	5	8	9
mol formula	C <sub>26</sub> H <sub>31</sub> B <sub>10</sub> FeOP	C <sub>16</sub> H <sub>20</sub> B <sub>10</sub> Fe <sub>2</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>18</sub> B <sub>8</sub> Fe <sub>2</sub> O <sub>4</sub>
fw	553.92	496.12	472.48
temp (K)	293(2)	298(2)	293(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
a (Å)	10.263(8)	8.1515(19)	13.781(2)
b (Å)	18.676(15)	11.133(3)	12.539(2)
c (Å)	14.737(12)	12.275(3)	13.112(2)
β (deg)	97.471(16)	92.320(4)	110.727(3)
Z	4	2	4
density (calcd) (Mg/m <sup>3</sup> )	1.314	1.480	1.481
abs coeff (mm <sup>-1</sup> )	0.617	1.325	1.389
<i>F</i> (000)	1142	500	952
cryst size (mm <sup>3</sup> )	0.05 × 0.15 × 0.2	0.1 × 0.2 × 0.5	0.25 × 0.25 × 0.15
θ range for data collecn (deg)	1.77–28.35	2.47–28.25	1.58–28.29
index ranges	−8 ≤ <i>h</i> ≤ 13 −22 ≤ <i>k</i> ≤ 24 −19 ≤ <i>l</i> ≤ 19	−10 ≤ <i>h</i> ≤ 10 −11 ≤ <i>k</i> ≤ 14 −12 ≤ <i>l</i> ≤ 16	−18 ≤ <i>h</i> ≤ 17 −16 ≤ <i>k</i> ≤ 15 −17 ≤ <i>l</i> ≤ 12
no. of rflns collected	17 140	6531	12 213
no. of indep rflns	6606 ( <i>R</i> (int) = 0.0972)	2523 ( <i>R</i> (int) = 0.0639)	4748 ( <i>R</i> (int) = 0.0385)
completeness to θ (%)	94.3	91.8	90.2
abs cor	SADABS	none	SADABS
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>	full-matrix least squares on <i>F</i> <sup>2</sup>
no. of data/restraints/params	6606/0/363	2523/0/136	4748/0/275
goodness of fit on <i>F</i> <sup>2</sup>	0.888	0.974	0.886
final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> 1 = 0.0725, <i>wR</i> 2 = 0.1791	<i>R</i> 1 = 0.0531, <i>wR</i> 2 = 0.1319	<i>R</i> 1 = 0.0460, <i>wR</i> 2 = 0.0913
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1947, <i>wR</i> 2 = 0.2293	<i>R</i> 1 = 0.0764, <i>wR</i> 2 = 0.1435	<i>R</i> 1 = 0.1048, <i>wR</i> 2 = 0.1067
largest diff peak and hole (e Å <sup>-3</sup> )	1.052 and −0.677	0.565 and −0.439	0.404 and −0.294



**Figure 1.** ORTEP diagram showing the molecular structure of 1-[( $\eta^5$ -cyclopentadienyl)(triphenylphosphine)carbonyliron]-1,12-dicarba-*closo*-dodecaborane (**5**).

**Molecular Structure of 1-[( $\eta^5$ -Cyclopentadienyl)(triphenylphosphine)carbonyliron]-1,12-dicarba-*closo*-dodecaborane (**5**).** The structure of **5**, confirmed by X-ray crystallography, is presented in Figure 1. A summary of the crystallographic data is presented in Table 2. The Fe–cage–H unit is linear (Fe1–C1–C12 = 177.9(3)°), and Fe1 is 1.722(4) Å from its Cp plane. Other selected bond distances and angles are given in Tables 3 and 4.

**Molecular Structure of 1,12-Bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,12-dicarba-*closo*-dodecaborane (**8**).** The structure of **8** was confirmed by X-ray crystallography and is presented in Figure 2. The molecule is centrosymmetric. A summary of the crystallographic data is presented in Table 2. The Fe–cage–Fe unit is linear (Fe1–C1–C12 = 177.56(16)°). The Cp carbon atoms are coplanar within 0.004(3) Å. Fe1 is 1.725(2) Å from its Cp plane. The Fe atom is 1.66(3) Å from the plane through the five Cp H atoms. The two

**Table 3.** Selected Bond Lengths (Å) for 1-[( $\eta^5$ -Cyclopentadienyl)(triphenylphosphine)carbonyliron]-1,12-dicarba-*closo*-dodecaborane (**5**)

Fe(1)–C(1L)	1.729(8)	C(1)–B(6)	1.745(9)
Fe(1)–C(1)	2.093(6)	C(1)–B(5)	1.751(9)
Fe(1)–C(2C)	2.089(7)	B(7)–C(12)	1.701(12)
Fe(1)–C(1C)	2.081(8)	B(8)–C(12)	1.685(11)
Fe(1)–C(3C)	2.085(8)	B(9)–C(12)	1.692(10)
Fe(1)–C(5C)	2.106(9)	B(10)–C(12)	1.689(11)
Fe(1)–C(4C)	2.158(9)	B(11)–C(12)	1.703(11)
Fe(1)–P(1)	2.271(2)	C(1L)–O(1L)	1.141(8)
C(1)–B(3)	1.711(10)	P(1)–C(13P)	1.832(6)
C(1)–B(4)	1.720(9)	P(1)–C(7P)	1.831(6)
C(1)–B(2)	1.739(9)	P(1)–C(1P)	1.842(6)

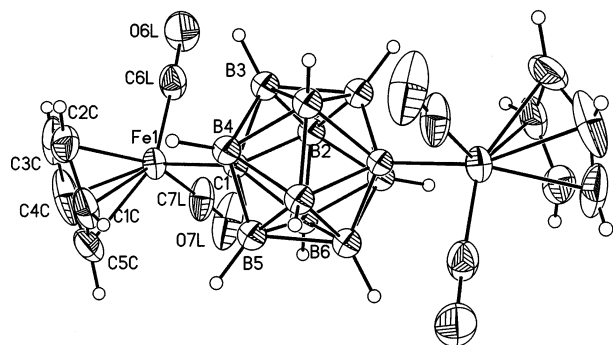
Fe atoms are 7.3588(15) Å apart, and the two cage C atoms are 3.246(6) Å apart. Other selected bond distances and angles are given in Tables 5 and 6.

