

limation at 80° onto a 0° cold finger; 46 mg (92%) of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,6-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> was obtained.

**Rearrangement of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,6-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.** A solution of 50 mg of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,6-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> in 5 ml of decane was heated at the reflux temperature for 4 hr. Column chromatography of the reaction mixture on silica gel eluted with hexane afforded a yellow band. The solvent was removed and a yellow solid was sublimed at 70° to a 0° probe. 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,10-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>, 38 mg (76%), was isolated.

**Rearrangement of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,7-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.** A 40-mg sample of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,7-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> was heated for 15 min in 5 ml of hexadecane at the reflux temperature. Column chromatography removed the hexadecane and the rearrangement product was eluted and further purified by thick-layer chromatography. The product was sublimed at 70° to a 0° cold finger yielding 20 mg (50%) of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,10-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.

**Rearrangement of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-3,10-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.** A 100-mg sample of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-3,10-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> was heated in 7 ml of refluxing hexadecane for 5 hr. Column chromatography followed by sublimation at 70° to a -78° probe yielded 85 mg (85%) of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,10-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.

**Rearrangement of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-4,5-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>.** A solid sample of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-4,5-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> was placed in an nmr tube which was then immersed in cyclooctane at the reflux temperature for 5 hr. CDCl<sub>3</sub> was added to the tube, and the <sup>1</sup>H and <sup>11</sup>B nmr spectra identified the product as 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-4,6-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>.

**Rearrangement of 4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-4-Co-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>.** A 0.268-g sample of 4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-4-Co-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> was added to 20 ml of hexane and heated to the reflux temperature for 15 hr. The products were separated by column chromatography using silica gel

eluted with hexane gradually enriched with dichloromethane. The bands that were separated were, in order of elution, 4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-4-Co-1,13-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (trace), 4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-4-Co-1,8-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (0.158 g, 60%), and 4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-4-Co-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (0.101 g, 37%). If the rearrangement were performed in benzene at the reflux temperature for 24 hr, only one band, consisting of 4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-4-Co-1,13-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (71%), was isolated.

**Kinetic Methods.** Kinetic runs at temperatures less than 60° were carried out in a constant temperature water bath. Others were carried out in an apparatus where a chamber containing the sample solution was suspended in a reservoir of refluxing liquid. A constant temperature of  $\pm 0.05^\circ$  could be maintained within the sample chamber.

Kinetic data for the rearrangement of 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-6,9-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> to 2-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-2-Co-1,6-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> were obtained by monitoring the increase in absorbance at 504 nm. In all other runs, aliquots were withdrawn from the samples at appropriate time intervals and injected into a high-pressure liquid chromatograph.<sup>28</sup> The absorbance of reactant and product was determined using a 280-nm uv detector and a strip-chart recorder. Individual peak areas were measured with a planimeter and, after corrections were made for differences in extinction coefficients at 280 nm, the concentration of each component was calculated. Plots of the log of the concentration of the reactants as a function of time gave first-order rate constants. Activation parameters were calculated from plots of  $\ln k$  vs.  $1/T$  using three temperatures for each reaction.

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## Direct Insertion of Transition Metals into Polyhedral Carboranes. Structurally Novel Mono-, Di-, and Trimetallic Small Cage Systems

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**Abstract:** Metallocarboranes of iron, cobalt, and nickel have been prepared by the direct reaction of the small polyhedral carboranes 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, or 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> with organometallic reagents in the gas phase or in solution, without the use of a prior cage-opening step. The novel six-vertex cages (CO)<sub>3</sub>FeC<sub>2</sub>B<sub>3</sub>H<sub>5</sub> and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-CoC<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, as well as the seven-vertex species (CO)<sub>3</sub>FeC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>CoC<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, were obtained from C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> and Fe(CO)<sub>5</sub> or ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> in the gas phase at elevated temperatures. Reactions of these metal reagents or ( $\pi$ -C<sub>5</sub>H<sub>4</sub>)Ni[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> with C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> gave primarily seven-vertex monometallic carboranes containing an MC<sub>2</sub>B<sub>4</sub> cage. The cobalt reagent and C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> gave mono-, di-, and trimetallic carborane species, including two isomers of the novel ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Co<sub>3</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> system. Nickel and iron monometallic carboranes of seven or eight vertices were obtained from C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> by analogous processes. The direct reaction of 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> at 300° gave a mixture of cobaltacarboranes which were predominantly isomers of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>. Molecular structures were assigned to the new compounds on the basis of <sup>11</sup>B and <sup>1</sup>H nmr spectra. Fine structure in the carborane CH <sup>1</sup>H nmr signals exhibited by several of the cobaltacarborane species was interpreted on the basis of H-C-B-H proton-proton coupling.

Of the many reported syntheses of metallocarboranes,<sup>1</sup> nearly all are variations on one or the other of two basic themes: (1) insertion of a metal atom into a neutral open-cage (nido) carborane, or (2) the opening of a closed polyhedral (closo) carborane framework to create a nido-carborane anion followed by the incorporation of a metal into the open face. The

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first method has been useful in limited applications, e.g., the synthesis of small metallocarboranes from nido-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>,<sup>2-6</sup> but cannot be considered a truly

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(5) L. G. Sneddon and R. N. Grimes, *J. Amer. Chem. Soc.*, **94**, 7161 (1972).

(6) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Amer. Chem. Soc.*, **94**, 1865 (1972).

Table I. 32.1-MHz  $^{11}\text{B}$  Nmr Data

Compd	Solvent	$\delta$ , <sup>a</sup> ppm (J, Hz)	Rel areas
1,2,4-(CO) <sub>3</sub> FeC <sub>2</sub> B <sub>3</sub> H <sub>5</sub> (I)	CCl <sub>4</sub>	-36.3 (197), -4.9 (190)	1, 2
1,2,3,5-(CO) <sub>4</sub> Fe <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>5</sub> (II)	CH <sub>2</sub> Cl <sub>2</sub>	-44.5 (163), -17.1 (160), -13.8 (163)	1, 1, <sup>b</sup> 1 <sup>b</sup>
1,2,4-( $\eta$ -C <sub>5</sub> H <sub>5</sub> )CoC <sub>2</sub> B <sub>3</sub> H <sub>5</sub> (III)	CH <sub>2</sub> Cl <sub>2</sub>	-16.1 (181), -2.7 (173)	1, 2
1,2,3,5-( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>5</sub> (IV)	CDCl <sub>3</sub>	-48.7 (156), -8.5 (150), -7.6 (146)	1, 1, <sup>b</sup> 1 <sup>b</sup>
1,2,4-[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P] <sub>2</sub> NiC <sub>2</sub> B <sub>3</sub> H <sub>6</sub> (VIII)	CH <sub>2</sub> Cl <sub>2</sub>	-3.2 <sup>c</sup>	
1,7,5,6-( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co <sub>2</sub> C <sub>2</sub> B <sub>3</sub> H <sub>7</sub> (XII)	CDCl <sub>3</sub>	-80.3 (139), +2.9 (161), +12.3 (166)	1, 2, 2
2,3,8,1,6-( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Co <sub>3</sub> C <sub>2</sub> B <sub>3</sub> H <sub>7</sub> (XIII)	CDCl <sub>3</sub>	-50.0 (146), -20.3 (137), -3.7 (137)	1, 2, 2
2,3,4,1,10-( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Co <sub>3</sub> C <sub>2</sub> B <sub>3</sub> H <sub>7</sub> (XIV)	CDCl <sub>3</sub>	-26.0 (153), +3.7 (153), +11.3 (131)	2, 2, 1

<sup>a</sup> Chemical shifts relative to externally referenced BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. Spectra of I-III and VIII were obtained on Varian HA-100 continuous-wave spectrometer; the others are Fourier transform spectra. <sup>b</sup> Estimated from overlapped peaks. <sup>c</sup> Broad singlet with  $W_{1/2}$  = 605 Hz.

general route inasmuch as few readily available *nido*-carboranes exist. The second approach, discovered and developed by Hawthorne and coworkers, has been widely employed in metallocarborane syntheses involving the C<sub>2</sub>B<sub>n</sub>-H<sub>n</sub> polyhedral carborane series.<sup>1a,b</sup> The opening of the polyhedron is normally accomplished by electron transfer from sodium naphthalide in ethereal solvents, producing a nido dianion into which a metal ion can be inserted to complete the "polyhedral expansion."<sup>7</sup> (An alternative technique, in which the cage is opened by removal of a boron atom by base attack,<sup>1</sup> is essentially limited to the icosahedral C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> systems.) The polyhedral expansion method is quite general and has been applied by Hawthorne and coworkers to polyhedra from C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> down to C<sub>2</sub>B<sub>6</sub>H<sub>8</sub> inclusive,<sup>7b</sup> and in our laboratory to 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub><sup>2,8</sup> and 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>.<sup>3</sup> We have found, however, that in the case of these smaller carboranes this technique gives rise to exceedingly complex reactions which produce in many cases nonexpanded products in which the metal replaces boron instead of adding to the original cage.<sup>2,3,8</sup> Moreover, in the case of C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> the metallocarborane yields were low, while similar treatment of C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> in several attempts gave no isolable metallocarboranes.<sup>3</sup>

Since metallocarboranes which might be derived from the smallest polyhedral carboranes are of considerable interest from a structural and bonding viewpoint, we have explored alternate routes to such compounds and have found that organometallic reagents of iron, cobalt, and nickel react directly with the lower carboranes to give small metallocarboranes, often in surprisingly good yield. Such reactions avoid a preliminary cage-opening step, are in most cases conducted in the gas phase and are exceedingly simple in execution, and give generally more tractable and easily separable product mixtures than those obtained in the sodium naphthalide treatment. Furthermore, this method is found to work well even with the thermally stable 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> and 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> systems, as well as with metallocarboranes themselves, and hence appears broadly applicable.

