

*N*-tetramethylethylenediamine (TMEDA) was added through the septum via a syringe. This mixture was stirred for 30 min at room temperature and then refluxed for an additional 30 min during which time the color changed from reddish orange to yellow. The solution was cooled to room temperature, the TMEDA removed in vacuo, and the reaction opened to the air. The residue was extracted with methylene chloride and chromatographed on silica gel TLC plates developed with a 20% methylene chloride-hexane solution. A single yellow band was collected which yielded 0.0243 g (0.0708 mmol,  $R_f$  0.54, 71.2% yield) of **9** as an air-stable solid; exact mass calcd for  $^{56}\text{Fe}^{11}\text{B}_3^{12}\text{C}_{19}^1\text{H}_{25}^+$  342.1585, found 342.1585.

**Preparation of  $(\text{C}_{16}\text{H}_{16})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$  (**10**).** A procedure analogous to that described above for the synthesis of **5** was employed to react 0.306 g (1.05 mmol) of **2** with 1.09 g (5.25 mmol) of [2.2]paracyclophane in 2 mL of dry, degassed triglyme at 175 °C for 6 h. The tube was treated as described above and the residue chromatographed on a  $2.5 \times 60$  ccm silica gel column which was eluted with a 9:1 methylene chloride-hexane solution. Two orange bands were collected. The first provided 0.066 g (0.2265 mmol) of unreacted **2**. The second colored band gave 0.121 g

(0.307 mmol,  $R_f$  0.76, 37.3% yield) of **10** as air-stable crystals: mp 151-153 °C; exact mass calcd for  $^{56}\text{Fe}^{11}\text{B}_4^{12}\text{C}_{22}^1\text{H}_{30}^+$  394.2069, found 394.2072.

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**Registry No.** 1, 8058-48-8; 2, 84583-03-9; 4, 95464-66-7; 5, 105472-21-7; 6, 105472-22-8; 7, 105472-23-9; 8, 105501-01-7; 9, 105472-20-6; 10, 105472-24-0;  $\text{FeCl}_2$ , 7758-94-3; [2.2]paracyclophane, 1633-22-3; fluorene, 7782-41-4; naphthalene, 91-20-3; 9,10-dihydroanthracene, 613-31-0.

**Supplementary Material Available:** Tables of unit-resolution mass spectroscopic data on compounds 1-10 (5 pages). Ordering information is given on any current masthead page.

## Organotransition-Metal Metallacarboranes. 9. *nido*-2,3-Dibenzyl-2,3-dicarbahexaborane(**8**) [ $(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_6$ ], a Versatile Multifunctional *nido*-Carborane: Iron-Polyarene Sandwich Compounds and Chromium Tricarbonyl $\pi$ -Complexes<sup>1</sup>

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The title carborane **1**, a nearly nonvolatile air- and water-stable liquid, has been prepared in multigram quantities from dibenzylacetylene (1,4-diphenyl-2-butyne) and  $\text{B}_5\text{H}_9$  in the presence of triethylamine. The multifunctional reactivity of **1** has been systematically explored via the preparation of a variety of mixed iron-carborane-polyarene complexes in which one or more of the three bonding rings in **1** ( $\text{C}_2\text{B}_3$  and two  $\text{C}_6$ ) are coordinated to metals. Thus, **1** was bridge-deprotonated to give the  $(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_5^-$  anion which in turn was treated with  $\text{FeCl}_2$  and  $\text{C}_8\text{H}_8^{2-}$  ion to form the cyclooctatriene complex  $(\eta^6\text{-C}_8\text{H}_{10})\text{Fe}[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]$  (**2**). The  $\text{C}_8\text{H}_{10}$  ligand in **2** is readily displaced by arenes on heating, affording sandwich complexes of general formula (arene) $\text{Fe}[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]$  where the arene is [2.2]paracyclophane (**3**), 9,10-dihydroanthracene (**4**), or fluorene (*o,o'*-diphenylenemethane) (**6**). The reaction of **4** with **2** at elevated temperature yielded the staggered triple-decker diiron species  $(\eta^6, \eta^6\text{-C}_{14}\text{H}_{12})\text{Fe}_2[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]_2$  (**5**). Complexes **2-6** are air-stable orange crystalline solids. Treatment of **2** with chromium hexacarbonyl in refluxing butyl ether/tetrahydrofuran resulted in complexation of one phenyl ring with a  $\text{Cr}(\text{CO})_3$  group, forming  $(2\text{-}[(\text{CO})_3\text{Cr}(\eta^6\text{-C}_6\text{H}_5)\text{CH}_2]\text{-3-PhCH}_2\text{-2,3-}\text{C}_2\text{B}_4\text{H}_4)\text{Fe}(\eta^6\text{-C}_6\text{H}_{10})$  (**7**); reaction of **7** with  $\text{Cr}(\text{CO})_6$  gave the dichromium species  $(2,3\text{-}[(\text{CO})_3\text{Cr}(\eta^6\text{-C}_6\text{H}_5)\text{CH}_2]_2\text{-2,3-}\text{C}_2\text{B}_4\text{H}_4)\text{Fe}(\eta^6\text{-C}_8\text{H}_{10})$  (**8**) in which both of the phenyl rings and the carborane face are coordinated to metals. Complexes **7** and **8** are yellow, moderately air- and light-stable solids. Characterization of compounds **1-8** was achieved via  $^{11}\text{B}$  and  $^1\text{H}$  NMR, IR, and mass spectroscopy, supported by an X-ray diffraction analysis of a dichromium complex of **1** which is reported in the following paper.

### Introduction

In the preceding paper<sup>1a</sup> and in earlier reports in this series,<sup>1b</sup> methods are described for the systematic construction of arene (or cyclic polyene)-transition metal-carborane  $\pi$ -complexes of specified design. These syntheses exploit several advantages afforded by *nido*- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$  carboranes as starting reagents,<sup>2</sup> including ease of preparation and handling, facile complexation by metal

ions on the  $\text{C}_2\text{B}_3$  face, and high chemical and thermal stability of the metal complexes formed. An additional synthetically important property of these complexes is their ability to undergo "decapitation" or base-induced removal of the apex BH unit (see Scheme I in the preceding report<sup>1a</sup>). This process forms a planar  $\text{C}_2\text{B}_3$  ring which can  $\eta^5$ -bond to a second metal, as in the  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_2\text{B}_3\text{H}_5)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$  isomers which provided the first examples of electrically neutral triple-decker sandwich complexes.<sup>3</sup>

(1) (a) Part 8: Spencer, J. T.; Grimes, R. N. *Organometallics*, first of three papers in this issue. (b) See ref 1a and references therein.

(2) Grimes, R. N. In Proceedings of the Anton Burg Symposium on Boron Chemistry, Los Angeles, CA, March 1985; Verlag Chemie International: Deerfield Beach, FL; in press.

(3) (a) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* 1974, 13, 1138. (b) Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* 1975, 97, 4213.

Table I. 115.8-MHz <sup>11</sup>B FT NMR Data

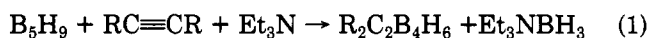
compd <sup>a</sup>	δ (J <sub>BH</sub> , Hz) <sup>b</sup>	rel areas
2,3-(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>6</sub> (1)	-0.43 (219), -2.53 (149), -46.37 (180)	1:2:1
(C <sub>8</sub> H <sub>10</sub> )Fe(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> (2)	13.04 (144), 7.26 (155), 3.33 (145)	1:1:2
(C <sub>16</sub> H <sub>18</sub> )Fe(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> (2a)	11.75, <sup>c</sup> 5.82, <sup>c</sup> 2.97 <sup>c</sup>	1:1:2
(C <sub>16</sub> H <sub>16</sub> )Fe(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> (3)	-8.52, <sup>c</sup> -11.60, <sup>c</sup> -13.96 <sup>c</sup>	1:1:2
(C <sub>14</sub> H <sub>12</sub> )Fe(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> (4)	3.35 (116), 0.46 (166), -2.93 (118)	1:1:2
(C <sub>14</sub> H <sub>12</sub> )Fe <sub>2</sub> [(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sub>2</sub> (5)	5.52, <sup>c</sup> 3.21, <sup>c</sup> 0.08 <sup>c</sup>	1:1:2
(C <sub>13</sub> H <sub>10</sub> )Fe(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> (6)	12.54 (134), 7.26 (150), 4.07 (138)	1:1:2
[(CO) <sub>3</sub> CrPhCH <sub>2</sub> ]-[PhCH <sub>2</sub> ] <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> )Fe(C <sub>8</sub> H <sub>10</sub> ) (7)	1.15 (135), -4.25 (156), -7.39 (140)	1:1:2
[(CO) <sub>3</sub> CrPhCH <sub>2</sub> ] <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> )Fe-(C <sub>8</sub> H <sub>10</sub> ) (8)	0.99, <sup>c</sup> -4.58, <sup>c</sup> -7.63 <sup>c</sup>	1:1:2

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub> solutions. <sup>b</sup> Relative to BF<sub>3</sub>·Et<sub>2</sub>O with positive shifts downfield. <sup>c</sup> J not measurable.