**Molecular Structure of 1,10-Bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,10-dicarba-*closo*-decaborane (**9**).** The structure of **9** was confirmed by X-ray crystallography and is presented in Figure 3. A summary of the crystallographic data is presented in Table 2. The Fe–cage–Fe unit is linear (Fe1–C1–C10 = 177.93(15)°, C1–C10–Fe2 = 178.23(15)°). The Cp carbon atoms are coplanar within 0.004(3) and 0.006(2) Å. Fe1 is 1.725(2) Å from its Cp plane, and Fe2 is 1.723(2) Å from its Cp plane. The Fe atoms are 1.64(2) and 1.63(2) Å from the planes through the 5 Cp H atoms, respectively. The two Fe atoms are 7.524(1) Å apart, and the two cage C atoms are 3.476(4) Å apart. The closest interatomic approach between two non-hydrogen atoms is 3.159(4) Å (O6A⋯O7A). A weak hydrogen interaction links C1L and O7A (C1L⋯H1L = 0.85(4) Å, H1L⋯O7A = 2.66(4) Å, C1L⋯O7A = 3.427(5) Å, C1L–H1L–O7A = 150(4)°). Other selected bond distances and angles are given in Tables 7 and 8.

**Discussion of Experimental Structures of 5, 8, and 9.** Comparable bond lengths for compounds **5**, **8**, and **9** are presented in Table 9. The Fe–C(carboranyl)

**Table 4. Selected Bond Angles (deg) for 1-[( $\eta^5$ -Cyclopentadienyl)(triphenylphosphine)carbonyliron]-1,12-dicarba-*closo*-dodecaborane (5)**

C(1L)-Fe(1)-C(1)	92.3(4)	C(1C)-Fe(1)-P(1)	95.6(2)
C(1L)-Fe(1)-C(2C)	81.3(4)	C(3C)-Fe(1)-P(1)	158.6(3)
C(1)-Fe(1)-C(2C)	130.4(3)	C(5C)-Fe(1)-P(1)	93.7(3)
C(1L)-Fe(1)-C(1C)	101.2(4)	C(4C)-Fe(1)-P(1)	121.7(4)
C(1)-Fe(1)-C(1C)	158.4(3)	B(3)-C(1)-Fe(1)	118.0(4)
C(2C)-Fe(1)-C(1C)	37.9(3)	B(4)-C(1)-Fe(1)	120.0(4)
C(1L)-Fe(1)-C(3C)	96.4(5)	B(2)-C(1)-Fe(1)	119.3(4)
C(1)-Fe(1)-C(3C)	96.9(3)	B(6)-C(1)-Fe(1)	122.2(4)
C(2C)-Fe(1)-C(3C)	36.5(3)	B(5)-C(1)-Fe(1)	122.4(4)
C(1C)-Fe(1)-C(3C)	65.1(4)	O(1L)-C(1L)-Fe(1)	176.9(8)
C(1L)-Fe(1)-C(5C)	144.3(4)	C(5C)-C(1C)-Fe(1)	69.1(4)
C(1)-Fe(1)-C(5C)	119.7(3)	C(2C)-C(1C)-Fe(1)	71.4(5)
C(2C)-Fe(1)-C(5C)	66.1(3)	C(3C)-C(2C)-Fe(1)	71.6(5)
C(1C)-Fe(1)-C(5C)	43.6(4)	C(1C)-C(2C)-Fe(1)	70.7(4)
C(3C)-Fe(1)-C(5C)	66.2(4)	C(2C)-C(3C)-Fe(1)	71.9(5)
C(1L)-Fe(1)-C(4C)	140.4(5)	C(4C)-C(3C)-Fe(1)	70.4(4)
C(1)-Fe(1)-C(4C)	91.8(3)	C(3C)-C(4C)-Fe(1)	65.6(5)
C(2C)-Fe(1)-C(4C)	66.4(4)	C(5C)-C(4C)-Fe(1)	70.2(5)
C(1C)-Fe(1)-C(4C)	67.0(4)	C(1C)-C(5C)-Fe(1)	67.3(5)
C(3C)-Fe(1)-C(4C)	44.0(4)	C(4C)-C(5C)-Fe(1)	74.6(6)
C(5C)-Fe(1)-C(4C)	35.2(3)	C(13P)-P(1)-Fe(1)	116.2(2)
C(1L)-Fe(1)-P(1)	96.4(3)	C(7P)-P(1)-Fe(1)	121.24(19)
C(1)-Fe(1)-P(1)	99.68(16)	C(1P)-P(1)-Fe(1)	113.29(18)
C(2C)-Fe(1)-P(1)	129.8(3)		

**Figure 2.** ORTEP diagram showing the molecular structure of 1,12-bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,12-dicarba-*closo*-dodecaborane (**8**).**Table 5. Selected Bond Lengths (Å) for 1,12-Bis-[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,12-dicarba-*closo*-dodecaborane (**8**)**