The only prior examples of direct metal insertion into polyhedral carboranes of which we are aware are the gas-phase reaction of 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> with Fe(CO)<sub>5</sub>, which we reported recently,<sup>2</sup> and several reactions of *closo*-2,3-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> with nickel group reagents, described by Spencer, Green, and Stone in a short communication.<sup>9</sup> In this paper we report the direct synthesis of

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(8) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, **95**, 2830 (1973).

iron, cobalt, or nickel metallocarboranes from 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>, and 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> and the structural characterization of several novel compounds obtained.

**General Procedure.** All of the reactions involving cobalt and iron reagents were conducted in the vapor phase without solvent, in an evacuated Pyrex "hot-cold" reactor described in the Experimental Section. Reactions of ethylenebis(triphenylphosphine)nickel were carried out in tetrahydrofuran (THF) solution at room temperature. In most instances, one or two major products were obtained, accompanied by minor or trace amounts of other compounds; of the latter species, only those considered structurally novel or otherwise significant were examined in detail. The new compounds were characterized from their  $^{11}\text{B}$  and  $^1\text{H}$  nmr, infrared, and electronic spectra (Tables I-IV, respectively) and from high-resolution mass spectroscopic analysis as described in the Experimental.

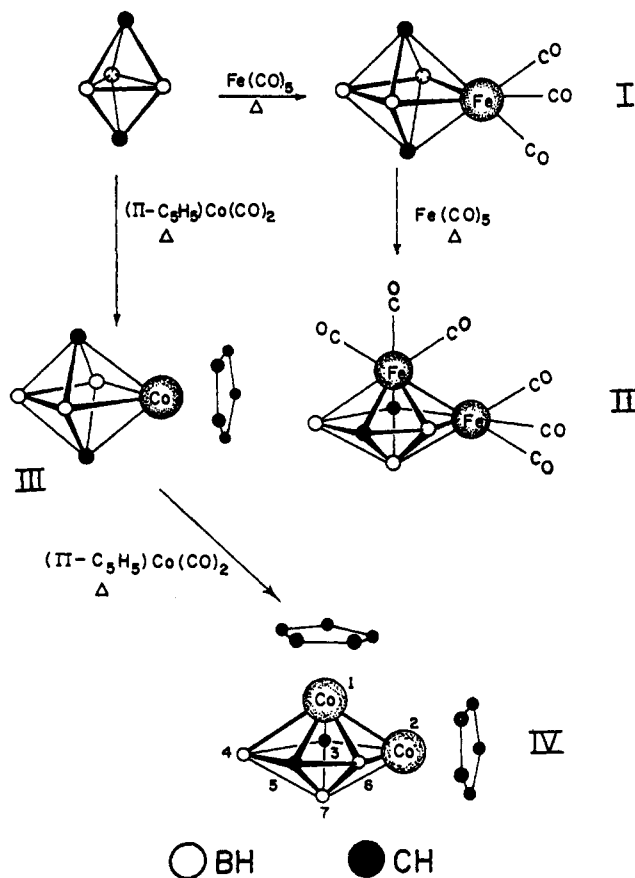
Table II. 100-MHz  $^1\text{H}$  Nmr Data

Compd	Solvent	$\delta$ , <sup>a</sup> ppm (J, Hz)			Rel areas
		C <sub>5</sub> H <sub>5</sub>	Cage CH	Other	
I	CCl <sub>4</sub>		-2.97	-3.69 (185) <sup>b</sup> -2.49 (181) <sup>c</sup>	2, 1 2
II	CCl <sub>4</sub>		-6.88 -4.37	-3.82 (192) <sup>d</sup> -2.55 (177) <sup>d</sup>	1, 2 1, 2
III	CDCl <sub>3</sub>	-5.03	-2.86	-2.92 (166) <sup>d</sup>	5, 2, 3
IV	CDCl <sub>3</sub>	-5.07	-8.29 -4.57		5, 1 5, 1
VIII	CDCl <sub>3</sub>		-5.08	-7.14 <sup>e</sup>	1, 15
XI	CDCl <sub>3</sub>	-4.82	-3.23 (3.4) <sup>f</sup>		5, 1
XII	CDCl <sub>3</sub>	-4.71	-8.63 -2.87		10, 1 1
XIII	CDCl <sub>3</sub>	-4.87	-10.65 (4.2) <sup>g</sup> -4.75		5, 1 10, 1
XIV	CDCl <sub>3</sub>	-4.75 <sup>i</sup>	-15.81 (2.4) <sup>i</sup> -4.74 <sup>i</sup>		10, 1 5, 1

<sup>a</sup> Chemical shifts relative to (CH<sub>3</sub>)<sub>4</sub>Si. Except where otherwise indicated, H- $^{11}\text{B}$  quartets were weak and/or masked by H-C peaks. Spectra of I-III and VIII were obtained on Varian HA-100 continuous-wave spectrometer; all others are Fourier transform nmr spectra. <sup>b</sup> H-B(6) quartet. <sup>c</sup> H-B(3,5) quartet. <sup>d</sup> H-B quartets, not specifically assignable. <sup>e</sup> Phenyl resonance. <sup>f</sup> Quartet-like multiplet in relative intensities 1:3:3:1 (see text). <sup>g</sup> Triplet-like multiplet. <sup>h</sup> Quartet-like multiplet. <sup>i</sup> Doublet. <sup>j</sup> C<sub>5</sub>H<sub>5</sub> singlets were resolved on an expanded scale with a separation of 0.8 Hz.

**Reactions of 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>.** The trigonal-bipyramidal carborane *closo*-1,5-dicarbapentaborane(5) reacted with excess iron pentacarbonyl at 230°, forming the orange liquids (CO)<sub>3</sub>FeC<sub>2</sub>B<sub>3</sub>H<sub>5</sub> (I) and (CO)<sub>6</sub>Fe<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> (II) in 13 and 1.4% yield, respectively. It appeared probable

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**Figure 1.** Reaction scheme for the gas-phase polyhedral expansion of 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>. Structures shown for metallocarborane products are proposed from spectroscopic data. An additional product of the cobalt reaction sequence is 1,7,2,4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> (V).

**Table III.** Infrared Absorptions, cm<sup>-1</sup>

I <sup>a</sup>	3040 (w), 2590 (m), 2550 (m), 2095 (vs), 2085 (m), 2050 (vs), 2030 (vs), 2000 (s), 1970 (w), 1260 (m)
II <sup>b</sup>	3040 (w), 2590 (m), 2550 (m), 2095 (vs), 2085 (m), 2050 (vs), 2030 (vs), 2000 (s), 1970 (w), 1260 (m), 1095 (m), 1010 (m)
III <sup>c</sup>	2617 (vs), 2590 (vs), 1820 (w), 1750 (w), 1660 (w), 1400 (w), 1115 (sh, m), 1095 (m), 1045 (w), 1025 (w), 1000 (m), 965 (w), 730 (m)
IV <sup>c</sup>	2550 (s), 2510 (s), 1810 (w), 1720 (w), 1600 (w), 1185 (w), 1130 (m), 1110 (m), 1005 (m), 805 (s)
VIII <sup>c</sup>	3040 (m), 2550 (vs), 1970 (w), 1900 (w), 1820 (w), 1665 (w), 1590 (w), 1575 (w), 1480 (s), 1435 (s), 1310 (w), 1170 (m), 1095 (s), 1060 (m), 1030 (w), 1000 (m), 870 (m), 850 (w), 680 (w)
XII <sup>c</sup>	3925 (w), 3120 (w), 3080 (w), 2530 (vs), 1820 (w), 1743 (w), 1676 (w), 1601 (w), 1414 (m), 1252 (w), 1134 (s), 1115 (m), 1094 (m), 1076 (w), 1008 (m), 898 (w), 845 (s), 821 (s), 798 (s), 657 (w)
XIII <sup>c</sup>	3925 (w), 3105 (w), 2460 (vs), 1816 (w), 1741 (w), 1662 (w), 1598 (w), 1415 (m), 1354 (w), 1116 (m), 1064 (s), 1030 (m), 1008 (m), 898 (w), 875 (m), 837 (s), 819 (vs), 804 (s)
XIV <sup>c</sup>	3920 (w), 3105 (w), 2485 (s), 1720 (w), 1603 (w), 1414 (w), 1103 (m), 1011 (m), 958 (m), 910 (w), 868 (m), 838 (s), 813 (s), 799 (m)