It was apparent to us that still greater versatility in this chemistry could be achieved if the R groups in R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> were themselves reactive toward metal reagents, as, for example, phenyl or benzyl. The C,C'-diphenyl derivative has presented a particular synthetic challenge and has only recently become available to us in workable quantities;<sup>4</sup> we shall report on it at a later time. However, the C,C'-dibenzyl carborane can be obtained on a bench scale (grams) by a modification of the standard R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> preparation<sup>5</sup> and has proved to be a particularly useful reagent. This paper describes the synthesis and characterization of 2,3-(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and some transition-metal-organometallic chemistry which illustrates its considerable utility as a versatile module in the construction of multiunit organotransition-metal complexes.

## Results and Discussion

**Synthesis of *nido*-2,3-(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>.** The usual route to *nido*-R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> carboranes (R = alkyl) employs the reaction of pentaborane(9) with the appropriate RC≡CR alkyne in the presence of a Lewis base.<sup>5</sup>



In the present case, the required dibenzylacetylene (1,4-diphenyl-2-butyne) is not available commercially and was prepared from *trans*-2,3-dibromo-2-butene-1,4-diol via a modification of a published procedure.<sup>6</sup> Alternatively, we found that the alkyne can be obtained less satisfactorily from 1,4-dichloro-2-butyne (Scheme I). Since neither dibenzylacetylene nor its precursor *trans*-2,3-dibromo-1,4-diphenyl-2-butene (Scheme I) has been well-characterized previously, we report <sup>1</sup>H NMR and infrared data on these compounds in Tables II and III; other information is included in the Experimental Section.

The formation of *nido*-2,3-(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (1) from B<sub>5</sub>H<sub>9</sub> proceeds as expected, with purification of the product via high-performance liquid chromatography (HPLC) in quantities of several grams per run. The dibenzylcarborane 1, characterized from its high-resolution <sup>11</sup>B and <sup>1</sup>H NMR, infrared spectra, and mass spectra (Tables I-IV), is a colorless, nearly nonvolatile liquid which exhibits no detectable reactivity toward air or water. In contrast, the analogous C,C'-dimethyl, -diethyl, and -dipropyl deriva-

Table II. 360-MHz <sup>1</sup>H FT NMR Data

compd <sup>a</sup>	δ <sup>b,c</sup>	rel areas
<i>trans</i> -(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> Br <sub>2</sub>	7.36 s (C <sub>6</sub> H <sub>5</sub> ), 4.17 s (CH <sub>2</sub> )	5:2
(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub>	7.43 m (C <sub>6</sub> H <sub>5</sub> ), 3.73 s (CH <sub>2</sub> )	5:2
1	7.28 m (C <sub>6</sub> H <sub>5</sub> ), 2.68 m (BH), 2.31 m (CH <sub>2</sub> ), 1.32 m (BHB)	5:2:2:1
2	7.28 m (C <sub>6</sub> H <sub>5</sub> ), 5.73 m (C <sub>8</sub> H <sub>10</sub> ), 3.82 t (C <sub>8</sub> H <sub>10</sub> ), 3.74 m (C <sub>8</sub> H <sub>10</sub> ), 3.50 m (C <sub>8</sub> H <sub>10</sub> ), 2.33 s (CH <sub>2</sub> ), 1.99 m (BH), 1.88 m (C <sub>8</sub> H <sub>10</sub> )	5:1:1:1:1:2:2:1
2a	7.26 m (C <sub>6</sub> H <sub>5</sub> ), 6.98 m (C <sub>16</sub> H <sub>18</sub> ), 5.04 m (C <sub>16</sub> H <sub>18</sub> ), 3.76 m (C <sub>16</sub> H <sub>18</sub> ), 3.66 m (C <sub>16</sub> H <sub>18</sub> ), 2.86 m (C <sub>16</sub> H <sub>18</sub> ), 2.78 m (C <sub>16</sub> H <sub>18</sub> ), 2.28 s (CH <sub>2</sub> ), 1.29 m (BH)	5:3:2:1:1:1:1:2:2
3	7.25 m (C <sub>6</sub> H <sub>5</sub> ), 6.51 br d (C <sub>6</sub> H <sub>4</sub> ), <sup>d</sup> 3.08 br d (CH <sub>2</sub> , paracyc), <sup>d</sup> 1.58 s (CH <sub>2</sub> , carborane), 1.24 m (BH)	5:4:4:2:2
4	[7.29 m (C <sub>14</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>5</sub> ), 7.23 m (C <sub>14</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>5</sub> ), 3.88 d (6.14 Hz, C <sub>14</sub> H <sub>12</sub> ), 3.84 d (6.14 Hz, C <sub>14</sub> H <sub>12</sub> ), 1.26 s (CH <sub>2</sub> ), 0.89 m (BH)]	[9]:1:1:2:2
5	[7.83 m (C <sub>14</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>5</sub> ), 7.26 m (C <sub>14</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>5</sub> ), 3.62 s (C <sub>14</sub> H <sub>12</sub> ), 2.37 s (CH <sub>2</sub> ), 1.16 m (BH)]	[7]:1:2:2
6	[7.62 m (C <sub>13</sub> H <sub>10</sub> , C <sub>6</sub> H <sub>5</sub> ), 7.30 m (C <sub>13</sub> H <sub>10</sub> , C <sub>6</sub> H <sub>5</sub> ), 4.06 d (21.0 Hz, C <sub>13</sub> H <sub>10</sub> ), 3.72 d (21.0 Hz, C <sub>13</sub> H <sub>10</sub> ), 2.42 s (CH <sub>2</sub> ), 1.05 m (BH)]	[18]:1:1:4:4
(CO) <sub>3</sub> Cr(C <sub>13</sub> H <sub>10</sub> )	7.39 m (C <sub>6</sub> H <sub>4</sub> ), 3.91 m, v br (CH <sub>2</sub> ), 3.38 m, v br (CH <sub>2</sub> )	8:1:1
7	7.28 br s (C <sub>6</sub> H <sub>5</sub> ), 7.18 br s (C <sub>6</sub> H <sub>5</sub> ), 5.68 m (C <sub>8</sub> H <sub>10</sub> ), 5.01 m (C <sub>8</sub> H <sub>10</sub> ), 3.66 d (13.9 Hz, C <sub>8</sub> H <sub>10</sub> ), 3.46 d (13.9 Hz, C <sub>8</sub> H <sub>10</sub> ), 1.96 m (C <sub>8</sub> H <sub>10</sub> ), 1.58 br s (CH <sub>2</sub> ), 0.90 m (BH)	5:5:2:2:2:2:2:4:4
8	7.40 br s (C <sub>6</sub> H <sub>5</sub> ), 5.92 m (C <sub>8</sub> H <sub>10</sub> ), 5.31 m (C <sub>8</sub> H <sub>10</sub> ), 3.62 d (11.6 Hz, C <sub>8</sub> H <sub>10</sub> ), 3.42 d (11.6 Hz, C <sub>8</sub> H <sub>10</sub> ), 1.84 m (C <sub>8</sub> H <sub>10</sub> ), 1.42 br s (CH <sub>2</sub> ), 1.06 m (BH)	5:1:1:1:1:1:2:2

<sup>a</sup> CDCl<sub>3</sub> solutions. <sup>b</sup> Legend: s = singlet, m = multiplet, d = doublet, t = triplet, br = broad. <sup>c</sup> Relative to SiMe<sub>4</sub>. <sup>d</sup> Unresolved doublet.

tives as well as parent 2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>7</sup> are readily attacked by oxygen and moisture; on the other hand, *nido*-2,3-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> is reported to be air- and water-stable.<sup>8</sup>

The electron-impact mass spectrum of 1 displays a strong parent envelope with a cutoff at *m/e* 257 (<sup>13</sup>C peak), and there is a close match between the calculated and observed intensities, indicating little fragmentation or hydrogen loss in the spectrometer. The 360-MHz proton

(4) Boyter, H. A.; Grimes, R. N., unpublished results.

