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Synthesis of New Metallacarborane Clusters from Coupled Carboranes

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A series of new cobaltacarborane clusters, derived from the coupled carboranes $(2,4\text{-}C_2B_5H_6)_2$ and $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$, have been prepared and structurally characterized. The thermal reaction of $(\eta\text{-}C_5H_5)Co(CO)_2$ with a mixture of $(2,4\text{-}C_2B_5H_6)_2$ isomers results in direct metal insertion and the formation of a number of multimetal complexes, including a set of six closely related compounds of the general formula $(\eta\text{-}C_5H_5)_2Co_2B_{10}H_{12}$. These compounds have been shown from their ^{11}B and ^1H NMR spectra to contain both metals in one cage and to consist of a $1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$– fragment bound to an unmetalated $C_2B_5H_6$– cage. Thus, the compounds differ only in the points of attachment of the two cages. In addition, these compounds have been found to undergo three different types of rearrangements, each of which occurs at a selected elevated temperature. The deprotonation of an isomeric mixture of the carborane $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$ by sodium hydride followed by the addition of sodium cyclopentadienide and anhydrous cobaltous chloride with an oxidative workup gives three sets of products, including several isomers with the general formulas $(CH_3)_2C_2B_4H_5\text{–}(CH_3)_2C_2B_3H_4Co(\eta\text{-}C_5H_5)$ and $(CH_3)_2C_2B_4H_5\text{–}(CH_3)_2C_2B_4H_3Co(\eta\text{-}C_5H_5)$ as well as the coupled metallacarborane $4,5'\text{-}[(CH_3)_2C_2B_4H_3Co(\eta\text{-}C_5H_5)]_2$.

Introduction

There have been few previous reports of complexes which contain a metal incorporated into a multicage carborane system. Examples include the synthesis of $(2,4\text{-}C_2B_5H_6)\text{–}((\eta\text{-}C_5H_5)CoC_2B_4H_5)$[1a] and $(2,4\text{-}C_2B_5H_6)\text{–}((\eta\text{-}C_5H_5)FeC_2B_4H_5)$[1b] by Grimes and the preparation of $(C_2B_8H_9)\text{–}((\eta\text{-}C_5H_5)_2Co_2C_2B_8H_9)$[2] by Hawthorne. Each of these complexes, however, was obtained in only low yields as a side product in a reductive polyhedral expansion reaction, and in each compound the two cages are linked by either a carbon–boron or a carbon–carbon bond. A second type of metal complex involving a linked carborane system can be prepared in good yields from the carbon–carbon-linked bis(carborane) $1,1'\text{-}(1,2\text{-}C_2B_{10}H_{11})_2$.[3] In these complexes which have the general formulas $M(C_2B_{10}H_{10}\text{–}C_2B_{10}H_{10})_2$[4] (M = Co, Ni, Cu), the transition metal is σ bonded to the available carbon sites on each cage and, to date, no complexes have been reported in which a metal has been incorporated into one or more of the cages of bis(carborane).

The limited number of multicage metallacarborane complexes can clearly be attributed to the lack of a convenient method for the synthesis of the parent linked carborane systems. Our recent discovery that the mercury-sensitized photolysis of either $2,4\text{-}C_2B_5H_7$ or $2,3\text{-}(CH_3)_2C_2B_4H_6$ results in the formation of the corresponding boron–boron-coupled carboranes is the first such high-yield synthesis.[5] The insertion of metals into these new coupled-cage systems offers a number of intriguing possibilities for the formation of multimetal, multicage molecules. As an illustration, we describe in this paper the synthesis and characterization of a variety of new cobaltacarborane complexes derived from the coupled carboranes $(2,4\text{-}C_2B_5H_6)_2$ and $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$.