<sup>a</sup> Gas phase. <sup>b</sup> CCl<sub>4</sub> solution vs. CCl<sub>4</sub>. <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> solution vs. CH<sub>2</sub>Cl<sub>2</sub>.

that II was formed by the attack of Fe(CO)<sub>5</sub> on I, and this was confirmed by allowing I to react with excess Fe(CO)<sub>5</sub> at 250° for 12 hr. These reactions are depicted schematically in Figure 1. The yield in the

**Table IV.** Electronic Spectra, CH<sub>3</sub>CN Solution

Compd	$\lambda_{\max}$ , m $\mu$ (log $\epsilon$ )
III	440 sh (2.11), 365 (2.47), 293 sh (3.30), 265 (4.33)
IV	605 (2.35), 440 sh (2.84), 380 sh (3.16), 300 (3.84), 270 (4.03)
V	670 sh (2.20), 555 (2.51), 371 (3.56), 303 (4.54)
VII	405 (2.31), 265 (4.31)
VIII	436 (2.86), 289 (4.22)
X	373 (2.58), 304 (3.59), 260 sh (3.94), 234 (4.12)
XI	630 sh (1.94), 525 sh (2.77), 434 (3.36), 375 sh (3.47), 350 sh (3.64), 298 sh (4.29), 280 (4.34), 238 (4.29)
XII	690 sh (2.34), 620 (2.39), 450 sh (3.06), 363 (3.85), 305 sh (3.88), 274 (4.22), 240 (4.32)
XIII	700 sh (2.01), 590 sh (2.44), 490 sh (2.99), 414 (3.55), 274 (4.49)
XIV	560 sh (2.75), 495 sh (2.88), 440 sh (3.12), 375 (3.61), 284 (4.25)
3,5,1,7-( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>6</sub>	550 sh (2.06), 435 (3.00), 330 sh (3.72), 292 (3.96), 263 sh (3.95), 240 (4.20)

first reaction is adversely affected by the decomposition of C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, which is unstable above 150°.

The <sup>11</sup>B and <sup>1</sup>H spectra of I are consistent with an octahedral cage structure as depicted in Figure 1, and this species accordingly is designated<sup>10</sup> 1,2,4-(CO)<sub>3</sub>Fe-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>. Alternative geometries having adjacent framework carbon atoms cannot be ruled out entirely but are considered unlikely since the original carborane has nonadjacent carbons (no case is known in which initially nonvicinal cage carbon atoms move together during metallocarborane synthesis, a particularly improbable occurrence at elevated temperatures since thermal isomerizations of carborane polyhedra tend to separate the carbons<sup>1d</sup>).

Compound I and its analog ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>3</sub>H<sub>5</sub> (*vide infra*) are the smallest known polyhedral metallocarboranes and are isoelectronic with the structurally established octahedral systems 1,2- and 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>11,12</sup> and B<sub>6</sub>H<sub>6</sub><sup>2-13</sup>. In a formal sense, I is generated from C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> by replacement of a BH unit with an Fe(CO)<sub>3</sub> group, both being two-electron donors to the cage system.

It is significant that I is also isoelectronic with a family of octahedral metal cluster molecules such as (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>4</sub>(CO)<sub>10</sub><sup>14</sup> and with the recently discovered metalloboron compound ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>B<sub>4</sub>H<sub>6</sub>,<sup>15</sup> for which an octahedral geometry containing a Co-Co bond has

(10) Numbers preceding the formulas designate the locations of framework metal and carbon atoms in that order, and the heteroatoms of highest atomic number are given the lowest cage numbers. The IUPAC system of numbering for inorganic boron compounds is followed here: *Pure Appl. Chem.*, **30**, 683 (1972).

(11) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **53**, 1899 (1970).

(12) (a) G. L. McKown and R. A. Beaudet, *Inorg. Chem.*, **10**, 1350 (1971); (b) V. S. Mastyukov, O. V. Dorofeeva, L. V. Vilkov, A. F. Zhigach, V. T. Laptev, and A. B. Petrunin, *J. Chem. Soc., Chem. Commun.*, 276 (1973); (c) E. A. McNeill, K. L. Gallaher, F. R. Scholer, and S. H. Bauer, *Inorg. Chem.*, **12**, 2108 (1973).

(13) R. Schaeffer, Q. Johnson, and G. Smith, *Inorg. Chem.*, **4**, 917 (1965).

(14) L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, **84**, 2450 (1962).

(15) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, **95**, 5078 (1973).

been postulated. The electronic relationship between the metalloboranes, metallocarboranes, and metal clusters has been discussed in several recent papers.<sup>16-19</sup>

The structure of II proved surprising. While one might have anticipated a symmetrical geometry in which the metal atoms occupy five-coordinate vertices at the apex positions of a pentagonal bipyramid, as has been established<sup>4</sup> for the analogous species 1,7,2,3-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, such a structure is eliminated by the <sup>11</sup>B and <sup>1</sup>H nmr spectra. These data show that all borons and both cage carbons are magnetically non-equivalent; assuming a gross pentagonal-bipyramidal geometry with nonadjacent carbon atoms (*vide supra*), the only structure for II compatible with the nmr spectra is 1,2,3,5-(CO)<sub>3</sub>Fe<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> (Figure 1).<sup>20</sup>

The isolation of this material from a high-temperature reaction is interesting, since no other diiron species was found, and a totally asymmetric metallocarborane might be expected to be unstable with respect to thermal rearrangement to a more symmetric isomer. Furthermore, the tendency of transition metal atoms to occupy five-coordinate in preference to four-coordinate vertices in metallocarboranes is well established, only one apparent exception<sup>7b</sup> having been reported prior to this paper.<sup>21</sup> Thus, the existence of II at 230–250° in the absence of other isomers implies a stabilizing factor which is possibly the direct metal–metal bond in the system. It is noteworthy that II is an isoelectronic analog of the organometallic cluster species (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>C<sub>4</sub>Fe<sub>3</sub>(CO)<sub>8</sub>, which is a pentagonal-bipyramidal cage system containing Fe(CO)<sub>2</sub> groups in one equatorial and both apex positions, the Fe–Fe bonds being bridged by CO groups.<sup>22</sup> Except for the bridging carbonyls, this molecule and II are structurally very similar,<sup>19</sup> both featuring direct metal–metal bonding interactions between apex and equatorial iron atoms in a pentagonal bipyramid.

The reaction of 1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> with cyclopentadienyl cobalt dicarbonyl at 230° produced a yellow-orange solid, ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>3</sub>H<sub>5</sub> (III), in 10% yield, plus traces of two dark green solids (IV and V) which have the composition ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>. From its <sup>11</sup>B and <sup>1</sup>H nmr spectra, III is proposed to be octahedral 1,2,4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, analogous to I. Again, there are no other possible octahedral structures if adjacent carbon isomers are ruled out.

Compound V has been identified as the previously characterized<sup>4</sup> 1,7,2,4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>. The structure of its isomer IV, like that of II, is indicated from the nmr data to be entirely asymmetric and accordingly

(16) K. Wade, *J. Chem. Soc., Chem. Commun.*, 792 (1971).

(17) K. Wade, *Inorg. Nucl. Chem. Lett.*, 8, 559 (1972).

(18) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973).

(19) R. N. Grimes, *Ann. N. Y. Acad. Sci.*, in press.

(20) This is easily seen by considering that in order to eliminate all symmetry in the cage system as required by the nmr data, the two five-coordinate (apex) vertices must be occupied by different groups. Neither of these, however, can be CH since the remaining CH would be equatorial and hence adjacent, contrary to the stated assumption. Thus, the apex positions are occupied by a metal and a BH group, with the remaining (equatorial) atoms arranged so that no C–C bonds and no mirror planes exist. Disregarding enantiomers, the 1,2,3,5 structure uniquely satisfies these conditions.