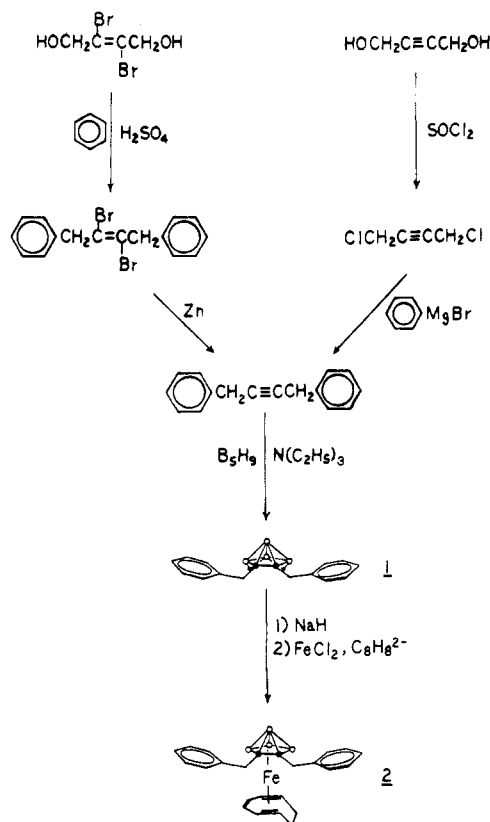
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Scheme I



and 115-MHz  $^{11}\text{B}$  NMR spectra are consistent with mirror symmetry in the molecule, in agreement with the proposed structure; this geometry is further supported by an X-ray structure determination on a bis(tricarbonylchromium) complex,  $[(\text{CO})_3\text{Cr}(\text{C}_6\text{H}_5\text{CH}_2)]_2\text{C}_2\text{B}_4\text{H}_6$ , described in the following paper.<sup>9</sup>

( $\eta^6$ -Cyclooctatriene)(dibenzylcarborane)iron (**2**). As anticipated for a *nido*- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$  carborane,<sup>7</sup> **1** readily undergoes bridge deprotonation on treatment with NaH in tetrahydrofuran, and the resulting  $(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_5^-$  anion combines with  $\text{Fe}^{2+}$  and  $\text{C}_8\text{H}_8^{2-}$  to generate the cyclooctatriene-iron-carborane sandwich complex ( $\eta^6$ - $\text{C}_8\text{H}_{10}$ ) $\text{Fe}[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]$  (**2**), an orange crystalline solid whose diethylcarborane analogue has been described previously.<sup>1b</sup> In addition to the desired compound **2**, obtained in 43% yield, a minor product characterized as  $(\text{C}_{16}\text{H}_{18})\text{Fe}[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]$  (**2a**) was isolated as orange crystals. The stereochemistry of the hydrocarbon ligand in **2a** has not been established, but from NMR and mass spectra we infer that it is a bicyclic system formed by attack of  $\text{C}_8\text{H}_8^{2-}$  on **2**. An apparently analogous  $(\text{C}_{16}\text{H}_{18})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$  complex was obtained earlier<sup>1b</sup> in the reaction of  $\text{Et}_2\text{C}_2\text{B}_4\text{H}_5^-$  ion with  $\text{FeCl}_2$  and  $\text{C}_8\text{H}_8^{2-}$ .

We anticipated that **2** would open the way to a large family of arene sandwich complexes containing the dibenzylcarborane moiety, provided that the  $\text{C}_8\text{H}_{10}$  ligand could be displaced by arenes as was observed previously<sup>1b</sup> with  $(\text{C}_8\text{H}_{10})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ . This is indeed the case, and we have exploited this property to selectively prepare a number of arene-iron-dibenzylcarborane species that are described in the following sections. The cyclooctatriene ligand in **2** is not, however, removed on treatment with the strong base  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$  (4-methyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2]octane). This observation is signif-

Table III. Infrared Absorptions ( $\text{cm}^{-1}$ , KBr Pellets)

compd	absorptions
<i>trans</i> -( $\text{PhCH}_2$ ) <sub>2</sub> $\text{Br}_2\text{C}_2$	3106 w, 3085 m, 3045 s, 2780 w, 2402 w, 2350 w, 2300 w, 1501 m, 1460 m, 1438 m, 1312 m, br, 1205 m, 1058 m, 946 s, 814 m, 766 s, 706 s, 610 s
$(\text{PhCH}_2)_2\text{C}_2^a$	3112 w, 3081 m, 3028 m, 2919 w, 2905 w, 1722 m, br, 1612 m, br, 1506 s, 1462 s, 1432 m, 1349 w, 1274 w, 1084 m, 1039 m, 738 vs, 708 vs, 618 w, br, 472 w, br
<b>1a</b> <sup>a</sup>	3165 sh, 3100 m, 3080 s, 3022 s, 2972 sh, 2938 s, 2864 s, 2608 vs, 1948 m, 1610 s, 1592 sh, 1501 vs, 1460 vs, 1388 w, 1115 m, br, 1082 m, 1037 sh, 987 m, 960 m, 921 w, 892 sh, 855 m, 822 w, 794 m, 752 s, 732 s, 704 vs (0% transmission below 520 $\text{cm}^{-1}$ )
<b>2</b>	3100 w, 3071 w, 3042 w, 2932 s, br, 2871 m, br, 2536 s, 1608 m, 1501 s, 1458 s, 1437 m, 1408 w, 1375 w, 1345 w, 1310 w, 1238 m, 1162 m, 1086 m, 1032 m, 888 m, 858 m, 806 m, 762 m, 727 s, 704 s, 670 w, 622 w, 472 m, 452 m, sh, 409 w, 352 w, 321 w (0% transmission below 275 $\text{cm}^{-1}$ )
<b>2a</b>	3104 w, 3079 w, 3047 w, 2978 s, 2940 s, 2884 m, 2544 s, 1724 m, br, 1612 m, 1502 m, 1460 m, 1440 s, br, 1401 w, 1372 m, 1323 m, 1308 w, 1265 m, 1210 s, br, 888 w, br, 865 w, 778 w, 733 w, 708 s, 478 s, br
<b>3</b>	2992 w, 2938 s, 2891 m, br, 2542 s, 1518 m, 1440 w, 1385 m, 1298 m, 1215 w, 1120 m, br, 855 m, 825 w, 796 w, 735 w, 675 w, 575 m, 500 w, 432 w
<b>4</b>	3078 w, 3038 w, 2932 vs, 2863 s, 2552 s, 2502 m, 1608 w, 1500 m, 1457 s, 1428 m, 1382 w, 1266 w, 1081 w, 1037 w, 882 w, 848 w, 810 w, 761 s, 732 s, 702 s, 500 w, 472 m, 422 w
<b>5</b>	3088 w, 3054 w, 2980 m, 2944 s, 2878 m, 2560 m, 1745 m, 1726 m, sh, 1688 m, 1608 m, 1592 w, sh, 1509 m, 1479 m, sh, 1466 m, 1393 w, 1298 m, 1272 s, 1183 w, 1106 s, br, 1032 s, br, 949 w, 882 w, 812 s, 760 w, 711 s, 612 w, 407 m
<b>6</b>	3100 w, 3000 s, 2956 s, 2985 m, 2545 s, 1478 m, 1465 m, 1445 m, 1432 m, 1409 m, 1398 m, 888 s, 852 m, 825 w, 808 w, 778 s, 732 s, 478 m
<b>7</b>	3052 w, 2942 m, 2862 w, 2560 s, 1982 vs, 1901 vs, br, 1505 m, 1464 m, 1388 w, 1357 w, 1312 w, 1225 w, 1168 w, 1090 w, 1073 m, 1048 m, 954 w, 888 m, 860 m, 842 w, 815 w, 772 m, 748 s, 712 s, 673 m, 642 m, 548 w, 480 m, 442 w
<b>8</b>	3108 w, 3044 w, 2942 m, 2865 w, 2572 s, 2542 s, 1978 vs, 1870 vs, br, 1502 m, 1462 m, 1162 m, 1074 w, 1038 w, 886 m, 857 m, 810 w, 772 w, 743 s, 718 m, 682 s, 642 s, 635 s, sh, 545 m, 490 m, br, 472 w, 320 w