Experimental Section

Materials. The coupled carboranes $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$ and $(2,4\text{-}C_2B_5H_6)_2$ were prepared by the mercury-sensitized photolysis of the parent carboranes.[5] Cyclopentadienylcobalt dicarbonyl $(\eta\text{-}C_5H_5)Co(CO)_2$ was obtained from Strem Chemical and vacuum distilled. Anhydrous $CoCl_2$ was obtained from $CoCl_2{\cdot}6H_2O$ by heating in vacuo at 180 °C. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich) and stored at −196 °C. Tetrahydrofuran (THF) solutions of sodium cyclopentadienide were prepared from the reaction of NaH (50% oil dispersion) and cyclopentadiene under vacuum with periodic venting of the resulting H_2. The THF was distilled from $LiAlH_4$. All other solvents were reagent grade. Preparative thin layer chromatography was conducted on 0.5-mm (20 × 20 cm) silica gel F-254 plates (Merck). Reversed-phase preparative thin layer chromatography was performed on 0.5-mm (20 × 20 cm) cellulose plates (Analtech) impregnated with Nujol.[6]

Instrumentation. Low- and high-resolution mass spectra (Table I) were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer. Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on a Jeol PS-100 Fourier transform spectrometer and are presented in Tables II and III respectively. ^1H NMR spectra at 220 MHz were obtained on a Varian HR-220 FT NMR spectrometer. Infrared spectra were recorded on a Hitachi Perkin-Elmer 521 spectrophotometer (Table IV). Ultraviolet spectra were obtained on a Cary 14 spectrophotometer and are presented in Table V. All melting points are uncorrected.

Table I. High-Resolution Mass Measurements

compd	ion	calcd mass	measd mass
I	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1356
II	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1294
III	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1336
IV	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1308
V	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1384
VI	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1301
VII	$^{12}C_{14}{}^{11}B_{10}{}^{1}H_{22}{}^{59}Co_2{}^+$	418.1316	418.1324
VIII	$^{12}C_{13}{}^{11}B_{7}{}^{1}H_{26}{}^{59}Co^+$	318.2018	318.2072
IX	$^{12}C_{13}{}^{11}B_{7}{}^{1}H_{26}{}^{59}Co^+$	318.2018	318.2022
X	$^{12}C_{13}{}^{11}B_{8}{}^{1}H_{25}{}^{59}Co^+$	328.2033	328.2102
XI	$^{12}C_{13}{}^{11}B_{8}{}^{1}H_{25}{}^{59}Co^+$	328.2033	328.2081
XII	$^{12}C_{18}{}^{11}B_{8}{}^{1}H_{28}{}^{59}Co_2{}^+$	450.1599	450.1535
XIII	$^{12}C_{14}{}^{11}B_{8}{}^{1}H_{24}{}^{59}Co_2{}^+$	398.1286	398.1303

Reaction of $(2,4\text{-}C_2B_5H_6)_2$ with $(\eta\text{-}C_5H_5)Co(CO)_2$. A 4.23-mmol sample of an isomer mixture of $(2,4\text{-}C_2B_5H_6)_2$ and 17 mmol of $(\eta\text{-}C_5H_5)Co(CO)_2$ were condensed into a 250-mL bulb equipped with a break-seal. The reaction bulb was sealed under vacuum and heated at 220 °C for 2 h. The bulb was then cooled to −196 °C and the noncondensables were removed in vacuo, after which time the bulb was warmed to room temperature and any volatile unreacted starting materials were removed. The flask was then opened to the air and the reaction mixture extracted with methylene chloride. The extract was filtered and chromatographed on silica gel TLC plates with carbon tetrachloride. Two main bands and several minor bands were isolated, all of which were shown to be complex isomer mixtures by ^1H NMR. Reversed-phase TLC was used to achieve final separation.[6] The first band (R_f 0.66, red-brown) was rechromatographed on reversed-phase plates in a 94:6 methanol–water eluent mixture and was separated into three compounds: I, $2\text{-}(1'\text{-}(2',4'\text{-}C_2B_5H_6))\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ (10 mg, mp 155–156 °C, R_f 0.58); II, $2\text{-}(3'\text{-}(2',4'\text{-}C_2B_5H_6))\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ (20 mg, mp 123–125 °C, R_f 0.49); III, $2\text{-}(5'\text{-}(2',4'\text{-}C_2B_5H_6))\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ (7 mg, mp 113.5–114.5 °C, R_f 0.44). The second band (R_f 0.58, red-brown) was found to consist of four compounds by reversed-phase TLC with a 96:4 methanol–water eluent mixture: the known $1,8,\text{-}5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$[1a] identified from its ^{11}B and ^1H NMR and mass spectra; IV, $3\text{-}(1'\text{-}(2',4'\text{-}C_2B_5H_6))\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ (6 mg, mp 136–137 °C, R_f 0.69); V, $3\text{-}(3'\text{-}(2',4'\text{-}C_2B_5H_6))\text{-}1,8,\text{-}5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ (12 mg, mp 132–134 °C, R_f 0.61); VI, $3\text{-}(5'\text{-}(2',4'\text{-}C_2B_5H_6))\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ (4 mg, R_f 0.57). The third band from the silica gel plates (green, R_f 0.38) broke up into several compounds when chromatographed on reversed-phase plates with a 86:14 methanol–water eluent mixture; only one compound