(21) The octahedral compounds I and III described herein and the previously reported<sup>16</sup> octahedral ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>B<sub>4</sub>H<sub>6</sub> also are presumed to contain four-coordinate metal groups, but in these cases there is of course no higher coordinate vertex available.

(22) R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, 3, 274 (1965).

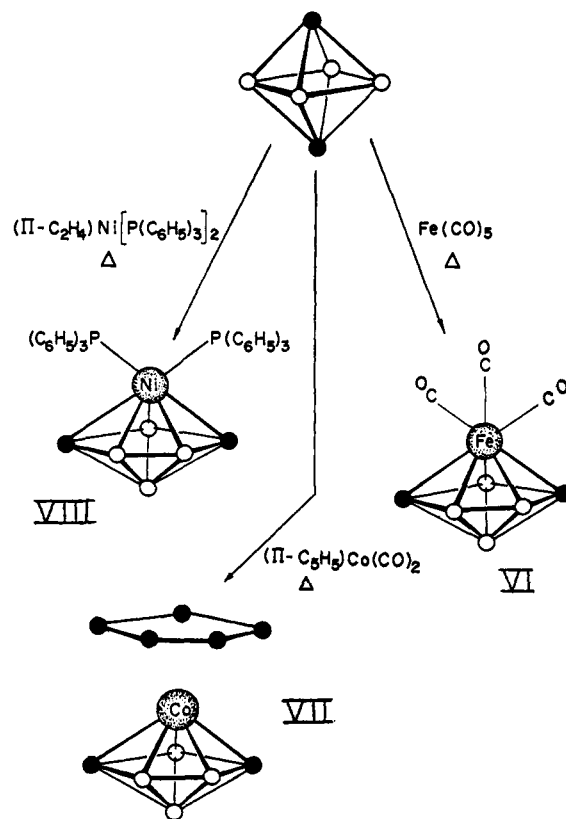
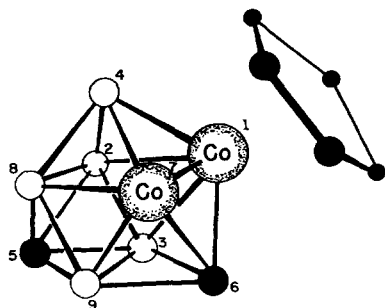


Figure 2. Reaction scheme for the gas-phase and solution polyhedral expansion of 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, showing proposed metallocarborane structures.

is designated 1,2,3,5-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>. As in the case of the analogous species II, the assumption of nonadjacent cage CH groups leads uniquely to this assignment.<sup>20</sup> Compound IV is the third ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> isomer to be characterized, the others being the established 1,7,2,3 and proposed 1,7,2,4 species;<sup>3,4</sup> both of the latter two molecules can be described as triple-decked metallocene analogs containing two formal Co<sup>3+</sup> ions sandwiched between two C<sub>5</sub>H<sub>5</sub><sup>-</sup> rings and a central C<sub>2</sub>B<sub>3</sub>H<sub>5</sub><sup>4-</sup> ring. A fourth isomer, believed to be 1,2,4,5-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, has been obtained together with IV and V in the pyrolysis of 1,7,2,3-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> and will be described elsewhere.<sup>23</sup>

**Reactions of 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>.** Since a number of metallocarboranes incorporating an MC<sub>2</sub>B<sub>4</sub> pentagonal-bipyramidal cage have been reported, some of them obtained from 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub>,<sup>2,3</sup> this type of metallocarborane system appears to have exceptional stability and might therefore be expected to form directly from C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>. This anticipated result was borne out in the gas-phase reactions of 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with Fe(CO)<sub>5</sub> and with ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> (Figure 2). In the former case the major product was the previously reported<sup>2</sup> species 1,2,4-(CO)<sub>3</sub>FeC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (VI) while the latter reaction generated 1,2,4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (VII) in 70% yield, identical with the compound obtained earlier<sup>8</sup> from 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> *via* sodium reduction in solution. The present direct-insertion synthesis represents a superior route to this metallocarborane, in view of the high yield and the simplicity of the one-step vapor-phase reaction. The

(23) V. R. Miller and R. N. Grimes, manuscript in preparation.



**Figure 3.** Schematic drawing of the proposed structure of 1,7,5,6-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (XII). One of the  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligands has been omitted for clarity.

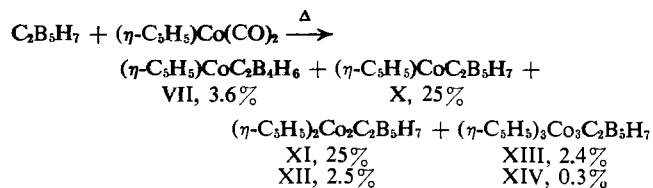
C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>-(C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> reaction also yielded a small quantity of 3,5,1,7-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, an eight-vertex polyhedron obtained previously<sup>8</sup> from C<sub>2</sub>B<sub>3</sub>H<sub>7</sub>, as well as traces of other metallocarboranes which were not identified.

The direct insertion of nickel into 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> was accomplished by treatment of the carborane with ethylenebis(triphenylphosphine)nickel in THF (Figure 2). The only isolated metallocarborane product was yellow 1,2,4-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NiC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (VIII) obtained in 10% yield as red-orange plates. This compound is isoelectronic with ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, (CO)<sub>3</sub>FeC<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, and other known seven-atom metallocarboranes, and the nickel atom has an 18-electron filled-shell configuration. The compound is evidently diamagnetic and exhibits a normal <sup>1</sup>H nmr spectrum, but the <sup>11</sup>B nmr spectrum consists of a single broad resonance with some indication of splitting. A similar effect has been noted in the <sup>11</sup>B nmr spectra of other formal nickel(II) metallocarboranes,<sup>3,24</sup> possibly indicating a paramagnetic contribution from a species in equilibrium with VIII in the solution. The indicated 1,2,4 structure is not established but can be assumed from the structures of the isoelectronic seven-atom iron and cobalt monometallocarboranes.

**Reactions of 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub>.** The high thermal stability of 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub>, which is unchanged at temperatures above 300° over indefinite periods, suggested that this carborane might be somewhat less reactive than its lower homologs with respect to direct metal insertion. Fortunately for our purposes, this was not found to be the case. The reaction with Fe(CO)<sub>5</sub> in the gas phase readily produced 1,2,4-(CO)<sub>3</sub>FeC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (VI) and the "expanded" eight-vertex product 3,1,7-(CO)<sub>3</sub>FeC<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (IX), as reported in an earlier study<sup>2</sup> (the latter species was formerly<sup>2</sup> numbered 4,1,8). The treatment of 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> with ( $\pi$ -C<sub>2</sub>H<sub>4</sub>)Ni[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> in THF at 25° yielded initially a violet species which is probably [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NiC<sub>2</sub>B<sub>5</sub>H<sub>7</sub>. This material was unstable and was not characterized but during chromatography on silica gel was converted to yellow 1,2,4-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NiC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (VIII), identical with the product obtained from 1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> as described above.

The vapor-phase reaction of 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> with ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> at 260° proved particularly fruitful from a synthetic viewpoint, giving a mixture of products as shown.

(24) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 1109 (1973).



Not only was a high (~60%) total yield of metallocarboranes obtained, but the two major products, X and XI, had formerly been accessible<sup>8</sup> only in low yield from the polyhedral expansion of C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> via sodium naphthalide reduction in THF. In addition, several new metallocarboranes were isolated, including a second isomer of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (XII) and two isomers of the previously unknown tricobalt system, XIII and XIV.

The proposed structures of X and XI, which are designated 3,1,7-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>5</sub>H<sub>7</sub> and 1,8,5,6-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>, have been discussed in an earlier paper<sup>8</sup> (the previous numbering of these species was 4,1,8 and 3,8,1,9, respectively). The argument advanced earlier<sup>8</sup> for the structure of XI has been strengthened by a re-determination of its <sup>1</sup>H nmr spectrum on a Fourier transform nmr spectrometer, which affords higher resolution and sensitivity than the original<sup>8</sup> spectrum obtained on a continuous wave (Varian HA-100) nmr spectrometer. While the gross features of the spectra are the same, the new spectrum shows the carborane H-C resonance as an apparent quartet with relative intensities 1:3:3:1 (*J* = 3.4 Hz), attributed to spin coupling of each equivalent H-C proton with three protons bonded to adjacent boron atoms.<sup>3,4,8</sup> These three BH groups need not be magnetically equivalent but must generate similar coupling constants in order to produce the pattern observed for XI. (We have observed apparent H-B-C-H coupling in the <sup>1</sup>H nmr spectra of other small metallocarboranes<sup>3,4,8</sup> but previously only seven-vertex cage systems were involved. In the present paper, we report for the first time observation of such coupling in polyhedra of nine and ten atoms.<sup>23</sup>)

The new isomer XII has been characterized as 1,7,5,6-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (Figure 3) from the 2:2:1 <sup>11</sup>B nmr pattern and the indications of equivalent ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co and nonequivalent CH units in the <sup>1</sup>H nmr spectrum. The only assumptions are that the gross geometry is a tricapped trigonal prism, that the cage carbons are nonadjacent (*vide supra*), and that the <sup>11</sup>B resonance at very low field arises from a unique four-coordinate BH group adjacent to cobalt,<sup>7b,8</sup> in which case the geometry is uniquely determined.