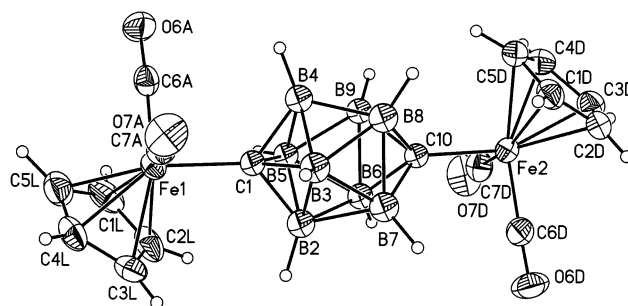
Fe(1)-C(7L)	1.765(4)	C(6L)-O(6L)	1.132(5)
Fe(1)-C(6L)	1.770(4)	C(7L)-O(7L)	1.132(4)
Fe(1)-C(1)	2.057(3)	C(1)-B(5)	1.723(5)
Fe(1)-C(4C)	2.063(4)	C(1)-B(2)	1.724(4)
Fe(1)-C(3C)	2.070(5)	C(1)-B(4)	1.727(4)
Fe(1)-C(5C)	2.080(5)	C(1)-B(6)	1.728(5)
Fe(1)-C(1C)	2.097(4)	C(1)-B(3)	1.730(4)
Fe(1)-C(2C)	2.098(4)		

distance is considerably longer (2.093(6) Å) for the monosubstituted **5** compared to that of the disubstituted compounds **8** (2.057(3) Å) and **9** (2.021(3) and 2.030(3) Å). Although both Fe-C(carboranyl) distances in **8** are required to be crystallographically equivalent, two different lengths are found in **9**. Compound **9** also exhibits the shortest Fe-C(carboranyl) distances in the series. This may be attributed to the greater s character associated with the cage carbon exo-bonding orbital of the 1,10-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> module present in **9**.<sup>8</sup>

The effect of the iron center on cage bonds can be seen when examining the carboranyl{Fe}C-B<sub>5</sub> distances in compounds **5** and **8**. These species can be directly compared, since they both contain icosahedral *p*-carborane cages. The average length of these bonds is 1.733(2)

**Table 6. Selected Bond Angles (deg) for 1,12-Bis-[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,12-dicarba-*closo*-dodecaborane (**8**)**

C(7L)-Fe(1)-C(6L)	93.3(2)	C(1)-Fe(1)-C(2C)	105.76(16)
C(7L)-Fe(1)-C(1)	91.80(14)	C(4C)-Fe(1)-C(2C)	63.9(2)
C(6L)-Fe(1)-C(1)	92.61(14)	C(3C)-Fe(1)-C(2C)	37.8(2)
C(7L)-Fe(1)-C(4C)	94.1(2)	C(5C)-Fe(1)-C(2C)	64.4(2)
C(6L)-Fe(1)-C(4C)	112.4(3)	C(1C)-Fe(1)-C(2C)	36.73(18)
C(1)-Fe(1)-C(4C)	153.9(3)	C(2C)-C(1C)-Fe(1)	71.7(2)
C(7L)-Fe(1)-C(3C)	125.3(3)	C(5C)-C(1C)-Fe(1)	69.7(3)
C(6L)-Fe(1)-C(3C)	88.7(2)	C(1C)-C(2C)-Fe(1)	71.6(3)
C(1)-Fe(1)-C(3C)	142.7(2)	C(3C)-C(2C)-Fe(1)	70.0(3)
C(4C)-Fe(1)-C(3C)	37.2(3)	C(4C)-C(3C)-Fe(1)	71.1(3)
C(7L)-Fe(1)-C(5C)	95.8(2)	C(2C)-C(3C)-Fe(1)	72.2(3)
C(6L)-Fe(1)-C(5C)	152.2(3)	C(3C)-C(4C)-Fe(1)	71.7(3)
C(1)-Fe(1)-C(5C)	113.2(3)	C(5C)-C(4C)-Fe(1)	70.2(3)
C(4C)-Fe(1)-C(5C)	40.9(3)	C(1C)-C(5C)-Fe(1)	71.0(2)
C(3C)-Fe(1)-C(5C)	64.7(3)	C(4C)-C(5C)-Fe(1)	68.9(3)
C(7L)-Fe(1)-C(1C)	131.0(2)	O(6L)-C(6L)-Fe(1)	176.7(4)
C(6L)-Fe(1)-C(1C)	135.3(2)	O(7L)-C(7L)-Fe(1)	176.9(3)
C(1)-Fe(1)-C(1C)	91.66(14)	B(5)-C(1)-Fe(1)	122.65(19)
C(4C)-Fe(1)-C(1C)	65.5(2)	B(2)-C(1)-Fe(1)	118.26(18)
C(3C)-Fe(1)-C(1C)	62.78(18)	B(4)-C(1)-Fe(1)	121.32(19)
C(5C)-Fe(1)-C(1C)	39.4(3)	B(6)-C(1)-Fe(1)	120.80(18)
C(7L)-Fe(1)-C(2C)	157.36(19)	B(3)-C(1)-Fe(1)	118.45(19)
C(6L)-Fe(1)-C(2C)	99.93(19)		

**Figure 3.** ORTEP diagram showing the molecular structure of 1,10-bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,10-dicarba-*closo*-decaborane (**9**).**Table 7. Selected Bond Lengths (Å) for 1,10-Bis-[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,10-dicarba-*closo*-decaborane (**9**)**

Fe(1)-C(7A)	1.752(4)	Fe(2)-C(3D)	2.104(4)
Fe(1)-C(6A)	1.763(4)	Fe(2)-C(5D)	2.110(4)
Fe(1)-C(1)	2.021(3)	C(6A)-O(6A)	1.137(4)
Fe(1)-C(4L)	2.089(4)	C(7A)-O(7A)	1.141(4)
Fe(1)-C(1L)	2.093(4)	C(6D)-O(6D)	1.143(4)
Fe(1)-C(3L)	2.094(4)	C(7D)-O(7D)	1.139(4)
Fe(1)-C(2L)	2.094(4)	C(1)-B(4)	1.604(5)
Fe(1)-C(5L)	2.098(4)	C(1)-B(5)	1.606(5)
Fe(2)-C(6D)	1.752(4)	C(1)-B(2)	1.611(5)
Fe(2)-C(7D)	1.759(4)	C(1)-B(3)	1.618(5)
Fe(2)-C(10)	2.030(3)	B(6)-C(10)	1.599(5)
Fe(2)-C(2D)	2.083(4)	B(7)-C(10)	1.612(5)
Fe(2)-C(1D)	2.089(4)	B(8)-C(10)	1.611(5)
Fe(2)-C(4D)	2.102(4)	B(9)-C(10)	1.601(5)