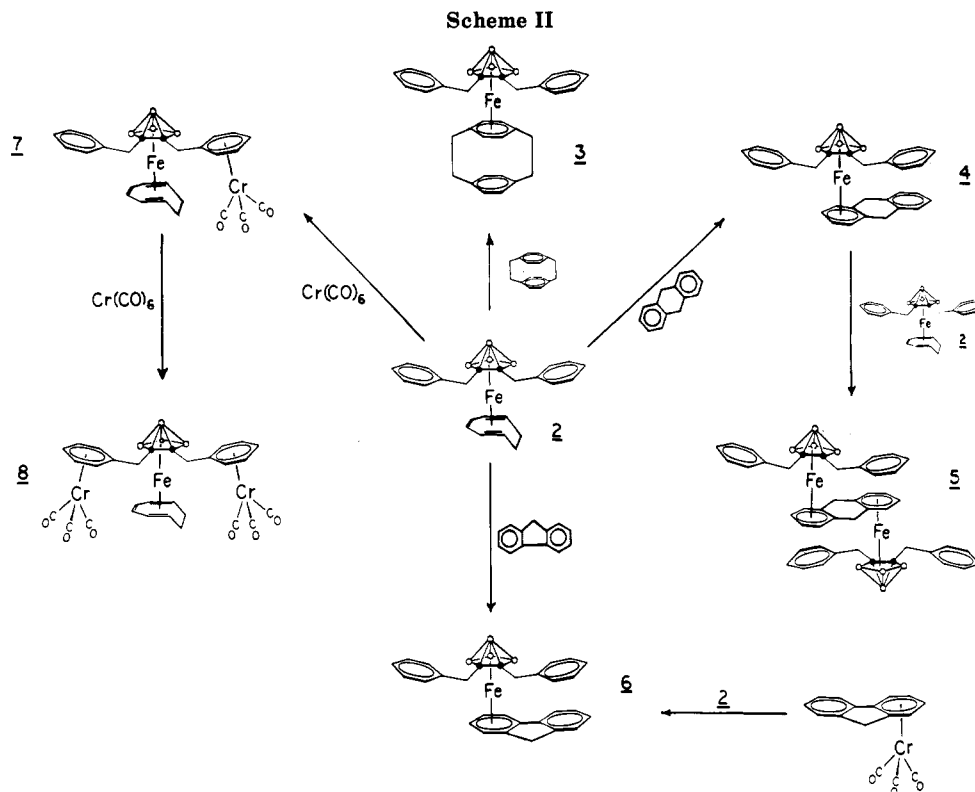
<sup>a</sup> Neat sample.

icant because phosphites of this kind are normally highly effective in displacing alkenes and other unsaturated organic ligands from transition-metal complexes.<sup>10</sup>

**Polyarene Sandwich Complexes.** The displacement of cyclooctatriene by arenes from  $(\eta^6\text{-C}_8\text{H}_{10})\text{Fe}(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)$  complexes is quite general, allowing the preparation of a wide variety of stable Fe(II) carborane complexes from readily available arenes.<sup>1b</sup> In the present study we focused

(9) Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics*, third of three papers in this issue.

(10) (a) Johnson, B. F.; Lewis, J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* 1974, 2, 251. (b) Cramer, R.; Seiwel, L. P. *J. Organomet. Chem.* 1975, 92, 245. (c) Hyde, C. L.; Darensbourg, D. S. *Inorg. Chem.* 1973, 12, 1286.



on polyarenes, hoping to obtain multidecker sandwich complexes which could be useful as building blocks for larger multilayer assemblies. Accordingly, **2** was heated with [2.2]paracyclophane<sup>11</sup> in triglyme, generating **3** (Scheme II). Complex **3** (like **4**, **5**, and **6** to be described below) was isolated via preparative plate chromatography on silica as a deep orange, air-stable crystalline solid, readily characterized from its <sup>11</sup>B and <sup>1</sup>H NMR, infrared, and mass spectra. The spectra are indicative of mirror symmetry in **3**, although rotation of either or both ligands in solution cannot be excluded.

The reaction of **2** with an excess of 9,10-dihydroanthracene yielded the sandwich complex  $(\eta^6\text{-C}_{14}\text{H}_{12})\text{Fe}[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]$  (**4**) and the staggered triple-decker diiron species  $(\eta^6, \eta^6\text{-C}_{14}\text{H}_{12})\text{Fe}_2[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]_2$  (**5**), both as orange air-stable crystals. Complex **5** was also obtained on heating **4** with an equivalent of **2** at 175 °C. Characterization of **4** and **5** was straightforward, both species exhibiting mass spectra in close agreement with the patterns calculated from natural isotopic distributions. The 360-MHz proton NMR resonances arising from the benzyl and dihydroanthracene benzene rings are nearly superimposed in both **4** and **5**, but the spectrum of **5** is simpler, as expected, reflecting its proposed symmetry; notably, two kinds of dihydroanthracene CH<sub>2</sub> protons are seen in **4**, while only one type is evident in **5**. The anti structure depicted for **5**, with iron-carborane units on opposite sides of the dihydroanthracene plane, is strongly preferred given the large steric bulk of the dibenzylcarborane moieties. Support for this structure is given by the crystallographically established geometry of the fluorene analogue of **5** (compound **7** in the preceding paper) which has the anti configuration.<sup>1a</sup> Thus far, satisfactory crystals of **5** have not been obtained.

The corresponding reaction of **2** with fluorene (*o,o'*-diphenylenemethane) gave  $(\eta^6\text{-C}_{13}\text{H}_{10})\text{Fe}[(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4]$

(**6**), an analogue of **4**, again demonstrating the general synthetic utility of the displacement of cyclooctatetraene from **2**. Compound **6**, another air-stable, orange solid, was also generated by a different route employing the reaction of  $(\eta^6\text{-fluorene})\text{chromium tricarbonyl}$  with **2** (Scheme II). This reaction was intended to produce a mixed bimetallic complex containing Fe(carborane) and Cr(CO)<sub>3</sub> units coordinated to the two arene rings in fluorene; however, the only isolable products were **6** and a Cr(CO)<sub>3</sub> complex of **2**, identical with **7** whose designed synthesis is reported below.