The two tricobalt isomers XIII and XIV were obtained only in low yield<sup>23a</sup> but are the first known subicosahedral metallocarboranes having more than two metal atoms [the only previously reported trimetallic system is a ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Co<sub>3</sub>C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> icosahedral cage prepared by polyhedral expansion of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)CoC<sub>2</sub>B<sub>7</sub>H<sub>9</sub> in solu-

(25) We have been able to detect fine structure in the carborane H-C <sup>1</sup>H nmr signals in some metallocarborane species but not in others, presumably due to variations in coupling constants and peak widths which in many instances obliterate the fine structure and give only a broad singlet. However, when observable this spectral feature has given valuable additional insight into the assignment of probable metallocarborane structures, as in compounds X-XIV in this paper and other species discussed elsewhere.<sup>3,4,8</sup>

(25a) NOTE ADDED IN PROOF. Recent work has shown that sealed-bulb reactions of C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> with (C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> produce XIII in much higher (~20%) yield.

tion<sup>26</sup>]. The more abundant isomer, XIII, is assigned the structure 2,3,8,1,6-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Co<sub>3</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (Figure 4a) based on a bicapped square antiprism, which is the normal gross geometry for a ten-atom polyhedron having a filled-shell ( $2n + 2$ )<sup>16,27</sup> electronic structure. The <sup>11</sup>B and <sup>1</sup>H nmr spectra suggest the presence of a mirror plane passing through the apices, on which are located one cobalt, one boron, and two nonequivalent cage carbon atoms, with two pairs of borons and a pair of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co groups located symmetrically with respect to the plane. Again assuming nonadjacent carbons and assigning the unique low-field <sup>11</sup>B nmr resonance to a four-coordinate BH group adjacent to cobalt,<sup>7b,8</sup> the only possible arrangements are the 2,3,8,1,6-, 2,3,6,1,8-, and 1,6,7,3,5-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Co<sub>3</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> isomers, the latter being somewhat less likely inasmuch as it contains cobalt in a four-coordinate apex position. The 2,3,8,1,6 isomer is favored because of the splitting of the <sup>1</sup>H nmr carborane CH signals into a 1:2:1 triplet and 1:3:3:1 quartet, respectively. An interpretation on the basis of H-B-C-H coupling between protons on adjacent cage atoms suggests that the two CH groups are linked directly to two and three BH units, respectively; this is the case in the 2,3,8,1,6 isomer but not in the 2,3,6,1,8 or 1,6,7,3,5 structures. It is also of interest to note that the triplet CH signal, which is assigned to H-C(1), appears at unusually low field for a carborane or metallocarborane cage CH resonance. This suggests that the interaction of the four-coordinate apex carbon with two adjacent cobalt atoms is somewhat similar to that in organocobalt clusters such as HCCo<sub>3</sub>(CO)<sub>9</sub>, which exhibits a <sup>1</sup>H nmr resonance at  $\delta$  -12.08 ppm relative to tetramethylsilane.<sup>28</sup>

The trace product XIV, an isomer of XIII, has a similar 1:2:2 <sup>11</sup>B nmr pattern, again indicative of a mirror plane passing through both apex positions of the bicapped square antiprism. The <sup>1</sup>H nmr spectrum of XIV has two unusual features: a very large shift (~10 ppm) between the two carborane CH resonances, one of which is at extremely low field ( $\delta$  -15.81 ppm), and a pair of C<sub>5</sub>H<sub>5</sub> resonances in a 2:1 area ratio which are very nearly superimposed with a separation of only 0.8 Hz. The mirror plane includes the unique ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co group, the unique boron, and the two nonequivalent CH groups. Furthermore, the absence of a <sup>11</sup>B nmr signal at very low field suggests that there are no four-coordinate BH units adjacent to cobalt.<sup>7b,8</sup> These considerations, plus the previously invoked assumption that the carbons are nonadjacent, limit the occupancy of the apex positions to either two carbons, or a carbon and a cobalt. However, the latter possibility is unlikely since the nearly identical chemical shifts of the C<sub>5</sub>H<sub>5</sub> signals in the <sup>1</sup>H nmr spectrum suggest that the three ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co moieties are in very similar electronic environments. Hence, the cobalts are all presumed to be in nonapical locations and the two CH groups occupy the apices. On this basis the remaining structures for XIV consistent with the data are the 2,3,4,1,10, 2,3,6,1,10, and 2,3,8,1,10 isomers. We favor the 2,3,4,1,10 structure (Figure 4b) for two reasons. First, the place-

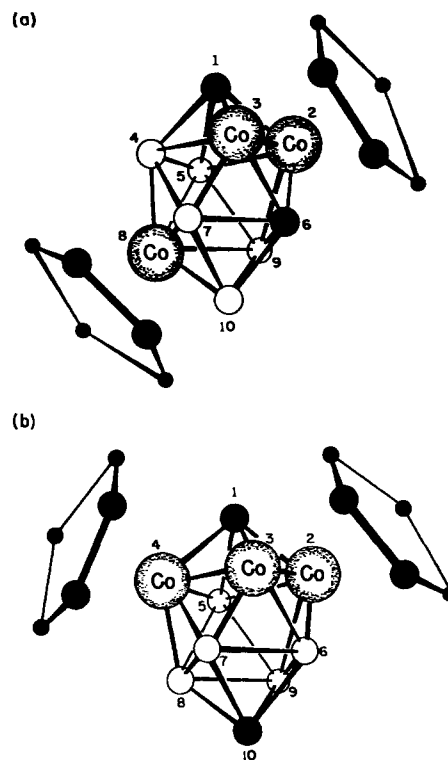


Figure 4. Schematic drawings of the proposed structures of (a) 2,3,8,1,6-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Co<sub>3</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (XIII) and (b) 2,3,4,1,10-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Co<sub>3</sub>C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> (XIV). In both structures the  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligand on Co(3) is omitted for clarity.

ment of C(1)-H adjacent to three cobalt atoms is consistent with the very low-field carborane H-C resonance [again comparable to HCCo<sub>3</sub>(CO)<sub>9</sub>, as noted for XIII] and also accounts for the large difference in chemical shift with respect to the other CH, since the latter is then adjacent to no metal atoms and consequently is in a very different electronic environment. Secondly, the low-field H-C resonance is a doublet, in agreement with its bonding to only one BH group; this feature is not consistent with either of the other isomers mentioned (the remaining CH resonance did not exhibit resolvable fine structure).

We emphasize that our interpretation of fine structure in the H-C <sup>1</sup>H nmr signals is tentative and has been employed only as a means of supplementing the main structural arguments which are based on the gross features of the nmr spectra.<sup>25</sup> Hopefully, the determination of many of these structures by X-ray diffraction studies will eventually place the H-C-B-H proton-proton coupling hypothesis on a firmer basis. Such coupling has been observed in at least one X-ray determined structure,<sup>3,4</sup> 2-CH<sub>3</sub>-1,7,2,3-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>, as well as in several other species whose gross geometry can be regarded as nearly certain, e.g., 1,2,3- and 1,2,4-( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Co<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>,<sup>3,8</sup> and thus far is consistent with the structure in all cases.

**Reaction of 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>.** Although our work on metallocarborane synthesis has centered on the smaller systems, the success of the direct-insertion method with C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, and C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>, and elsewhere with (CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>,<sup>9</sup> led us to investigate the extension of the technique to 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (*o*-carborane). Earlier attempts at direct reaction of Ni[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub> or Pt[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub> with 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> or 1,2-(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> in solution

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have been reported to be unsuccessful.<sup>9</sup> However, in this work the gas-phase thermal reaction of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  with  $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$  in a sealed tube gave a complex mixture of metallocarboranes. Mass spectroscopic and tlc analysis indicated that most of these products were isomers of  $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_9\text{H}_{11}$ , and since all possible isomers of this icosahedral system have previously been characterized,<sup>29</sup> the isolation of individual products was not carried out. One of the more abundant products was, however, identified as  $3,1,9\text{-}(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_9\text{H}_{11}$  (compound 1c in ref 29) from its ir and  $^1\text{H}$  nmr spectra by comparison with literature values.<sup>29</sup> Conceivably, the initial insertion of cobalt generates a thermally unstable 13-vertex<sup>30</sup>  $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_{10}\text{H}_{12}$  species which subsequently degrades, by loss of boron, to one or more 12-vertex compounds; the latter species can then undergo thermal rearrangement<sup>29</sup> to produce other isomers.