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Table II. 32.1-MHz ^{11}B NMR Data

compd[a]	δ[b] (*J*, Hz)[c]	rel area
I	+114.2 (156.0), +4.9, −11.5, −21.5 (178.3)	1:5:3:1
II	+114.5 (133.7), +4.3, −11.8, −21.5 (178.3)	1:5:2:2
III	+116.0 (160.0), +4.5,[d] −11.1, −21.5 (173.8)	1:5:2:2
IV	+115.6 (156.0), +4.9, −10.5, −20.5 (182.7)	1:5:3:1
V	+115.2 (144.8), +4.7,[d] −10.5, −20.8 (178.3)	1:5:2:2
VI	+115.2 (144.8), +7.6, +4.6, −10.4, −20.9 (178.3)	1:3[f]:2[f]:2:2
VII	+79.8, +4.9, −3.5, −10.4, −20.8 (173.8)	1:3:2[f]:2:2
VIII	+2.1, −5.7, −44.5 (177.8)	4:2:1
IX	+2.4, −1.7, −5.9, −45.0 (177.8)	2[f]:3[f]:1[f]:1
X	+10.4,[d] +5.6, −2.4, −45.8 (178.3)	3[f]:2[f]:2:1
XI	+14.2, +9.7, +4.5, −4.2, −42.6 (177.8)	1[f]:1[f]:3[f]:2:1
XII	+7.3[e]	
XIII	+23.5 (155.5), +5.7 (137.7), +0.5 (173.3), −4.2 (111.1), −6.6 (123.3), −10.4 (144.4), −16.3 (177.8)	1:1:2:1:1:1:1

[a] All complexes were run in CCl_4 with internal C_6D_6 lock except XIII (pure $CDCl_3$). [b] Chemical shifts are relative to external $BF_3 \cdot O(C_2H_5)_2 = 0$. Positive sign indicates a downfield shift. [c] All chemical shifts are measured from the proton-decoupled spectra; because of the heavy overlapping of peaks coupling constants are given only when a doublet is clearly defined. [d] Peak contains a shoulder on downfield side. [e] Contains a slight shoulder on upfield side; very broad resonance, $W_{1/2} = 380$ Hz. [f] Estimated from overlapping peaks.

Table III. Proton NMR Data

compd[a]	C_5H_5[b]	cage C–H[b] (assignt)	B–H (assignt)[c]	rel area
$2,4\text{-}C_2B_5H_7$[d]		5.89 (2, 4)	4.93 (3), 4.05 (5, 6), 0.03 (1, 7)	2:1:2:2
$1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$[d]	4.82	3.91 (5, 6)	13.11 (4), 4.21 (3, 9), 0.11 (2, 7)	5:2:1:2:2
I	4.67 4.65	5.18 (2′, 4′)[e] 3.73 (5 or 6) 3.37 (5 or 6)	12.53 (4), 4.10 (3 or 9) 3.95 (3 or 9; 5′, 6′) −0.03 (7), −0.17 (7′)	5:5:2:1:1:1:1:3:1:1
II	4.75 4.73	5.10 (2′, 4′)[f] 3.96 (5 or 6) 3.91 (5 or 6)	13.14 (4), 4.28 (3, 9) 3.96 (5′, 6′), −0.03 (7) −0.28 (1′, 7′)	5:5:2:4:1:2:1:2
III	4.64	5.39 (2′ or 4′), 5.01 (2′ or 4′), 3.86 (5,6)	13.06 (4), 4.25 (3, 9) 3.86 (6′), −0.08 (7), −0.23 (1′, 7′)	10:1:1:3:1:2:1:2
IV	4.62 4.61	5.68 (2′, 4′)[e] 3.51 (5, 6)	12.97 (4), 5.10 (3′), 4.24 (5′, 6′) 3.79 (9), 0.28 (7′), −0.11 (2 or 7), −0.32 (2 or 7)	5:5:2:2:1:1:2:1:1:1:1
V	4.72 4.65	5.67 (2′, 4′)[f] 4.22 (5 or 6) 4.01 (5 or 6)	13.21 (4), 4.32 (9) 4.22 (5′, 6′), 0.17 (2, 7 or 1′, 7′) 0.06 (1′, 7′ or 2, 7)	5:5:2:3:1:1:1:2:2
VI	4.71 4.68	5.60 (2′, 4′)[f] 4.11 (5 or 6) 3.84 (5 or 6)	13.04 (4), 5.01 (3′) 4.11 (9, 6′), 0.19 (2, 7 or 1′, 7′)	5:5:2:3:1:1:1:4
VII	4.50 4.43	8.12 (6) 5.50 (2′, 4′) 2.47 (5)		5:5:1:2:1