The proposed structure of **6** is consistent with the spectroscopic data in Tables I-IV; the proton NMR spectrum is closely similar to that of the diethylcarborane analogue.<sup>1a</sup>

**Complexes Involving  $\pi$ -Coordination at the Benzyl Groups.** As a further exploration of the versatility of these complexes, we investigated the ability of **2** to coordinate to metal groups via its carborane-attached benzyl units. Accordingly, employing conditions similar to those used elsewhere in the preparation of  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$  complexes,<sup>1,2</sup> **2** was refluxed with chromium hexacarbonyl in 10:1 butyl ether-THF to give the monosubstituted species  $(2\text{-}[(\text{CO})_3\text{Cr}(\eta^6\text{-C}_6\text{H}_5)\text{CH}_2]\text{-3-(PhCH}_2\text{)-2,3-C}_2\text{B}_4\text{H}_4)\text{Fe}(\eta^6\text{-C}_8\text{H}_{10})$  (**7**). Reaction of **2** with excess Cr(CO)<sub>6</sub> effected coordinated coordination of Cr(CO)<sub>3</sub> to both benzyl rings, forming the corresponding dichromium complex  $(2,3\text{-}[(\text{CO})_3\text{Cr}(\eta^6\text{-C}_6\text{H}_5)\text{CH}_2]_2\text{-2,3-C}_2\text{B}_4\text{H}_4)\text{Fe}(\eta^6\text{-C}_8\text{H}_{10})$  (**8**), both compounds being isolated as orange solids. Complex **8** was also obtained directly from **7** by treatment with Cr(CO)<sub>6</sub> in refluxing butyl ether-THF. In the proton NMR spectrum of **7** the complexed and uncomplexed C<sub>6</sub>H<sub>5</sub> rings give rise to clearly distinguishable resonances, the signal at higher field being assigned to the (CO)<sub>3</sub>Cr-coordinated ring as usual. The spectrum of **8**, in contrast, is simpler and fully consistent with the mirror symmetry of the proposed structure (Scheme II). Both **7** and **8** are somewhat

(11) For a recent review of the [2<sub>n</sub>]cyclophanes and their transition-metal complexes, see: Boekelheide, V. *Top. Curr. Chem.* 1984, 113, 87.

(12) Top, S.; Jaouen, G. *J. Organomet. Chem.* 1974, 182, 381.

Table IV. Selected Mass Spectroscopic Data

compd	<i>m/e</i>	rel intensity <sup>a</sup>	assignt	
<i>trans</i> -(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> Br <sub>2</sub>	369	1.8 (2.4)	<sup>13</sup> C <sup>12</sup> C <sub>15</sub> <sup>81</sup> Br <sub>2</sub> H <sub>14</sub> <sup>+</sup>	
	368	12.8 (13.9)	} parent envelope	
	366	27.9 (27.9)		
	364	13.4 (13.9)		
	205	55.5		<sup>12</sup> C <sub>16</sub> H <sub>13</sub> <sup>+</sup>
	(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub>	128	100.0	<sup>12</sup> C <sub>10</sub> H <sub>8</sub> <sup>+</sup>
		91	82.0	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>
77		23.9	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	
207		10.4 (17.9)	<sup>13</sup> C <sup>12</sup> C <sub>15</sub> H <sub>14</sub> <sup>+</sup>	
206		100.0 (100)	<sup>12</sup> C <sub>16</sub> H <sub>14</sub> <sup>+</sup>	
128		51.9	<sup>12</sup> C <sub>10</sub> H <sub>8</sub> <sup>+</sup>	
115		34.4	<sup>12</sup> C <sub>9</sub> H <sub>7</sub> <sup>+</sup>	
(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>8</sub> (1)	91	85.4	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	77	14.6	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	257	16.2 (16.4)	<sup>13</sup> C <sup>12</sup> C <sub>15</sub> <sup>11</sup> B <sub>4</sub> H <sub>20</sub> <sup>+</sup>	
	256	99.3 (99.3)	} parent envelope	
	255	98.1 (97.9)		
	254	47.0 (47.2)		
	253	13.4 (13.6)		
	178	18.9	} parent - C <sub>6</sub> H <sub>5</sub> envelope	
	177	31.0		
	176	91.5		
	175	100.0		
	174	80.0		
	173	48.5		
172	20.4			
(C <sub>8</sub> H <sub>10</sub> )Fe[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] (2)	91	88.5	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	417	4.3 (4.5)	<sup>13</sup> C <sup>12</sup> C <sub>23</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>28</sub> <sup>+</sup>	
	416	16.2 (16.2)	} parent envelope	
	415	17.2 (14.7)		
	414	10.8 (6.1)		
	413	5.7 (1.7)		
	412	2.6 (0.4)	} parent - C <sub>8</sub> H <sub>10</sub> envelope	
	312	49.2		
	311	57.7		
	310	79.1		
	309	70.4		
	308	43.3		
	307	24.3		
(C <sub>16</sub> H <sub>18</sub> )Fe[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] (2a)	134	100.0	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	91	54.6	<sup>13</sup> C <sup>12</sup> C <sub>31</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>36</sub> <sup>+</sup>	
	521	1.3 (0.8)	<sup>12</sup> C <sub>32</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>36</sub> <sup>+</sup>	
	520	2.4 (2.4)	parent - C <sub>6</sub> H <sub>6</sub>	
	442	10.0	parent - C <sub>16</sub> H <sub>18</sub>	
	310	4.3	FeC <sub>8</sub> H <sub>8</sub> <sup>+</sup>	
	160	73.9	FeC <sub>6</sub> H <sub>6</sub> <sup>+</sup>	
	134	51.8	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
(C <sub>16</sub> H <sub>16</sub> )Fe[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] (3)	91	100.0	<sup>12</sup> C <sub>32</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>34</sub> <sup>+</sup>	
	518	0.1	parent - C <sub>16</sub> H <sub>16</sub>	
	310	28.6	<sup>56</sup> Fe <sup>12</sup> C <sub>16</sub> H <sub>16</sub> <sup>+</sup>	
	264	100.0	<sup>12</sup> C <sub>16</sub> H <sub>16</sub> <sup>+</sup>	
	208	5.6	<sup>12</sup> CH <sub>2</sub> <sup>12</sup> C <sub>6</sub> H <sub>4</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	104	43.7	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
(C <sub>14</sub> H <sub>12</sub> )Fe[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] (4)	91	58.6	<sup>13</sup> C <sub>2</sub> <sup>12</sup> C <sub>28</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>30</sub> <sup>+</sup>	
	492	3.2 (3.3)	} parent envelope	
	491	19.7 (19.0)		
	490	61.4 (61.4)		
	489	58.0 (50.8)		
	488	27.0 (20.9)	} parent - C <sub>14</sub> H <sub>12</sub> envelope	
	487	7.9 (5.8)		
	311	48.9		
	310	92.7		
	309	100.0		
308	75.8			
(C <sub>14</sub> H <sub>12</sub> )Fe <sub>2</sub> [(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sub>2</sub> (5)	178	92.7	<sup>12</sup> C <sub>14</sub> H <sub>10</sub> <sup>+</sup>	
	91	52.2	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	800	0.05	<sup>13</sup> C <sup>12</sup> C <sub>45</sub> <sup>56</sup> Fe <sub>2</sub> <sup>11</sup> B <sub>8</sub> H <sub>47</sub> <sup>+</sup>	
	547	0.19	} parent - (PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> envelope	
	546	0.58		
	545	0.55		
	544	0.28		
	543	0.13	<sup>12</sup> C <sub>30</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>30</sub> <sup>+</sup>	
	490	6.5	<sup>12</sup> C <sub>16</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>18</sub> <sup>+</sup>	
310	11.5			
208	96.8			
180	88.8	<sup>12</sup> C <sub>14</sub> H <sub>12</sub> <sup>+</sup>		