This reaction is evidently the first instance of heteroatom insertion into a closed icosahedral carborane framework in the absence of a preliminary cage-opening treatment such as reduction with sodium or attack by Lewis bases. However, the extent to which this approach represents a useful synthetic route is not clear; the advantage of a simple, one-step operation is evident but the abundance of isomers is a drawback. The latter problem might be overcome by controlling the reaction conditions or by trapping the original product species before they can rearrange, but such possibilities are outside the scope of this investigation and were not examined.

## Conclusions

These results suggest strongly that direct metal insertion into polyhedral carboranes is a synthetic approach of potentially broad applicability. Including the work reported elsewhere on  $\text{C}_2\text{B}_9\text{H}_{11}$ ,<sup>6</sup> the method has been successfully employed in the preparation of metallocarboranes from  $\text{C}_2\text{B}_n\text{-}_2\text{H}_n$  polyhedra in which  $n = 5, 6, 7, 11,$  and  $12$ . It is reasonable to expect that the  $\text{C}_2\text{B}_6\text{H}_8$ ,  $\text{C}_2\text{B}_7\text{H}_9$ , and  $\text{C}_2\text{B}_8\text{H}_{10}$  species will undergo similar metal insertions. The yields of metallocarboranes obtained are, in general, comparable to those of other methods, and in the reactions of  $\text{C}_2\text{B}_3\text{H}_5$ ,  $\text{C}_2\text{B}_4\text{H}_6$ , and  $\text{C}_2\text{B}_5\text{H}_7$  with  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  they are substantially larger. In addition, the transition metal reagents employed have been sufficiently varied to demonstrate some versatility in the choice of attacking groups.

An inherent problem with the method is that there is no control over the position of metal insertion into the cage, but this is true of most other metallocarborane synthetic routes as well. For example, while the incorporation of metals into the  $1,2\text{-C}_2\text{B}_9\text{H}_{11}^{2-}$  ion proceeds exclusively at the open-face (3) position, there is no known way to vary the location of the open face in the ion.<sup>1</sup> A particular difficulty arising in the direct insertion technique at elevated temperatures is that thermally less stable isomers are likely to rearrange to more stable species unless, as suggested above, the initially formed compounds can be trapped or removed from the reaction zone. Notwithstanding these limitations, the direct insertion method offers a useful new

route to metallocarboranes from commercially available reagents, requiring only simple and relatively fast manipulations, and in general avoids the complicating side reactions (e.g., metallocene formation) associated with other synthetic techniques.

The new compounds reported herein extend the previous limits of known metallocarborane structural features in several directions. The six-vertex species I and III are novel, as are the seven-vertex compounds II and IV which evidently incorporate metal atoms in adjacent four- and five-coordinate vertices. The isolation of X, formerly only a trace product, in substantial yield as a thermally and hydrolytically stable compound has forced us to revise an earlier tentative hypothesis<sup>8</sup> that this eight-vertex system might be inherently unstable with respect to degradation to  $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_4\text{H}_6$ . Finally, the formation of the tricobalt species XIII and XIV directly from  $2,4\text{-C}_2\text{B}_5\text{H}_7$  raises the possibility that direct gas-phase reactions of dicobalt metallocarboranes with  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  might generate metallocarboranes containing more than three cobalt atoms. The preparation and study of such multimetal cage species is potentially important in its relationship to the metal clusters<sup>19</sup> and could eventually develop into a synthetic bridge between the latter field and boron cage chemistry.

## Experimental Section

**Materials.** 1,6-Dicarba-*closo*-hexaborane(6) ( $\text{C}_2\text{B}_4\text{H}_6$ ), 2,4-dicarba-*closo*-heptaborane(7) ( $\text{C}_2\text{B}_5\text{H}_7$ ), and 1,5-dicarba-*closo*-pentaborane(5) ( $\text{C}_2\text{B}_3\text{H}_5$ ) were purchased from Chemical Systems, Inc., Irvine, Calif., and purified by glpc (30% Apiezon L on Chromosorb W at 25–45°). Ethylenebis(triphenylphosphine)nickel was prepared by the literature method.<sup>31</sup> All other reagents were reagent grade and used as received. Tetrahydrofuran (THF) was dried over  $\text{LiAlH}_4$  before use.

**Spectra.** Boron-11 nmr spectra at 32.1 MHz and proton nmr spectra at 100 MHz were obtained on either a Varian HA-100 spectrometer or a JEOL PS-100P pulse Fourier transform spectrometer interfaced to a JEOL-Texas Instrument EC-100 computer system. Unit-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. High-resolution mass spectra were recorded on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source and interfaced to a PDP-8I computer. All high-resolution spectra were obtained under chemical ionizing conditions in argon-water as described in an earlier paper,<sup>8</sup> and the exact masses of several peaks in each spectrum corresponding to different isotopic combinations<sup>8</sup> were determined and found to be in satisfactory agreement with the calculated values (masses of parent or  $P + 1$  peaks are given below). Infrared spectra were obtained on a Beckman IR-8 instrument, and electronic spectra were recorded on a Cary 14 spectrophotometer. Elemental analyses were conducted by the Schwarzkopf Micro-analytical Laboratory, Woodside, N. Y.

**General Procedure.** Except where otherwise indicated, all reactions were run in high vacuum systems or in an inert atmosphere. Thin-layer and column chromatography were conducted on silica gel in air. "Hot-cold" reactions were run in an evacuated cylindrical Pyrex tube 24 mm in diameter, connected to a vacuum line with a greaseless Teflon stopcock containing a Viton O-ring. The reactor was maintained in a vertical position with its central portion heated by a Variac-controlled heating tape, and the lower section was immersed in a flask containing a liquid whose temperature was adjusted as desired.

**Reaction of  $1,5\text{-C}_2\text{B}_3\text{H}_5$  with  $\text{Fe}(\text{CO})_5$ .** The hot-cold reactor described above was charged with 2.78 mmol of  $\text{C}_2\text{B}_3\text{H}_5$  and 6.0 mmol of  $\text{Fe}(\text{CO})_5$  *in vacuo*. The hot zone was heated to 230° while the lower end was maintained at 25–30° for 11 hr. At this time the tube was opened to the vacuum line and the volatiles were removed. The pure orange liquids  $1,2,4\text{-(CO)}_3\text{FeC}_2\text{B}_3\text{H}_5$  (I, 64.7 mg, 0.320 mmol) and  $1,2,3,5\text{-(CO)}_4\text{FeC}_2\text{B}_3\text{H}_5$  (II, 11.5 mg, 0.034

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mmol) were obtained by repeated fractionation through  $-23$  and  $0^\circ$  traps, respectively. A 0.286-mmol quantity of  $C_2B_3H_5$  was recovered. The yields of I and II based upon  $C_2B_3H_5$  consumed were 12.8 and 1.4%, respectively. Mass spectroscopic analyses: calcd for  $^{12}C_8^{11}B_3^{56}Fe^{16}O_3^+H_5^+$  (I),  $m/e$  202; found 202, with a 3-boron pattern in the parent region and successive loss of three CO groups evidenced by similar groupings at  $m/e$  174, 146, and 118. Calcd mass for II ( $P + 1$  peak from protonation by chemical ionization in  $Ar/H_2O$ ), 342.9140; found, 342.9161. The spectrum also exhibited a 3-boron pattern and successive loss of six CO groups.

**Reaction of  $C_2B_3H_5Fe(CO)_5$  with  $Fe(CO)_5$ .** The hot-cold reactor was charged with I (64.7 mg, 0.32 mmol) and  $Fe(CO)_5$  (6.0 mmol). The hot zone was maintained at  $250^\circ$  and the lower end at  $25^\circ$  for 12 hr. Vacuum line fractionation as above gave II (4.9 mg, 0.0143 mmol, 4.5% yield). No I was recovered.