compd[a]	C_5H_5[b]	methyl[b]	bridge protons[c]	rel area
VIII	4.75	2.19, 2.03 1.80, 1.77	−0.57, −6.14, −6.42	5:3:3:3:3:2:1:1
IX	4.67	1.96, 1.80	−0.48, −0.68, −5.63, −6.36	5:6:6:1:1:1:1
X	4.55	2.28, 2.24, 2.08, 2.07	−1.51	5:3:3:3:3:2
XI	4.77	2.36, 2.28, 2.26, 2.14	−0.47	5:3:3:3:3:2
XII	4.76, 4.59	2.48, 2.23, 2.14, 2.04		5:5:3:3:3:3
XIII	5.45, 5.30	2.40, 2.35		5:5:3:3

[a] All samples run in CCl_4 solvent with C_6D_6 lock, except XIII (pure $CDCl_3$). Negative sign indicates an upfield shift in ppm from internal Me_4Si (=0). [b] All cyclopentadienyl, methyl, and cage C–H resonances were observed at 220 MHz. [c] Terminal and bridging B–H resonances were observed at 100 MHz with ^{11}B decoupling. [d] Reference 22. [e] Unresolved multiplet due to proton–proton coupling. [f] Doublet due to proton–proton coupling.

was isolated in sufficient yield to characterize, complex VII (2 mg, R_f 0.60), as described in the Results section. Several less mobile bands were also separated on silica gel plates and shown to be complex mixtures of three-cobalt (R_f 0.35) and four-cobalt (R_f 0.32, 0.14 and 0.09) systems. Due to the small amounts present complete characterization was not possible; however, some indications of the gross structures could be ascertained from the spectroscopic data and are discussed in the Results section.

Thermal Rearrangements. At 220 °C. A 12-mg sample of compound II was sealed in an evacuated glass tube and heated at 220 °C for 2 h. Analysis of the sample by TLC and ^1H NMR showed it to consist of a mixture of compound II and compound V. Reheating for 20 h, gave the same result. The relative amounts of compounds II and V were calculated by carefully integrating the H–(C) resonances at 5.67 and 5.10 ppm of the ^1H NMR of the mixture; this gave a ratio of *II*:V as 2.18:1. The same experiment, except starting with compound V, was performed and gave similar results. A ratio of II:V was calculated to be 2.27:1.

A similar experiment was performed with the green adjacent cobalt isomer, compound VII. After a very small sample (1 mg) was heated at 220 °C for 2 h, the sample was found to consist of complex VII and another new green compound as shown by TLC. Due to the very small amounts of these two compounds the relative ratio of these complexes could not be accurately measured.

At 330–350 °C. A 10-mg sample of compound II was sealed in an evacuated glass tube and heated at 330–350 °C for 2 h. Separation by TLC in CCl_4 gave four bands, two red-brown bands which were identified as compounds II and V and two new green bands (R_f 0.40 and 0.32). Owing to the small amounts, complete characterization of these two green bands was not possible; however, partial analyses could be accomplished on the basis of ^{11}B NMR and ^1H NMR spectra. For example, the ^{11}B NMR spectra of both green compounds are very similar to the spectrum of green complex VII. That is, both spectra contain a doublet of intensity 1 near +80.0 ppm, characteristic of the adjacent cobalt compound $1,7,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ (+80.3 ppm).[1c] A doublet of intensity 2 near −20.0 ppm is also present in both spectra