Table IV (Continued)

compd	<i>m/e</i>	rel intensity <sup>a</sup>	assignt	
(C <sub>13</sub> H <sub>10</sub> )Fe[(PhCH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] (6)	149	100.0		
	91	50.7	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	
	478	4.5 (1.6)	<sup>13</sup> C <sub>2</sub> <sup>12</sup> C <sub>27</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>28</sub> <sup>+</sup>	
	477	9.7 (9.6)	parent envelope	
	476	31.7 (31.7)		
	475	28.7 (26.4)		
	474	14.9 (10.8)		
	473	7.2 (3.0)		
	310	61.0	<sup>12</sup> C <sub>18</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>18</sub> <sup>+</sup>	
	166	58.8	<sup>12</sup> C <sub>13</sub> H <sub>10</sub> <sup>+</sup>	
91	100.0	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>		
[(CO) <sub>3</sub> CrPhCH <sub>2</sub> ][PhCH <sub>2</sub> ] <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> Fe(C <sub>8</sub> H <sub>10</sub> ) (7)	553	1.7 (1.6)	<sup>13</sup> C <sup>12</sup> C <sub>26</sub> <sup>56</sup> Fe <sup>52</sup> Cr <sup>16</sup> O <sub>3</sub> <sup>11</sup> B <sub>4</sub> H <sub>28</sub> <sup>+</sup>	
	552	2.6 (4.1)	parent envelope	
	551	3.3 (3.3)		
	550	2.0 (1.5)		
	549	1.1 (0.5)		
	548	0.5 (0.2)		
	468	100.0	parent - 3CO	
	416	4.8	parent - Cr(CO) <sub>3</sub>	
	[(CO) <sub>3</sub> CrPhCH <sub>2</sub> ] <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> Fe(C <sub>8</sub> H <sub>10</sub> ) (8)	688	0.01	<sup>12</sup> C <sub>30</sub> <sup>56</sup> Fe <sup>52</sup> Cr <sub>2</sub> <sup>16</sup> O <sub>6</sub> <sup>11</sup> B <sub>4</sub> H <sub>28</sub> <sup>+</sup>
		660	0.06	parent - CO
552		1.3	parent - Cr(CO) <sub>3</sub>	
468		44.3	parent - Cr(CO) <sub>6</sub>	
416		31.6	parent - 2 Cr(CO) <sub>3</sub>	
310		100.0	<sup>12</sup> C <sub>18</sub> <sup>56</sup> Fe <sup>11</sup> B <sub>4</sub> H <sub>18</sub> <sup>+</sup>	
91		58.6	<sup>12</sup> C <sub>6</sub> H <sub>5</sub> <sup>12</sup> CH <sub>2</sub> <sup>+</sup>	

<sup>a</sup> Values in parentheses are calculated intensities for the parent group, based on natural isotope abundances and normalized to the most intense observed peak in the parent group.

light-sensitive, although samples of each exposed to light and air for several weeks exhibited only partial decomposition.

### Conclusions

The utility of (PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> as a synthetic building-block reagent lies in its special combination of properties: while exhibiting high intrinsic stability toward air oxidation and hydrolysis, it nevertheless undergoes the bridge-deprotonation, apex BH removal, and metal-complexation reactions that are characteristic of R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> *nido*-carboranes;<sup>13</sup> as an added feature, the phenyl groups can themselves be π-complexed to transition metals. Moreover, the mixed-sandwich complex (η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (2) exhibits facile replacement of its cyclooctatriene ligand by arenes, allowing the designed synthesis of an essentially unlimited variety of organo-transition-metal sandwich species. Further development of (PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> chemistry appears in the following paper.<sup>9</sup>

### Experimental Section

**Materials.** Except as noted, solvents were employed as described in the preceding paper.<sup>1a</sup> Used as received were *trans*-2,3-dibromo-2-butene-1,4-diol (Aldrich), zinc metal (Mallinkrodt), 1,4-butanediol (Aldrich), phenylmagnesium bromide (Aldrich), B<sub>5</sub>H<sub>9</sub> (U.S. Government Stockpile), [2.2]paracyclophane (Aldrich), fluorene (Aldrich), 9,10-dihydroanthracene (Aldrich), and chromium hexacarbonyl (Strem). Anhydrous ferrous chloride (Alfa) was stored under dry nitrogen prior to use. Cyclooctatetraene (Aldrich, 98%) was stored cold and distilled in vacuo before being used. Sodium hydride (Alfa, 50% in mineral oil) was washed twice with anhydrous hexane prior to use. Dipotassium cyclooctatetraenide (K<sub>2</sub>C<sub>8</sub>H<sub>8</sub>) was prepared in THF (tetrahydrofuran) by the procedure of Streitwieser et al.<sup>14</sup>

**Instrumentation.** Instruments and apparatus employed in

this work are described in the preceding article.<sup>1a</sup>

**Preparation of 1,4-Diphenyl-2-butyne.** Two approaches were employed for the synthesis of this alkyne, as described below. Method A is based on a procedure described earlier<sup>6</sup> but with significant modification and is preferred owing to its simpler experimental procedure and higher yields.

**Method A.** Typically, 300.0 g (1.220 mol) of *trans*-2,3-dibromo-2-butene-1,4-diol was suspended in 1000 mL of dry benzene in a 2-L round-bottom flask equipped with a magnetic stirrer and a 500-mL addition funnel charged with 375 mL of concentrated sulfuric acid. The acid was added dropwise to the butene suspension over a 2-h period with vigorous stirring, while the temperature was maintained below 40 °C. During this time the reaction became homogeneous and gradually turned black. The mixture was stirred at room temperature for an additional 12 h, after which time it was washed with 5 L of water and the benzene layer collected, dried, and evaporated. This afforded 227.8 g (51.0% yield) of a dark solid which was identified from its <sup>1</sup>H NMR, IR, and mass spectra, and melting point as *trans*-2,3-dibromo-1,4-diphenyl-2-butene. This material was transferred to a 2-L round-bottom flask equipped with a water condenser and magnetic stirrer, to which was added 1300 mL of absolute ethanol and 92.8 g (1.42 mol) of zinc metal. This mixture was refluxed for 12 h, cooled to room temperature, and extracted with 1 L of benzene. The benzene layer was filtered and the solvent removed. The product was purified either by vacuum distillation (bp<sub>12</sub> 190–194 °C) or by HPLC using a silica gel column eluted with 1:1 benzene-hexane to obtain 72.3 g (56.4%) of the colorless liquid product.

**Method B.** In a typical experiment, to a solution of 61.49 g (0.50 mol) of 1,4-dichlorobutyne (either prepared from the action of thionylchloride on 1,4-butanediol or purchased commercially) in 500 mL of anhydrous ether at ice temperature was added dropwise 1.0 mol of phenylmagnesium bromide in ether (either purchased commercially or prepared via the reaction of 157.0 g (1.0 mol) of bromobenzene and 24.3 g (1.0 mol) of magnesium in 750 mL of dry ether). The mixture was allowed to warm slowly to room temperature and stirred for 12 h. To this mixture was added carefully 500 mL of water followed by extraction with 1500 mL of ether. The ether layer was separated and dried with magnesium sulfate and the solvent removed, after which the residue solidified upon standing. Vacuum fractional distillation at 0.5 torr yielded first a large fraction consisting primarily of biphenyl followed by 11.9 g of the desired liquid product (bp<sub>0.5</sub> 145–147 °C; 11.6%).

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**Preparation of 2,3-Dibenzyl-2,3-*nido*-dicarbahexaborane** [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, **1**]. Into each of several (typically four) 500-mL Pyrex reactor bulbs,<sup>5b</sup> each equipped with a Teflon high vacuum stopcock, was placed ca. 6.4 g (31 mmol) of 1,4-diphenyl-2-butyne and 3.1 g (31 mmol) of triethylamine. Each reactor was attached to the vacuum line via a ball-and-socket ground glass joint, and the contents were frozen with liquid nitrogen, followed by evacuation of the flask. The contents of each reactor were degassed by three repetitions of the thaw, refreeze, and evacuate cycle. To each bulb was added 1.95 g (31.0 mmol) of B<sub>5</sub>H<sub>9</sub> at liquid-nitrogen temperature by high vacuum distillation. (*Caution*: B<sub>5</sub>H<sub>9</sub> is toxic and spontaneously inflames or explodes on exposure to air). Each bulb was then warmed to 0 °C in an ice bath with constant stirring, during which time the color of the viscous solution became orange and the mixture evolved gas rapidly. The bulbs were allowed to warm slowly to room temperature and the contents stirred for 3 days, following which the reaction bulbs were evacuated at high vacuum for 45 min to remove unreacted B<sub>5</sub>H<sub>9</sub>. The bulbs were filled with dry nitrogen at 1 atm and opened to the air, after which the contents were extracted with 400 mL of dry hexane and the hexane was removed by rotary evaporation to yield a yellowish oil. The product was purified by either conventional column chromatography (using a 2.5 × 60 cm silica gel column eluted with *n*-hexane) or HPLC (Porasil column eluted with hexane). Elution of the column provided initially a small amount of unreacted alkyne followed by the pure carborane and finally (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NBH<sub>3</sub>. Excellent separation of the components was achieved, yielding typically 1.4 g/bulb (17.4% yield based on B<sub>5</sub>H<sub>9</sub> employed) of the pure, colorless liquid product. The procedure thus affords ca. 5–6 g of the dibenzylcarborane **1** in a four-bulb synthesis. In developing this procedure our primary interest was in generating bench-scale quantities of carborane rather than in optimizing yields; however, with adjustment of reaction conditions it should be possible to approach the yields achieved<sup>5b</sup> in the synthesis of the *C,C'*-diethyl derivative (2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>), ca. 25–30%.