**Reaction of 1,5- $C_2B_3H_5$  with  $(\eta-C_5H_5)Co(CO)_2$ .** The hot-cold reactor was charged with 3.59 mmol of  $C_2B_3H_5$  and 3.90 mmol of  $(\eta-C_5H_5)Co(CO)_2$ . The central portion of the tube was heated to  $230^\circ$ , while the lower end was maintained at  $60^\circ$  in an oil bath. After 14 hr the tube was cooled in liquid nitrogen, the noncondensables were removed, and an additional 2.14 mmol of  $C_2B_3H_5$  was added. The reactor was again heated for 24 hr, after which time the above procedure was repeated and another 2.14 mmol of  $C_2B_3H_5$  was added. The reaction was then allowed to continue for 48 hr with periodic interruptions to permit removal of noncondensables. At this point the reactor was opened to the vacuum line and the volatiles were removed. Repeated fast distillation of the volatiles into a  $0^\circ$  trap allowed unreacted  $(\eta-C_5H_5)Co(CO)_2$  to pass. No  $C_2B_3H_5$  was recovered. The material retained in the  $0^\circ$  trap was combined with a solution obtained by extracting the residue in the reactor with  $CH_2Cl_2$ , and the resulting mixture was separated by preparative thin-layer chromatography. Development on silica gel plates with carbon tetrachloride as eluent gave yellow-orange 1,2,4- $(\eta-C_5H_5)CoC_2B_3H_5$  (III, 135 mg, 0.750 mmol), dark green 1,2,3,5- $(\eta-C_5H_5)_2Co_2C_2B_3H_5$  (IV, 0.9 mg, 0.003 mmol), and dark green 1,7,2,4- $(\eta-C_5H_5)_2Co_2C_2B_3H_5$  (V, 10.2 mg, 0.033 mmol). The yields were 9.5, 0.04, and 0.42%, respectively, based on the total quantity of  $C_2B_3H_5$  employed. Calculated masses: for III (parent peak), 186.0393; found, 186.0407; for IV ( $P + 1$  peak), 311.0194; found, 311.0188. Compound V was identified from its  $^{11}B$  nmr, ir, and mass spectra in comparison with those of a known<sup>3,4</sup> sample.

**Reaction of 1,6- $C_2B_4H_6$  with  $Fe(CO)_5$ .** The hot-cold reactor was charged with 2.2 mmol of  $C_2B_4H_6$  and 3.0 mmol of  $Fe(CO)_5$  *in vacuo*. The hot zone was maintained at  $130^\circ$  for 1 hr and then at  $190^\circ$  for an additional 4 hr, while the lower end of the reactor was immersed in a  $25^\circ$  bath. The volatiles were fractionated through a  $-23^\circ$  trap and all material passing through was returned to the reactor. After an additional 12 hr at  $210$ – $225^\circ$ , the volatiles were again fractionated through a  $-23^\circ$  trap. The  $-23^\circ$  condensate from both fractionations was combined and fractionated repeatedly through a  $0^\circ$  trap until the more volatile  $Fe(CO)_5$  was separated. The material remaining in the  $0^\circ$  trap was an orange liquid which was identified from ir and mass spectra as 1,2,4- $(CO)_3FeC_2B_4H_6$  (VI), identical with the compound previously obtained<sup>2</sup> in the reaction of 2,4- $C_2B_3H_7$  and  $Fe(CO)_5$ . A  $CH_3(CO)_6Fe_2C_2B_3H_4$  species was also detected in the sample and was presumed to have formed from a  $CH_3-1,5-C_2B_3H_4$  impurity in the carborane reagent (the presence of this material was confirmed by glpc, infrared, and mass spectroscopic analysis of the 1,6- $C_2B_4H_6$  sample). There was no evidence of new metallocarborane species among the products and the reaction was not studied further.

**Reaction of 1,6- $C_2B_4H_6$  with  $(\eta-C_5H_5)Co(CO)_2$ .** A mixture of 0.78 mmol of  $C_2B_4H_6$  and 3.4 mmol of  $(\eta-C_5H_5)Co(CO)_2$  was allowed to react in the hot-cold apparatus at  $270$ – $280^\circ$  for 70 hr. The more volatile materials were distilled into a vacuum line while cooling the reaction vessel at  $0^\circ$  and were separated by trap-to-trap fractionation to give 1.7 mmol of  $(\eta-C_5H_5)Co(CO)_2$  and 0.50 mmol of  $C_2B_4H_6$ . The reaction vessel was opened to the air, the solids were extracted with  $CH_2Cl_2$ , and the extract was evaporated onto a small amount of silica gel, placed on top of a silica gel column (100 ml of dry solid) prepared in hexanes, and eluted with benzene-hexane mixtures. The first major band was identified from its ir and mass spectra as the known<sup>8</sup> 1,2,4- $(\eta-C_5H_5)CoC_2B_4H_6$  (VII): yield 39 mg (0.20 mmol, 70% based on  $C_2B_4H_6$  consumed). The next band was identified as the known<sup>8</sup> 3,5,1,7- $(\eta-C_5H_5)_2Co_2C_2B_4H_6$  (previously<sup>8</sup> numbered 3,4,1,7) from its ir and mass spectra. The yield was 5 mg (0.015 mmol, 5% based on  $C_2B_4H_6$  consumed). The less mobile material on the column was not characterized.

**Reaction of 1,6- $C_2B_4H_6$  with  $(\pi-C_2H_4)Ni[P(C_6H_5)_3]_2$ .** Under a nitrogen atmosphere 1.83 mmol of  $(\pi-C_2H_4)Ni[P(C_6H_5)_3]_2$  was placed in a 100-ml Schlenk tube which was connected to a vacuum line, and 1,6- $C_2B_4H_6$  (1.83 mmol) and THF (30 ml) were added at  $-196^\circ$ . The reaction mixture was allowed to warm to room temperature with stirring. During this period the solution changed from a rusty brown to a bright red color with substantially no  $H_2$  evolution.

After a total reaction period of 3 hr, the solvent was removed and the product extracted with benzene. The benzene extract was rapidly passed through a silica gel column with benzene as the eluent. The recovered red-orange fraction was chromatographed on a silica gel column with a 50/50 hexane-benzene mixture. Recrystallization from methylene chloride-hexane yielded 120 mg (0.183 mmol, 10%) of red-orange plates of 1,2,4- $[(C_6H_5)_3P]_2NiC_2B_4H_6$  (VIII). *Anal.* Calcd for  $C_{38}H_{36}B_6P_2Ni$ : C, 69.51; H, 5.53; B, 6.58; Ni, 8.94. Found: C, 69.38; H, 5.51; B, 6.56; Ni, 9.09.

**Reaction of 2,4- $C_2B_3H_7$  and  $(\pi-C_2H_4)Ni[P(C_6H_5)_3]_2$ .** 2,4- $C_2B_3H_7$  (4.32 mmol) and THF (30 ml) were distilled into a flask containing 4.32 mmol of  $(\pi-C_2H_4)Ni[P(C_6H_5)_3]_2$ . The mixture was stirred at room temperature for 4 hr and filtered, and solvent was removed from the filtrate to give a reddish-brown material. Attempts to purify this substance by chromatography resulted in extensive decomposition. When hexane and hexane-benzene mixtures were used as eluents, a violet-colored band separated on the column, but after a few minutes the color faded to light brown, then yellow. Collection of this fraction followed by recrystallization from methylene chloride-hexane gave 110 mg (0.178 mmol, 4.1%) of VIII, identified from its  $^{11}B$  nmr and ir spectra.