Å for **5** with a range from 1.711(10) to 1.751(9) Å. Compound **8** has an average length of 1.726(4) Å and a range of 1.723(5) to 1.730(4) Å for the same types of bonds. Moreover, a comparison of the carboranyl C-B<sub>5</sub> distances associated with both ends of the **5** molecule demonstrates the dramatic effect of carboranyl carbon substitution. The average carboranyl C-B<sub>5</sub> distance within the portion of the molecule  $\sigma$ -bonded to iron is 1.733(2) Å, as mentioned previously, while the average carboranyl C-B<sub>5</sub> distance for the portion of the molecule  $\sigma$ -bonded to hydrogen is 1.694(8) Å.

**Table 8.** Selected Bond Angles (deg) for 1,10-Bis-[( $\eta^5$ -cyclopentadienyl)dicarbonyl-iron]-1,10-dicarbido-*closo*-dodecaborane (**9**)

C(7A)–Fe(1)–C(6A)	91.94(17)	C(6A)–Fe(1)–C(5L)	94.01(18)
C(7A)–Fe(1)–C(1)	90.54(15)	C(1)–Fe(1)–C(5L)	152.14(17)
C(6A)–Fe(1)–C(1)	91.80(15)	C(4L)–Fe(1)–C(5L)	38.34(16)
C(7A)–Fe(1)–C(4L)	91.82(17)	C(1L)–Fe(1)–C(5L)	39.20(18)
C(6A)–Fe(1)–C(4L)	125.96(18)	C(3L)–Fe(1)–C(5L)	65.34(19)
C(1)–Fe(1)–C(4L)	142.03(17)	C(2L)–Fe(1)–C(5L)	65.3(2)
C(7A)–Fe(1)–C(1L)	155.08(19)	O(6A)–C(6A)–Fe(1)	176.9(3)
C(6A)–Fe(1)–C(1L)	94.75(19)	O(7A)–C(7A)–Fe(1)	178.0(3)
C(1)–Fe(1)–C(1L)	113.2(2)	C(2L)–C(1L)–Fe(1)	70.6(3)
C(4L)–Fe(1)–C(1L)	64.95(18)	C(5L)–C(1L)–Fe(1)	70.6(3)
C(7A)–Fe(1)–C(3L)	102.47(18)	C(1L)–C(2L)–Fe(1)	70.5(3)
C(6A)–Fe(1)–C(3L)	158.48(18)	C(3L)–C(2L)–Fe(1)	70.4(2)
C(1)–Fe(1)–C(3L)	103.81(16)	C(4L)–C(3L)–Fe(1)	70.3(2)
C(4L)–Fe(1)–C(3L)	38.94(16)	C(2L)–C(3L)–Fe(1)	70.4(2)
C(1L)–Fe(1)–C(3L)	65.66(18)	C(5L)–C(4L)–Fe(1)	71.2(2)
C(7A)–Fe(1)–C(2L)	140.0(2)	C(3L)–C(4L)–Fe(1)	70.7(2)
C(6A)–Fe(1)–C(2L)	128.1(2)	C(4L)–C(5L)–Fe(1)	70.4(2)
C(1)–Fe(1)–C(2L)	89.88(16)	C(1L)–C(5L)–Fe(1)	70.2(3)
C(4L)–Fe(1)–C(2L)	64.95(18)	B(4)–C(1)–Fe(1)	127.4(2)
C(1L)–Fe(1)–C(2L)	38.96(19)	B(5)–C(1)–Fe(1)	125.7(2)
C(3L)–Fe(1)–C(2L)	39.17(18)	B(2)–C(1)–Fe(1)	128.3(2)
C(7A)–Fe(1)–C(5L)	116.42(19)	B(3)–C(1)–Fe(1)	129.7(2)

**Table 9.** Comparative Bond Lengths (Å) for Compounds **5**, **8**, and **9**

	<b>5</b>	<b>8</b>	<b>9</b>
Fe–C(carboranyl)	2.093(6)	2.057(3)	2.021(3), 2.030(3)
Fe–C(CO)	1.729(8)	1.765(4)–1.770(4)	1.752(4)–1.763(4)
Fe–Cp(plane)	1.722(4)	1.725(2)	1.725(2), 1.723(2)
C–B <sub>5</sub> (carboranyl)	1.733(2)	1.726(4)	1.609(8)
{Fe–}–C–B <sub>5</sub> (av)			
C–O	1.141(8)	1.132(4), 1.132(5)	1.137(4), 1.141(4) 1.139(4), 1.143(4)
C–B <sub>5</sub> (carboranyl)	1.694(0)	N/A	N/A
{H–}–C–B <sub>5</sub> (av)			

The C–O distances in compounds **5**, **8**, and **9** are very similar (~1.137 Å). Interestingly, the Fe–C(CO) bond lengths of the symmetric compounds, **8** and **9**, are much longer (~0.03 Å) than that of **5**. This observation may be explained by the fact that the more tightly bound CO in **5** is a result of competition with a weaker PPh<sub>3</sub> ligand for  $\pi$ -back-bonding electrons from iron. Species **8** and **9** each contain iron centers equipped with two strongly back-bonding and mutually competitive CO ligands. Thus, **8** and **9** would be expected to have weaker individual Fe–C(CO) bonds.