The pure dibenzylcarborane is remarkably stable toward air and moisture with no decomposition observed after 1 month of standing open to the air. The compound has a very low vapor pressure (<0.05 torr) at room temperature.

**Preparation of (C<sub>8</sub>H<sub>10</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**2**) and (C<sub>16</sub>H<sub>18</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**2a**).** A solution of K<sub>2</sub>C<sub>8</sub>H<sub>8</sub> was prepared in vacuo from 0.535 g (5.14 mmol) of cyclooctatetraene and 0.402 g (10.3 mmol) of potassium metal in 50 mL of dry THF by standard procedures<sup>14</sup> employing a three-flask apparatus similar to that described previously.<sup>15</sup> This solution, after being stirred at room temperature for 1 h, was filtered onto 0.655 g (5.17 mmol) of anhydrous FeCl<sub>2</sub> in a 250-mL flask immersed in liquid nitrogen. A solution of Na<sup>+</sup>[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>]<sup>-</sup> was prepared by the reaction of 0.132 g (5.50 mmol) of sodium hydride and 1.24 g (4.84 mmol) of **1** in 50 mL of dry THF. The reactants were combined in vacuo at liquid-nitrogen temperature and allowed to warm to room temperature, during which time hydrogen evolution was observed. After being stirred for 30 min at room temperature, the reaction was filtered onto the FeCl<sub>2</sub> at liquid nitrogen temperature, and the noncondensable gas was pumped off. The 250-mL reaction flask was slowly warmed to -63 °C over a 3-h period with constant stirring. The reaction mixture was then allowed to warm slowly to room temperature and was stirred at this temperature for an additional 12 h, after which the flask was filled with dry nitrogen at 1 atm and opened to the air. The solution was filtered through 2 cm of silica gel and washed with THF until the washings were colorless; subsequently the THF was removed by rotary evaporation to yield a dark red residue. The two products were separated and purified by column chromatography (2.5 × 50 cm silica gel eluted with 1:1 CH<sub>2</sub>Cl<sub>2</sub>/hexane). Two dark red-orange bands were collected, the first of which (*R<sub>f</sub>* 0.91 in CH<sub>2</sub>Cl<sub>2</sub> and 0.47 in 30% CH<sub>2</sub>Cl<sub>2</sub>-hexane) was recrystallized from a minimum of methylene chloride to yield 0.867 g (43.1%) of (C<sub>8</sub>H<sub>10</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**2**) as an orange, crystalline, air-stable solid. Exact mass calcd for <sup>56</sup>Fe<sup>11</sup>B<sub>4</sub><sup>12</sup>C<sub>24</sub><sup>1</sup>H<sub>28</sub><sup>+</sup> 416.1913, found 416.1931. The second band (*R<sub>f</sub>* 0.55 in CH<sub>2</sub>Cl<sub>2</sub> and 0.15 in 30% CH<sub>2</sub>Cl<sub>2</sub>-hexane) was recrystallized from 1:1 CH<sub>2</sub>Cl<sub>2</sub>-hexane to yield 0.139

g (5.52%) of (C<sub>16</sub>H<sub>18</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**2a**) as an orange, crystalline, air-stable solid.

**Attempted Reaction of (C<sub>8</sub>H<sub>10</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**2**) with P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub>.** To a 250-mL round-bottom flask equipped with a magnetic stirrer were added 0.075 g (0.180 mmol) of [(C<sub>8</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]Fe(C<sub>8</sub>H<sub>10</sub>), 0.857 g (5.79 mmol) of P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub> (prepared by the method of Verkade et al.<sup>16</sup>), and 75 mL of anhydrous THF. The reaction was warmed to 45 °C and stirred under dry nitrogen (1 atm) for 12 h. The reactor was cooled to room temperature and the solvent removed in vacuo. The residue was chromatographed on silica gel TLC plates developed with methylene chloride. A single orange band was collected, which afforded a quantitative yield of unreacted **2** (identified from its <sup>1</sup>H and <sup>11</sup>B NMR spectra, *R<sub>f</sub>* values, and mass spectra). Unreacted P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub> was also recovered.

**Preparation of (C<sub>16</sub>H<sub>18</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**3**).** Into a 20-mL Pyrex tube equipped with a ball joint for attachment to a vacuum system were placed 0.178 g (0.428 mmol) of **2**, 0.265 g (1.27 mmol) of [2.2]paracyclophane, and 2 mL of dry triglyme. The tube was degassed three times on the vacuum line by successive thawing, refreezing, and evacuation cycles, following which it was sealed off under vacuum with a torch. The reaction tube was heated to 175 °C for 12 h and then cooled to room temperature. The reactor was opened to the air, extracted with methylene chloride, and filtered and the solvent removed in vacuo. The dark orange residue was chromatographed on silica gel TLC plates which were developed with 30% methylene chloride-hexane solution. Two orange bands were isolated, the first of which (*R<sub>f</sub>* 0.47) gave 0.025 g of unreacted **2**. The second band (*R<sub>f</sub>* 0.37) produced 31.0 mg (16.4% yield based on **2** consumed) of (C<sub>16</sub>H<sub>18</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**3**) as an orange, air-stable, crystalline solid.

**Preparation of (C<sub>14</sub>H<sub>12</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**4**) and (C<sub>14</sub>H<sub>12</sub>)Fe<sub>2</sub>[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub> (**5**).** Into a Pyrex tube identical with that employed in the previous synthesis were placed 0.114 g (0.274 mmol) of **2** and 0.480 g (2.66 mmol) of 9,10-dihydroanthracene. The tube was evacuated to 1 × 10<sup>-4</sup> torr, sealed with a torch, heated to 175 °C for 4 1/2 h, and allowed to cool to room temperature. The reactor was opened to the air, and the contents were extracted with methylene chloride. This solution was filtered, the solvent removed in vacuo, and the residue chromatographed on a 2.5 × 60 cm silica gel column which was eluted with 1:1 methylene chloride-hexane. Three orange bands were collected, the first of which (*R<sub>f</sub>* 0.26) consisted of 0.012 g of unreacted **2**. The second band (*R<sub>f</sub>* 0.20) yielded 0.039 g (32.1%) of (C<sub>14</sub>H<sub>12</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**4**) as an air-stable solid. The final orange band (*R<sub>f</sub>* 0.11) produced 0.025 g (12.6%) of (C<sub>14</sub>H<sub>12</sub>)Fe<sub>2</sub>[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub> (**5**) as an air-stable crystalline solid. Compound **5** was also synthesized via the reaction of **2** with **4** in a 1:1 stoichiometric ratio under reaction conditions identical with those just described.

**Preparation of (C<sub>13</sub>H<sub>10</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**6**).** A procedure analogous to that described for the preceding syntheses was employed to react 0.184 g (0.442 mmol) of **2** with 0.367 g (2.21 mmol) of fluorene at 175 °C for 6 h. The contents were extracted as described in the preceding syntheses, affording 0.0720 g (34.2% yield) of (C<sub>13</sub>H<sub>10</sub>)Fe[(PhCH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (**6**) as orange, air-stable crystals.