**Reaction of 2,4- $C_2B_3H_7$  with  $(\eta-C_5H_5)Co(CO)_2$ .** A mixture of 2.90 mmol of  $C_2B_3H_7$  and 2.70 mmol of  $(\eta-C_5H_5)Co(CO)_2$  was allowed to react in the hot-cold apparatus at  $260$ – $270^\circ$  for 50 hr. The more volatile materials were distilled onto a vacuum line while cooling the reaction vessel at  $0^\circ$  and were separated using trap-to-trap fractionation to give 2.1 mmol of  $C_2B_3H_7$  and 1.8 mmol of  $(\eta-C_5H_5)Co(CO)_2$ . The reaction vessel was opened to the air and a  $CH_2Cl_2$  extract was evaporated onto a small amount of silica gel, placed on a silica gel column (100 ml of dry solid) prepared in hexanes, and eluted with a benzene-hexane mixture. The first band (44 mg, 0.21 mmol, 26%) was crystallized from pentane at  $-78^\circ$  and identified as the known<sup>8</sup> 3,1,7- $(\eta-C_5H_5)_2CoC_2B_3H_7$  (X, previously<sup>8</sup> numbered 4,1,8). The second band (5.8 mg, 0.029 mmol, 3.6%) was identified as 1,2,4- $(\eta-C_5H_5)CoC_2B_3H_6$  from its ir and mass spectra.<sup>8</sup> The third band (69 mg, 0.20 mmol, 25%) was crystallized from warm hexane and identified as the known<sup>8</sup> 1,8,5,6- $(\eta-C_5H_5)_2Co_2C_2B_3H_7$  (XI, formerly<sup>8</sup> numbered 3,8,1,9). The fourth band (7.1 mg, 0.020 mmol, 2.5%) was characterized as green 1,7,5,6- $(\eta-C_5H_5)_2Co_2C_2B_3H_7$  (XII) and was purified by crystallization from pentane at  $-78^\circ$  (calcd mass, 334.0458; found, 334.0497). The fifth band (8.7 mg, 0.019 mmol, 2.4%) was characterized as brown 2,3,8,1,6- $(\eta-C_5H_5)_3Co_3C_2B_3H_7$  (XIII) and was crystallized by slowly evaporating a hexane solution (calcd mass of protonated species, 459.0260; found, 459.0261). The sixth band (1.3 mg, 0.0028 mmol, 0.3%) was characterized as brown 2,3,4,1,10- $(\eta-C_5H_5)_3Co_3C_2B_3H_7$  (XIV) and was purified by preparative tlc on silica gel using 50% benzene in hexane (calcd mass of protonated species, 459.0260; found, 459.0255). All yields given are based on  $C_2B_3H_7$  consumed.

**Reaction of 1,2- $C_2B_{10}H_{12}$  with  $(\eta-C_5H_5)Co(CO)_2$ .** A mixture of 1.01 mmol of 1,2- $C_2B_{10}H_{12}$  and 2.13 mmol of  $(\eta-C_5H_5)Co(CO)_2$  was sealed into an evacuated 100-ml Pyrex bulb and heated at  $300^\circ$  for 1 hr. After cooling, the bulb was opened to the air and the  $CH_2Cl_2$  extract was evaporated onto a small amount of silica gel, placed on top of a silica gel column (100 ml of dry solid) prepared in hexane, and eluted with various benzene-hexane mixtures. The first fraction contained mainly  $C_2B_{10}H_{12}$ . The second yellow band (17 mg, 0.06 mmol) was crystallized by evaporation of a hexane solution and was shown to be the previously reported<sup>29</sup> 3,1,9- $(\eta-C_5H_5)CoC_2B_9H_{11}$  (compound 1c in ref 29) from its  $^1H$  nmr, ir, and mass spectra. The mass spectra of other fractions (yellow to brown) indicated their major components to be  $(\eta-C_5H_5)CoC_2B_9H_{11}$  isomers which were not identified, plus trace amounts of other products. There was no clear evidence for a  $(\eta-C_5H_5)CoC_2B_{10}H_{12}$  species. Approximately 0.5 mmol of 1,2- $C_2B_{10}H_{12}$  was recovered, and the total yield of metallocarborane was  $\sim 70$  mg (50% based on carborane consumed). In a similar reaction at  $250^\circ$  for 3 hr, only about 10% of the carborane reacted, yielding again primarily  $(\eta-C_5H_5)CoC_2B_9H_{11}$  isomers.



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## Synthesis and Reactions of Nucleophilic Complexes of Rhodium(I) Containing *o*-(Diphenylphosphino)-*N,N*-dimethylaniline<sup>1</sup>

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**Abstract:** The complexes  $[\text{Rh}(\text{PN})_2]\text{X}$  ( $\text{X} = \text{Cl}, \text{PF}_6, \text{SbF}_6, \text{BPh}_4, \text{ClO}_4$ ) where PN is *o*-(diphenylphosphino)-*N,N*-dimethylaniline are described. The trans addition of  $\text{Cl}_2$  and  $\text{CH}_3\text{I}$  gives  $[\text{RhCl}_2(\text{PN})_2]\text{X}$  and  $[\text{RhCH}_3\text{I}(\text{PN})_2]\text{X}$ . Oxygen and cyanogen add to give  $[\text{RhO}_2(\text{PN})_2]\text{X}$  and  $[\text{Rh}(\text{CN})_2(\text{PN})_2]\text{X}$  where the adduct groups occupy cis positions.  $[\text{Rh}(\text{PN})_2]\text{X}$  adds carbon monoxide to form  $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{X}$  where the dimethylamino arms of the chelate are displaced. Heating the dicarbonyl in boiling toluene favors the reverse reaction.  $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$  reacts with  $\text{CH}_3\text{I}$  to give  $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$  because of the likely presence of iodide in the reaction medium. The low conductivity of  $\text{RhCl}(\text{PN})_2$  is due to ion pairing. The complexes  $\text{RhClCO}(\text{PN})$ ,  $\text{RhCl}(\text{PF}_3)(\text{PN})$ , and  $\text{Rh}(\text{C}_6\text{H}_5\text{O}_2)(\text{PN})$  have been isolated.  $\text{RhClCO}(\text{PN})$  is converted into  $[\text{Rh}(\text{PN})_2(\text{CO})_2]\text{PF}_6$  by reaction with PN and  $\text{NH}_4\text{PF}_6$  under a CO atmosphere.  $\text{RhClCO}(\text{PN})$  adds allyl chloride to form  $\text{RhCl}_2(\sigma\text{-C}_3\text{H}_5)\text{CO}(\text{PN})$ .  $\text{RhClCO}(\text{PN})$  reacts with  $\text{CH}_3\text{I}$  in the presence of NaI to give  $\text{RhI}_2(\text{COCH}_3)\text{CO}(\text{PN})$ . Two separate isomers of the acetyl complex have been isolated. The number of nonequivalent *N*-methyl resonances for the coordinated dimethylamino group is used to identify the stereochemistry of many of the above complexes.  $\text{Ir}_2\text{Cl}_2(\text{cyclooctene})_4$  reacts with PN and  $\text{NH}_4\text{PF}_6$  to give  $[\text{IrHCl}(\text{PN})_2]\text{PF}_6$ .

Platinum metal complexes of substituted phosphines have become of considerable importance recently because of their use as homogeneous catalysts. The features which appear to be desirable are a low oxidation state, a high basicity or nucleophilicity, and an ability to undergo facile ligand dissociation to generate coordinately unsaturated intermediates. One of the most significant complexes of the group VIII metals which have been used in this work is chlorotris(triphenylphosphine)rhodium(I). The catalytic hydrogenation of olefins using this complex has been studied in considerable detail,<sup>2</sup> and it has been found that dissociation of a triphenylphosphine ligand is a necessary and fundamental step in the hydrogenation mechanism. This requirement of a low-valent complex to dissociate one or more ligands in order to be catalytically active has been found to be critically important in a number of cases. At the onset of work on the catalytic activity of these compounds there was no way to predict in advance that these coordinated  $\pi$ -acceptor ligands would show the necessary lability. Since this is an important aspect of the direct synthesis of compounds of likely catalytic activity, it appeared to us that it would be valuable to prepare nucleophilic complexes which would predictably displace ligands in the presence of incoming electrophiles or  $\pi$  acceptors. We believe that the results of this work represent one of the first successful attempts to synthesize compounds having such desirable features.

Our approach to this problem has been to prepare low-valent complexes of substituted amines. Since, however, an amino group will not stabilize a low-valent transition metal complex because of the failure of such a ligand to be involved in  $d-\pi$  back-bonding, it is necessary for  $\pi$ -acid ligands to be also present in order for the compounds to be isolable. The compound *o*-(diphenylphosphino)-*N,N*-dimethylaniline (Figure 1) can be conveniently used as a ligand for complexes of this type since the presence of the diphenylphosphino group will effectively stabilize low-valent transition metal complexes. The dimethylamino arm can then coordinate through the nitrogen to form a chelate complex, which can be verified in a convenient manner from the chemical shift of the dimethylamino group in the <sup>1</sup>H nmr spectrum. A further advantage of the use of an amine as ligand for a low-valent complex is that the coordination of a basic  $\sigma$ -donor ligand will confer a high nucleophilicity to the complex. This combination of features, lability to generate coordinately unsaturated complexes and nucleophilicity of the central metal atom, is the main requirement for an active homogeneous catalyst.<sup>3,4</sup> This paper reports the synthesis and chemistry of some rhodium complexes which have been specifically designed to be nucleophilic and to contain ligands which can be replaced by incoming  $\pi$ -acceptor ligands.

*o*-(Diphenylphosphino)-*N,N*-dimethylaniline, abbreviated PN, has been used as a chelating ligand in a number of group VIII complexes. These compounds

(1) See T. Rauchfuss and D. M. Roundhill, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., 1973, Abstract No. 153.

(2) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(3) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(4) G. N. Schrauzer, Ed., "Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971.