## Conclusions

A series of  $\eta^5$ -CpFe(CO)<sub>2</sub>-substituted *closo*-carboranes has been synthesized. These compounds are yellow crystalline solids, except for 1-[CpFe(PPh<sub>3</sub>)(CO)]-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**5**), which is red. Cyclic voltammetry measurements with all of these  $\eta^5$ -CpFe(CO)<sub>2</sub>-substituted carboranes reveal that 1,12-[ $\eta^5$ -CpFe(CO)<sub>2</sub>]<sub>2</sub>-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**8**) and 1,10-[ $\eta^5$ -CpFe(CO)<sub>2</sub>]<sub>2</sub>-1,10-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> (**9**) each show two similar, but distinctly different, irreversible one-electron oxidations, which suggests that they exhibit through-cage electronic communication. Molecular structures derived from X-ray diffraction studies are provided for 1-[ $\eta^5$ -CpFe(PPh<sub>3</sub>)(CO)]-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**5**), 1,12-[ $\eta^5$ -CpFe(CO)<sub>2</sub>]<sub>2</sub>-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**8**), and 1,10-[ $\eta^5$ -CpFe(CO)<sub>2</sub>]<sub>2</sub>-1,10-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> (**9**). The Fe–C(carboranyl) bond distance observed in each of these species may be rationalized in terms of cage carbon hybridization effects, among others.

## Experimental Section

**General Considerations.** All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Argon gas was dried by passage through a column of reduced chromium oxide on silica. Diethyl ether was dried over sodium benzophenone ketyl and freshly distilled prior to use. All carboranes were obtained from Katchem Ltd. and used as purchased. The  $\eta^5$ -CpFe(CO)<sub>2</sub>Cl precursor was synthesized by modification of literature methods.<sup>11</sup> 1,12-Bis(ethynyl)-1,12-dicarbido-*closo*-dodecaborane was prepared as described by literature methods.<sup>12</sup> All other chemicals were used as purchased from various sources. Infrared spectra were obtained using a Nicolet Nexus 470 FTIR. All NMR spectra were recorded at room temperature using a Bruker ARX500 spectrometer. The EI and CI mass spectra were obtained on a VG Autospec spectrometer. Cyclic voltammetry measurements were recorded using a Princeton Applied Research Potentiostat Model 263A with "PowerCV" software. Redox potentials were measured in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> solutions containing 100 mM (Bu<sub>4</sub>N)<sup>+</sup>(PF<sub>6</sub>)<sup>−</sup> as the electrolyte vs an Ag/AgCl reference electrode.

**Synthesis of 1-[( $\eta^5$ -Cyclopentadienyl)dicarbonyliron]-1,2-dicarbido-*closo*-dodecaborane (**1**).** To a solution of 1,2-dicarbido-*closo*-dodecaborane (1.00 g, 6.93 mmol) in Et<sub>2</sub>O (30 mL) was added <sup>n</sup>BuLi (1.6 M in hexanes, 4.33 mL, 6.93 mmol) dropwise at −78 °C. After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to −78 °C and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (1.47 g, 6.93 mmol) was added at once. The solution was warmed to ambient temperature and stirred for 15 h. Solvent was removed in vacuo, and the reddish brown residue was redissolved in benzene, the solution was extracted with H<sub>2</sub>O (2 × 30 mL), and the organic phase was flashed through activated basic alumina (Aldrich, Brockmann I, ~150 mesh) with petroleum ether/benzene (1:1) as the eluant. The yellow first fraction was collected, and the solvent was removed, leaving the crystalline product **1** (1.53 g, 69%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>;  $\delta$  (ppm)): 3.67 (5H, s, Cp), 3.50–1.60 (10H, m, br, BH), 2.02 (1H, s, br, CH). <sup>13</sup>C NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>;  $\delta$  (ppm)): 213.32, 86.79, 68.03, 61.25. <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, C<sub>6</sub>D<sub>6</sub>, BF<sub>3</sub>·Et<sub>2</sub>O external):  $\delta$  (ppm) −0.39 (1B), −2.33 (1B), −6.70 (4B), −9.96 (2B), −13.64 (2B). FTIR (KBr; cm<sup>−1</sup>): 3070, 2963, 2928, 2859, 2603, 2032, 1980. HRMS (EI; *m/z*): calcd for C<sub>9</sub>H<sub>16</sub>B<sub>10</sub>FeO<sub>2</sub>, 322.1449; found, 322.1433 (M<sup>+</sup>, monoisotopic mass).

**Synthesis of 1-[( $\eta^5$ -Cyclopentadienyl)dicarbonyliron]-1,7-dicarbido-*closo*-dodecaborane (**2**).** To a solution of 1,7-dicarbido-*closo*-dodecaborane (1.00 g, 6.93 mmol) in Et<sub>2</sub>O (30 mL) was added <sup>n</sup>BuLi (1.6 M in hexanes, 4.33 mL, 6.93 mmol) dropwise at −78 °C. After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to −78 °C and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (1.47 g, 6.93 mmol) was added at once. The solution was warmed to ambient temperature and stirred for 15 h. Solvent was removed in vacuo, and the reddish brown residue was redissolved in benzene, the solution was extracted with H<sub>2</sub>O (2 × 30 mL), and the organic phase was flashed through activated basic alumina (Aldrich, Brockmann I, ~150 mesh) with petroleum ether/benzene (1:1) as the eluant. The yellow first fraction was collected, and the solvent was removed, leaving the crystalline product **2** (0.77 g, 35%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>;  $\delta$  (ppm)): 3.80 (5H, s, Cp), 3.30–1.80 (10H, m, br, BH), 2.38 (1H, s, br, CH). <sup>13</sup>C NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>;  $\delta$  (ppm)):

(11) Johnson, E. C.; Meyer, T. J.; Winterton, N. *Inorg. Chem.* **1971**, *10*, 1673. The preparation was modified to optimize the yield by deoxygenating all solvents prior to use and reducing the drying time over MgSO<sub>4</sub> from overnight to 1 h. This increased the product yield to 85%.