In an alternative synthesis, 0.106 g (0.255 mmol) of **2** and 0.219 g (0.725 mmol) of (<sup>η</sup><sup>6</sup>-fluorene)chromium tricarbonyl (vide infra) were sealed into a 20-mL Pyrex tube under vacuum, as described above, and heated at 160 °C for 4 h. Extraction of the contents with CH<sub>2</sub>Cl<sub>2</sub> and elution from a silica plate with 30% CH<sub>2</sub>Cl<sub>2</sub> in hexane gave four orange fractions consisting of unreacted (C<sub>13</sub>-H<sub>10</sub>)Cr(CO)<sub>3</sub> (0.008 g, *R<sub>f</sub>* 0.53), complex **7** (0.011 g, 9.2%, *R<sub>f</sub>* 0.49), unreacted **2** (0.016 g, *R<sub>f</sub>* 0.46), and **6** (0.021 g, 10.3%, *R<sub>f</sub>* 0.38).

**Synthesis of (C<sub>13</sub>H<sub>10</sub>)Cr(CO)<sub>3</sub>.** This complex was prepared via a modification of the procedure of Fischer and Kriebitzsch.<sup>17</sup> Into an apparatus similar to that used in the preparation of **7** and **8** (vide infra) were placed 8.30 g (50.0 mmol) of sublimed fluorene and 11.0 g (50.0 mmol) of Cr(CO)<sub>6</sub>. To this were added 250 mL

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of anhydrous dibutyl ether and 25 mL of anhydrous THF under a dry nitrogen atmosphere. The mixture was refluxed for 24 h during which time the colorless mixture became bright yellow-orange. The solution was cooled to room temperature, opened to the air, and filtered and the solvent removed in vacuo. The residue was chromatographed on a 2.5 × 60 cm silica gel column eluted with 20% methylene chloride-hexane. The colorless unreacted fluorene was eluted from the column first near the solvent front. This was followed by a yellow band which yielded 2.84 g (18.8%) of  $(C_{13}H_{10})Cr(CO)_3$ . This complex was isolated as a yellow-orange, moderately air-stable, crystalline solid which was stored in the dark under nitrogen prior to use.

**Preparation of  $[2-((CO)_3CrPhCH_2)-3-PhCH_2-2,3-C_2B_4H_4]Fe(C_8H_{10})$  (7) and  $[(CO)_3CrPhCH_2)_2C_2B_4H_4]Fe(C_8H_{10})$  (8).** A 0.230-g (0.553-mmol) sample of 2 and 1.216 g (5.53 mmol) of  $Cr(CO)_6$  were placed in a 250-mL round-bottom flask equipped with a condenser and magnetic stirrer. Anhydrous dibutyl ether (100 mL) and 10 mL of anhydrous THF were added, and the mixture was refluxed under dry nitrogen for 48 h, during which time the color gradually changed from colorless to orange. The reactor was cooled to room temperature and the solvent removed in vacuo, the orange residue was dissolved in a minimum of methylene chloride, and the solution was chromatographed by using 30%  $CH_2Cl_2$ -hexane as eluent. Two distinct orange bands were collected. The first band ( $R_f$  0.49) produced 0.132 g (43.1%) of 7 as an orange, crystalline, moderately air-stable solid. The

second band ( $R_f$  0.24) yielded 0.065 g (17.2%) of 8, again as a moderately air-stable, orange crystalline solid.

Complex 8 was also prepared directly from 7. In a typical experiment, 0.100 g (0.181 mmol) of 7 and 0.398 g (1.81 mmol) of  $Cr(CO)_6$  were placed in a 250-mL round-bottom flask, equipped as described above, and 100 mL of dibutyl ether and 10 mL of THF were added. The mixture was refluxed for 48 h, after which it was cooled to room temperature and the solvent removed in vacuo to give an orange residue. This material was purified as described to yield 0.065 g (52.1%) of 8.

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**Registry No.** 1, 105472-14-8; 2, 105472-15-9; 3, 105472-16-0; 4, 105472-17-1; 5, 105500-99-0; 6, 105472-18-2; 7, 105472-19-3; 8, 105501-00-6;  $B_5H_9$ , 19624-22-7;  $FeCl_2$ , 7758-94-3;  $P(OCH_2)_3CCH_3$ , 1449-91-8;  $Cr(CO)_6$ , 13007-92-6; *trans*-2,3-dibromo-2-butene, 21285-46-1; *trans*-2,3-dibromo-1,4-diphenyl-2-butene, 105456-31-3; 1,4-diphenyl-2-butyne, 33598-23-1; 1,4-butyne diol, 110-65-6; 1,4-dichlorobutyne, 821-10-3; cyclooctatetraene, 629-20-9; [2.2]-paracyclophane, 1633-22-3; 9,10-dihydroanthracene, 613-31-0; fluorene, 86-73-7; ( $\eta^5$ -fluorene)chromium tricarbonyl, 33635-16-4.

## Organotransition-Metal Metallocarboranes. 10. $\pi$ -Complexation of *nido*-( $PhCH_2$ )<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> at the C<sub>2</sub>B<sub>3</sub> and C<sub>6</sub> Rings. Synthesis and Crystal Structures of *nido*-2,3-[(CO)<sub>3</sub>Cr( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>]<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and (PhCH<sub>2</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub>, a Nonfluxional C<sub>4</sub>B<sub>8</sub> Cluster<sup>1</sup>

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Reaction of the *C,C'*-dibenzyl-*nido*-carborane  $(PhCH_2)_2C_2B_4H_6$  (1) with NaH in THF followed by  $FeCl_2$  forms a red complex,  $[(PhCH_2)_2C_2B_4H_4]_2FeH_2$  (2), which on treatment with O<sub>2</sub> generates a tetrabenzyl tetracarbon carborane,  $(PhCH_2)_4C_4B_8H_8$  (3). Compound 3 is nonfluxional in solution, in contrast to previously studied  $R_4C_4B_8H_8$  species where R = Me, Et, or *n*-Pr, and an X-ray diffraction study of 3 disclosed that the C<sub>4</sub>B<sub>8</sub> cage is locked into an open-cage geometry as a consequence of severe intramolecular crowding of the benzyl groups. Reaction of 2 with  $CpCo(CO)_2$  generates  $[(PhCH_2)_2C_2B_4H_4]_4FeCoCp$  (4), for which a wedged structure is proposed. Treatment of 1 with  $Cr(CO)_6$  produces the mono- and dichromium complexes  $(CO)_3Cr(PhCH_2)_2C_2B_4H_6$  (5) and  $(CO)_6Cr_2(PhCH_2)_2C_2B_4H_6$  (6) as moderately air-sensitive solids which were characterized from NMR, IR, and mass spectra and an X-ray crystallographic investigation of 6. Crystal data for 3:  $M_r$  507, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 10.007$  (2) Å,  $b = 22.681$  (6) Å,  $c = 13.692$  (2) Å,  $\beta = 110.18$  (2)°,  $V = 2917$  Å<sup>3</sup>,  $R = 0.053$  for 3813 reflections having  $F_o^2 > 3\sigma(F_o)^2$ . Crystal data for 6:  $M_r$  521, space group  $Pnam$ ,  $Z = 4$ ,  $a = 11.914$  (2) Å,  $b = 6.927$  (1) Å,  $c = 28.729$  (6) Å,  $V = 2371$  Å<sup>3</sup>,  $R = 0.044$  for 1678 reflections having  $F_o^2 > 3\sigma(F_o)^2$ .

The carborane derivative *nido*-2,3-dibenzyl-2,3-dicarba-hexaborane  $(PhCH_2)_2C_2B_4H_6$  (1) with its multifunctional capability for  $\pi$ -coordination to transition metals has considerable potential for exploitation in organometallic synthesis. As described elsewhere,<sup>1</sup> the conjugate base

anion of 1,  $(PhCH_2)_2C_2B_4H_5^-$ , in combination with transition-metal ions and arene ligands forms isolable, stable mixed-ligand sandwich complexes. Here we are concerned with somewhat different aspects of dibenzylcarborane chemistry, namely, the formation of bis(dibenzylcarboranyl)metal complexes and their oxidative fusion properties and the reactivity of the benzyl groups in 1 itself toward metal complexation. Our primary purpose in this study was to explore the steric and/or electronic influence

(1) Part 9: Spencer, J. T.; Grimes, R. N. *Organometallics*, second of three papers in this issue.

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