Table IV. Infrared Spectra (cm^{-1})

I[a]	3025 w, 2922 w, 2860 w, 2600 vs, 2540 vs, 2485 vs, 1815 w, 1740 w, 1412 m, 1090 m, 1058 s, 1022 w, 992 sh, 920 w, 878 w, 840 m, br, 675 w, 642 w, 620 w, 604 w
II[a]	3025 w, 2920 w, 2860 w, 2600 vs, 2535 vs, 2480 vs, 1814 w, 1740 w, 1410 m, 1285 sh, 1260 m, 1092 s, 1060 s, 1044 s, 1000 m, 932 w, 900 w, 837 m, br, 674 w, 620 w, 605 w
III[a]	3090 w, 3025 w, 2915 w, 2845 w, 2595 vs, 2525 vs, 2478 vs, 1810 w, 1735 w, 1408 m, 1153 m, 1090 s, 1058 s, 1038 s, 990 m, 955 sh, 925 w, 835 m, br, 665 w, 630 w, 600 w
IV[a]	3090 w, 3030 w, 2920 w, 2850 w, 2600 vs, 2525 sh, 2480 vs, 1812 w, 1735 w, 1410 m, 1190 w, 1058 s, 1020 w, 992 sh, 915 w, 835 m, br, 670 w
V[a]	3080 w, 3032 w, 2930 w, 2605 vs, 2530 sh, 2485 vs, 1812 w, 1740 w, 1410 m, 1288 m, 1128 m, 1065 s, 1042 s, 1000 w, 938 w, 900 w, 835 m, br, 672 w, 648 w
VI[a]	3100 w, 2920 w, 2850 w, 2605 vs, 2520 sh, 2480 vs, 1810 w, 1735 w, 1410 m, 1168 m, 1065 s, 1040 s, 985 sh, 835 m, br
VIII[b]	2920 s, 2850 m, 2565 sh, 2540 vs, 2490 sh, 1860 w, 1744 m, 1566 w, 1512 w, 1460 sh, 1446 m, 1438 sh, 1420 w, 1370 w, 1010 m, 910 w, 892 m, 826 s, 768 w, 745 w, 720 w, 670 w, 642 w
IX[b]	2950 sh, 2920 m, 2855 m, 2550 vs, 2530 sh, 1860 w, 1618 w, 1540 m, 1437 m, 1411 m, 1362 m, 1250 m, 1085 m, 1004 s, 975 sh, 905 w, 878 m, 844 w, 822 s, 795 m, 765 w, 738 w, 718 w, 660 w, 622 w
XI[b]	3100 w, 2940 m, 2915 m, 2860 w, 2535 vs, 2500 sh, 1960 w, 1502 m, 1433 m, 1405 m, 1358 m, 1247 w, 1090 w, 1030 sh, 992 s, 956 m, 882 m, 853 m, 818 s, 800 sh, 748 m, 725 w, 702 w, 665 w, 640 w, 620 m
XII[b]	3050 w, 2916 w, 2855 w, 2515 vs, 1430 w, 1409 m, 1365 w, 1098 m, 995 m, 856 w, 820 s, 786 w, 768 s, 738 m, 698 s, 620 w, 570 w

[a] Solution (CCl_4 vs. CCl_4); NaCl cells. [b] KBr disk.

Table V. Electronic Spectra (Acetonitrile Solutions)

compd	λ_{max}, nm (log ϵ)
I	535 sh (2.51), 442 (3.20), 360 (3.45), 309 sh (4.1), 2.84 (4.23), 237 (4.20)
II	535 sh (2.53), 445 (3.14), 360 (3.32), 306 sh (4.09), 282 (4.19) 2.38 (4.17)
III	530 sh (2.49), 442 (3.12), 355 (3.43), 306 sh (4.07), 2.82 (4.18), 238 (4.15)
IV	535 sh (2.36), 445 (2.96), 350 sh (3.40), 303 (4.01), 279 (4.07), 2.43 (4.08)
V	535 sh (2.62), 445 (3.18), 348 sh (3.62), 303 (4.27), 277 (4.31), 242 (4.31)
VI	535 sh (2.53), 442 (3.08), 350 sh (3.42), 303 (4.20), 281 (4.20), 2.40 (4.22)
VIII	385 sh (3.17), 346 (3.40), 270 (3.77), 239 (3.86)
IX	400 sh (3.23), 345 (3.68), 266 (4.05), 238 (4.17)
XI	445 sh (2.72), 366 (3.39), 293 sh (3.75), 260 (3.99)
XII	528 sh (2.23), 411 (3.20), 270 (4.46), 219 (4.26)