(12) Batsanov, A. S.; Fox, M. A.; Howard, J. A. K.; MacBride, H.; Wade, K. *J. Organomet. Chem.* **2000**, *610*, 20.

214.18, 86.65, 63.98, 60.10.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)):  $-1.18$  (2B),  $-7.87$  (4B),  $-11.83$  (2B),  $-13.03$  (2B). FTIR (KBr;  $\text{cm}^{-1}$ ): 3070, 2957, 2923, 2854, 2583, 2025, 1971; HRMS (EI;  $m/z$ ): calcd for  $\text{C}_9\text{H}_{16}\text{B}_{10}\text{FeO}_2$ , 322.1449; found, 322.1438 ( $\text{M}^+$ , monoisotopic mass).

**Synthesis of 1-[( $\eta^5$ -Cyclopentadienyl)dicarbonyliron]-1,12-dicarba-closo-dodecaborane (3).** To a solution of 1,12-dicarba-closo-dodecaborane (1.00 g, 6.93 mmol) in  $\text{Et}_2\text{O}$  (30 mL) was added  $^n\text{BuLi}$  (1.6 M in hexanes, 4.33 mL, 6.93 mmol) dropwise at  $-78^\circ\text{C}$ . After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to  $-78^\circ\text{C}$  and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (1.47 g, 6.93 mmol) was added at once. The solution was warmed to ambient temperature and stirred for 15 h. Solvent was removed in vacuo, and the reddish brown residue was redissolved in benzene, the solution was extracted with  $\text{H}_2\text{O}$  ( $2 \times 30$  mL), and the organic phase was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with petroleum ether/benzene (2:1) as the eluant. The yellow first fraction was collected, and the solvent was removed, leaving the crystalline product **3** (1.53 g, 69%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 3.75 (5H, s, Cp), 3.20–1.80 (10H, m, br, BH), 2.17 (1H, s, br, CH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 214.29, 86.58, 64.67, 63.76.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)):  $-8.53$  (5B),  $-12.36$  (5B). FTIR ( $\text{CCl}_4$  solution;  $\text{cm}^{-1}$ ): 3065, 2961, 2926, 2855, 2607, 2036, 1990. HRMS (EI;  $m/z$ ): calcd for  $\text{C}_9\text{H}_{16}\text{B}_{10}\text{FeO}_2$ , 322.1449; found, 322.1460 ( $\text{M}^+$ , monoisotopic mass).

**Synthesis of 1-[( $\eta^5$ -Cyclopentadienyl)dicarbonyliron]-1,10-dicarba-closo-decaborane (4).** To a solution of 1,10-dicarba-closo-decaborane (1.00 g, 8.29 mmol) in  $\text{Et}_2\text{O}$  (60 mL) was added  $^n\text{BuLi}$  (2.0 M in hexanes, 4.36 mL, 8.71 mmol) dropwise at  $-78^\circ\text{C}$ . After it was warmed to ambient temperature and stirred for 8 h, the solution was cooled again to  $-78^\circ\text{C}$  and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (1.85 g, 8.71 mmol) was added at once. The solution was warmed to ambient temperature and stirred for 26 h. The reaction mixture was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with benzene as the eluant as a workup procedure. The yellow first fraction was collected, and the solvent was removed, leaving the crude product. Another flash column was run through basic alumina as before, but with petroleum ether as the eluting solvent. The yellow first fraction was collected and the solvent was removed, leaving the crystalline product **4** (1.52 g, 62%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 6.33 (1H, s, br, CH), 4.10 (5H, s, Cp), 2.90–1.60 (8H, m, br, BH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 215.56, 96.22 (cage CH, only one observed), 86.73.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)):  $-8.98$  (4B),  $-11.10$  (4B). FTIR (KBr;  $\text{cm}^{-1}$ ): 3100, 2957, 2924, 2854, 2590, 2031, 1975. HRMS (EI;  $m/z$ ): calcd for  $\text{C}_9\text{H}_{14}\text{B}_8\text{FeO}_2$ , 297.1131; found, 297.1125 ( $\text{M}^+$ ).

**Synthesis of 1-[( $\eta^5$ -Cyclopentadienyl)(triphenylphosphine)carbonyliron]-1,12-dicarba-closo-dodecaborane (5).** To a deoxygenated solution of **3** (0.500 g, 1.56 mmol) in dry benzene (15 mL) in a quartz reaction vessel was added triphenylphosphine (0.614 g, 2.34 mmol). This was photolyzed with a mercury source UV lamp (Hanovia, 450 W, 250 nm) for 3 h under an argon atmosphere. The reaction mixture was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with benzene as the eluant as a workup procedure. A red fraction was collected, and the solvent was removed in vacuo, leaving the crude product, which was recrystallized from benzene/heptane to give the red crystalline product **5** (0.839 g, 97%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 7.74 (3H, s, br), 7.38 (6H, s, br), 7.03 (6H, s, br), 3.93 (5H, s, Cp), 3.10–1.80 (10H, m, br, BH), 2.21 (1H, s, br, CH).  $^{13}\text{C}$ - $\{^{31}\text{P}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 214.67, 134.15 (d,  $J = 19.5$  Hz), 132.39 (d,  $J = 9.7$  Hz), 131.52 (d,  $J = 2.5$  Hz), 128.51 (d,  $J = 11.8$  Hz), 86.30, 65.13, 64.28.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)):  $-8.48$  (5B),

$-12.58$  (5B). FTIR ( $\text{CCl}_4$  solution;  $\text{cm}^{-1}$ ): 3073, 3058, 2928, 2858, 2596, 2036, 1990, 1946. LRMS (EI;  $m/z$ ): calcd for  $\text{C}_{26}\text{H}_{31}\text{B}_{10}\text{FeOP}$  554.2 ( $\text{M}^+$ ),  $\text{C}_{25}\text{H}_{31}\text{B}_{10}\text{FeP}$  526.4 ( $\text{M}^+ - \text{CO}$ ); found, 526.2 ( $\text{M}^+ - \text{CO}$ ).

**Synthesis of Bis(12-[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,12-dicarba-closo-dodecaboran-1-yl)mercury (6).** To a solution of **3** (1.06 g, 3.30 mmol) in  $\text{Et}_2\text{O}$  (40 mL) was added  $^n\text{BuLi}$  (1.2 M in pentane, 2.75 mL, 3.30 mmol) dropwise at  $-78^\circ\text{C}$ . After allowing to warm to ambient temperature and stirred for 5 h, the solution was cooled again to  $-78^\circ\text{C}$  and mercury(II) chloride (0.450 g, 1.65 mmol) was added at once. The solution was then heated at reflux for 24 h. After the solution was cooled to ambient temperature, the solvent was removed in vacuo and the greenish yellow residue was redissolved in benzene, the solution was extracted with  $\text{H}_2\text{O}$  ( $2 \times 30$  mL), and the organic phase was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with petroleum ether/benzene (2:1) as the eluant. The yellow first fraction was the unreacted starting material **3**. The remaining yellow fraction was flashed out of the column with benzene and collected, and the solvent was removed, leaving the powdery product **6** (0.67 g, 48%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 3.71 (10H, s, Cp), 3.30–1.70 (20H, m, br, BH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 214.33, 86.58, 62.11, 61.31.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)):  $-6.25$  (10B),  $-9.55$  (10B).  $^{199}\text{Hg}\{^1\text{H}\}$  NMR (89.6 MHz,  $\text{C}_6\text{H}_6$ , 1.0 M  $\text{PhHgCl}$  in  $[\text{D}_6]\text{DMSO}$  external;  $\delta$  (ppm)):  $-1163$ . FTIR ( $\text{CCl}_4$  solution;  $\text{cm}^{-1}$ ): 2958, 2928, 2856, 2588, 2036, 1990. HRMS (CI;  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{30}\text{B}_{20}\text{Fe}_2\text{HgO}_4$ , 839.2545; found, 839.2600 ( $\text{M}^+$ ).

**Synthesis of Bis(10,10'-[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,10-dicarba-closo-decaboran-1,1'-yl)mercury (7).** To a solution of **4** (0.600 g, 2.02 mmol) in  $\text{Et}_2\text{O}$  (40 mL) was added  $^n\text{BuLi}$  (2.5 M in hexanes, 0.90 mL, 2.22 mmol) dropwise at  $-78^\circ\text{C}$ . After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to  $-78^\circ\text{C}$  and mercury(II) chloride (0.274 g, 1.01 mmol) was added at once. The solution was warmed slowly to ambient temperature and then was heated at reflux for 19 h. After the solution was cooled to ambient temperature, the reaction mixture was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with benzene as the eluant as a workup procedure. Solvent was removed in vacuo, and another flash column was run through basic alumina as before, but with petroleum ether as the eluting solvent. An early yellow fraction was collected and confirmed to be the unreacted starting material **4**. The remaining yellow fraction was flashed out of the column with benzene and collected, and the solvent was removed, leaving the powdery product **7** (0.120 g, 15%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 4.18 (10H, s, Cp), 3.00–1.70 (16H, m, br, BH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 215.77, 86.80, (cage CH carbons not observed).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)):  $-7.36$  (8B),  $-9.70$  (8B).  $^{199}\text{Hg}\{^1\text{H}\}$  NMR (89.6 MHz,  $\text{C}_6\text{H}_6$ , 1.0 M  $\text{Ph}_2\text{Hg}$  in  $\text{CH}_2\text{Cl}_2$  external;  $\delta$  (ppm)):  $-1028$ . FTIR (KBr;  $\text{cm}^{-1}$ ): 3118, 2956, 2925, 2854, 2572, 2029, 1974. HRMS: not determined.

**Synthesis of 1,12-Bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,12-dicarba-closo-dodecaborane (8).** To a solution of **3** (0.38 g, 1.19 mmol) in  $\text{Et}_2\text{O}$  (50 mL) was added  $^n\text{BuLi}$  (1.7 M in pentane, 0.700 mL, 1.19 mmol) dropwise at  $-78^\circ\text{C}$ . After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to  $0^\circ\text{C}$  and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (0.280 g, 1.32 mmol) was added at once. The solution was heated at reflux for 20 h. The reaction mixture was cooled to ambient temperature, and solvent was removed in vacuo. The reddish brown residue was redissolved in benzene, the solution was extracted with  $\text{H}_2\text{O}$  ( $2 \times 30$  mL), and the organic phase was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with petroleum ether/benzene (2:1) as the eluant. The yellow first fraction was confirmed to be the monosubstituted starting material **3**. The

remaining yellow fraction was flashed out of the column with benzene. The solvent was removed, leaving the crystalline product **8** (0.400 g, 67%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 3.83 (10H, s, Cp), 3.30–2.15 (10H, m, br, BH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 214.74, 86.61, 61.11.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)): –7.03 (10B). FTIR ( $\text{CCl}_4$  solution;  $\text{cm}^{-1}$ ): 2956, 2928, 2856, 2581, 2033, 1987. HRMS (CI;  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{20}\text{B}_{10}\text{Fe}_2\text{O}_4$ , 496.1073; found, 496.1080 ( $\text{M}^+$ ).