and can be assigned to the two equivalent apex BH units on a 2,4-$C_2B_5H_6$ cage; this rules out bonding from an apex boron. A good ^1H NMR of the lower green band was obtained and consisted of two cyclopentadienyl resonances at 4.75 and 4.69 ppm, a C–H resonance of intensity 2 at 5.58, assignable to the equivalent C–H units of a symmetrically substituted 2,4-$C_2B_5H_6$ cage, and two other C–H resonances, each of intensity 1 at 8.98 and 3.13 ppm. These latter two resonances are characteristic of 1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$. From this data, and from the fact that these two green compounds were derived from compound II, a compound in which the $C_2B_5H_6$ cage is bound to the metallacarborane cage by the 3′ position, we feel that both green compounds consist of a 2′,4′-$C_2B_5H_6$ cage bonded at the 3′ position to a 1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2B_5H_6$ cage. There are two possible positions of bonding to the metallacarborane cage, the 2- or the 3-position; the apex 4-position is ruled out by the presence of the downfield doublet near +80.0 ppm in the ^{11}B NMR spectra. Thus these two green compounds must be 2-(3′-(2′,4′-$C_2B_5H_6$))-1,7,-5,6-$(\eta\text{-}C_5H_5)Co_2C_2B_5H_6$ and 3-(3′-(2′,4′-$C_2B_5H_6$))-1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ and are the adjacent cobalt analogues of the two red isomers which were in equilibrium at 220 °C. In a separate experiment, the same four compounds were also produced when one of the green compounds was heated at 330–350 °C for 2 h. Heating complex VII at 330–350 °C also gave similar results.

At 390–400 °C. A 6-mg sample of compound II was sealed in an evacuated glass tube and heated at 390–400 °C. After 2 h the tube was cooled to room temperature and opened to the air, and the reaction mixture was extracted with methylene chloride. Some decomposition had occurred leaving nonsoluble solid material in the reaction tube. Separation of the extract by TLC on silica gel plates in CCl_4 again yielded two red-brown bands and two green bands. However, further analysis by reversed-phase TLC revealed that each band actually consisted of a mixture of three compounds, giving a total of 12 compounds produced from the initial complex II. The two red-brown bands were found to consist of compounds I, II, III and IV, V, VI, respectively, by comparison of R_f values with those of the known compounds. Each of the two green bands was shown by reversed-phase TLC (methanol–water, 86:14) to also consist of three compounds, giving a total of six green bands. Two of these compounds were identified as 2-(3′-(2′,4′-$C_2B_5H_6$))-1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ and 3-(3′-2′,4′-$C_2B_5H_6$))-1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$, which were previously found to be in equilibrium at 340 °C. Because the remaining four green compounds were not previously characterized, the identity of these compounds could not be definitely established. However, ^{11}B and ^1H NMR spectra of these compounds indicate that they are the other four possible (discounting bonding at the apex position of the metallacarborane cage) boron–boron bonded isomers of 2′,4′-$C_2B_5H_6$-1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$.