**Synthesis of 1,10-Bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,10-dicarba-closo-decaborane (9).** To a solution of 1,10-dicarba-closo-decaborane (0.500 g, 4.15 mmol) in  $\text{Et}_2\text{O}$  (25 mL) was added  $n\text{BuLi}$  (2.5 M in hexanes, 3.65 mL, 9.13 mmol) dropwise at  $-78^\circ\text{C}$ . After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to  $-78^\circ\text{C}$  and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (1.94 g, 9.13 mmol) was added at once. The solution was warmed again to ambient temperature and stirred for 20 h. The reaction mixture was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with benzene as the eluant as a workup procedure. Solvent was removed in vacuo, and another flash column was run through basic alumina as before, but with petroleum ether/benzene (5:1) as the eluting solvent. An early yellow fraction was collected and confirmed as the monosubstituted compound **4**. The remaining yellow fraction was flashed out of the column with benzene. The solvent was removed, leaving crude product **9**, which was recrystallized from benzene/heptane (0.730 g, 37%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 4.20 (10H, s, Cp), 2.90–1.80 (8H, m, br, BH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 216.03, 92.53, 86.71.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)): –7.45 (8B). FTIR (KBr;  $\text{cm}^{-1}$ ): 3116, 2956, 2926, 2855, 2566, 2017, 1969. HRMS (EI;  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{18}\text{B}_8\text{Fe}_2\text{O}_4$ , 473.0697; found, 473.0695 ( $\text{M}^+$ ).

**Synthesis of 1,12-Bis(2-[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]ethyn-1-yl)-1,12-dicarba-closo-dodecaborane (10).** To a solution of 1,12-bis(ethynyl)-1,12-dicarba-closo-dodecaborane (0.200 g, 1.04 mmol) in  $\text{Et}_2\text{O}$  (15 mL) was added  $n\text{BuLi}$  (2.5 M in hexanes, 0.920 mL, 2.29 mmol) dropwise at  $-78^\circ\text{C}$ . After it was warmed to ambient temperature and stirred for 3 h, the solution was cooled again to  $-78^\circ\text{C}$  and ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride (1.94 g, 9.13 mmol) was added at once. The solution was warmed again to ambient temperature and was stirred for 20 h. As a workup procedure, the reaction mixture was flashed through activated basic alumina (Aldrich, Brockmann I,  $\sim 150$  mesh) with benzene as the eluant. Solvent was removed in vacuo, and another flash column was run through basic alumina as before, but with petroleum ether/benzene (3:2) as the eluting solvent. An early orange fraction eluted and was confirmed to be a mixture of the monosubstituted compound and unreacted ( $\eta^5$ -cyclopentadienyl)iron dicarbonyl chloride. The remaining yellow fraction was flashed out of the column with benzene. The solvent was removed, leaving crude product **10**, which was recrystallized from benzene/heptane (0.200 g, 35%).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 3.80 (10H, s, Cp), 3.70–2.50 (10H, m, br, BH).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ;  $\delta$  (ppm)): 212.54, 84.77. (alkynyl and carboranyl carbons not observed).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160.5 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  external;  $\delta$  (ppm)): –11.45 (10B). FTIR (KBr;  $\text{cm}^{-1}$ ): 3101, 2958, 2925, 2854, 2611, 2122, 2040, 1984. HRMS (EI;  $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{20}\text{B}_{10}\text{Fe}_2\text{O}_4$ , 544.1075; found, 544.1084 ( $\text{M}^+$ ).

**Collection and Reduction of X-ray Data.** All X-ray data were collected using a Bruker SMART ccd diffractometer. Data were corrected for Lorentz and polarization effects and for absorption (**5** and **9**), but not for extinction. Intensities did not decay during the course of the experiment. Programs used in this work are those supplied with the Bruker SMART ccd diffractometer. The isotropic displacement parameters for hydrogen atoms were based on the values for the attached atoms. Scattering factors for H were obtained from Stewart et al.,<sup>13</sup> and those for other atoms were taken from ref 14.

**Collection and Solution of X-ray Data for 1-[( $\eta^5$ -Cyclopentadienyl)(triphenylphosphine)carbonyliron]-1,12-dicarba-closo-dodecaborane (5).** A red crystalline plate obtained from a heptane solution was mounted on a thin glass fiber. Unit cell parameters were determined from a least-squares fit of 905 reflections ( $5.17 < 2\theta < 56.16^\circ$ ). These dimensions and other parameters, including conditions of data collection, are summarized in Table 2. Atoms were located by use of heavy-atom methods. All non-hydrogen atoms were included with anisotropic displacement parameters. All hydrogen atoms were kept in calculated positions.

**Collection and Solution of X-ray Data for 1,12-Bis[( $\eta^5$ -Cyclopentadienyl)dicarbonyliron]-1,12-dicarba-closo-dodecaborane (8).** A yellow crystalline needle obtained from a benzene/heptane solution was cut and mounted on a thin glass fiber. Unit cell parameters were determined from a least-squares fit of 894 reflections ( $4.94 < 2\theta < 52.61^\circ$ ). Atoms were located by use of statistical methods. With the exception of the  $\text{C}_2\text{B}_{10}$  moiety, all non-hydrogen atoms were included with anisotropic displacement parameters. Position parameters were refined for all cyclopentadienyl hydrogen atoms. Carboranyl hydrogen atoms were kept in calculated positions.

**Collection and Solution of X-ray Data for 1,10-Bis[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]-1,10-dicarba-closo-decaborane (9).** A yellow crystalline parallelepiped obtained from a benzene/heptane solution was cut and mounted on a thin glass fiber. Unit cell parameters were determined from a least-squares fit of 905 reflections ( $6.32 < 2\theta < 55.40^\circ$ ). Atoms were located by use of statistical methods. With the exception of the  $\text{C}_2\text{B}_8$  moiety, all non-hydrogen atoms were included with anisotropic displacement parameters. Positional parameters were refined for all hydrogen atoms.

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**Supporting Information Available:** Tables of bond distances and angles, anisotropic thermal parameters, hydrogen coordinates and thermal parameters, torsion angles, and hydrogen bonds; these data are also available in electronic form as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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