Metallacarboranes from $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$. Approximately 25 mL of dry THF was condensed into a removable trap which contained 700 mg (3.4 mmol) of $[(CH_3)_2C_2B_4H_5]_2$. This solution was transferred via Schlenk techniques under nitrogen to a 100-mL flask containing 6.8 mmol of NaH, cooled to −196 °C and evacuated. The solution was then warmed to room temperature and stirred with periodic venting of the resulting H_2. Stirring was continued until hydrogen evolution had subsided. This solution was then combined with a THF solution containing 20 mmol of sodium cyclopentadienide, filtered, and added dropwise to a stirred suspension of anhydrous $CoCl_2$ (20 mmol) in 50 mL of THF. An immediate reaction occurred and the deep blue solution turned dark brown-green. Stirring was continued overnight, after which time the solvent was removed under reduced pressure and 100 mL of water was added. Air was bubbled through this suspension with stirring for 2 h. The suspension was then filtered and the residue extracted with methylene chloride followed by acetone. Preparative TLC of the extract on silica gel plates with carbon tetrachloride gave a number of products. The first band (yellow, R_f 0.73) was rechromatographed with hexane; repeated development gave two compounds, VIII (2 mg, mp 126–127 °C) and IX (3 mg, mp 119.5–120 °C). The second band (orange, R_f 0.42) was separated into two compounds when chromatographed on reversed-phase plates (methanol–water 92:8). Only the lower band was present in a sufficient amount to characterize, X (1 mg). The third band was the major product XI (orange, 12 mg, mp 134.5–135.5 °C, R_f 0.35). The fourth band (R_f 0.27) was identified as known 2,3-$(CH_3)_2$-1,2,3-$(\eta\text{-}C_5H_5)CoC_2B_4H_4$[7a] from its ^{11}B and ^1H NMR and mass spectra. The fifth band (orange, R_f 0.19) was further purified by rechromatographing with a 60:40 hexane–benzene eluent mixture: XII (2 mg, mp 213–216 °C). The origin was rechromatographed in benzene; this gave a dark green compound, XIII (1 mg, R_f 0.50), which was identified as the C,C-substituted dimethyl derivative of the known $(\eta\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$[8] on the basis of its spectroscopic data given in the tables.

Results and Discussion

Cobaltacarboranes from $(2,4\text{-}C_2B_5H_6)_2$. Two general methods have been previously employed to form transition-metal complexes of the small *closo*-carboranes. The first method involves polyhedral expansion by direct metal insertion with the aid of an appropriate organometallic reagent. For example, direct metal insertions have been observed in the reactions of $(\eta\text{-}C_5H_5)Co(CO)_2$ or $Fe(CO)_5$ with 1,5-$C_2B_3H_5$,[1c] 1,6-$C_2B_4H_6$,[1c] or 2,4-$C_2B_5H_7$[1b,c] and in the reaction of Pt(styrene)$(PEt_3)_2$ with 2,4-$C_2B_5H_7$.[1d] The second method of metal insertion requires the initial reduction of the carborane cage with sodium napthalide, followed by the addition of a suitable metal halide. This second method often leads to some cage fragmentation; for example, the reduction of 2,4-$C_2B_5H_7$ followed by addition of NaC_5H_5 and anhydrous $CoCl_2$ gives 1,2,4-(η-C_5H_5)$CoC_2B_4H_6$,[1a] a four-boron cluster, as the main product. We, therefore, chose a modification of the direct insertion method for the incorporation of metals into the coupled carborane (2,4-$C_2B_5H_6$)$_2$. It was hoped that this would allow the basic five-boron cages to remain intact and thus give a more tractable set of products. In addition, it was also not known what effect the addition of sodium napthalide would have on the boron–boron σ bond.[9]

The mercury-sensitized photolysis of 2,4-$C_2B_5H_7$ at 2537 Å has been shown to yield six boron–boron-bonded isomers of the coupled carborane (2,4-$C_2B_5H_6$)$_2$.[5] Because of the tedious and time consuming procedures required to separate these isomers, prior separation before reaction was not practical. Furthermore, it was felt (and later shown to be true) that under the reaction conditions employed for metal insertions, extensive isomerization would occur to reestablish an isomeric mixture; therefore, all reactions described in this paper start with the unseparated mixture of isomers. The thermal reaction of (η-C_5H_5)Co(CO)$_2$ with (2,4-$C_2B_5H_6$)$_2$ at 220 °C for 2 h results in the production of six closely related red-brown metallacarboranes as primary products. The mass spectra of these six compounds are identical, each containing a sharp cutoff at *m/e* 418 with strong fragments ions at *m/e* 189 (($^{59}Co^{12}C_{10}{}^{1}H_{10}$)$^+$) and 124 (($^{59}Co^{12}C_5{}^{1}H_5$)$^+$). Exact mass measurements of the parent ions (Table I) for each compound are in agreement with an empirical formula of (η-C_5H_5)$_2Co_2$-($C_2B_5H_6$)$_2$.

Two types of structures can be suggested for compounds I–VI: (1) a coupled system containing one metal in each cage or (2) a two-cage compound consisting of a dicobalt metallacarborane cage bound to an unmetalated $C_2B_5H_6$ unit. The spectroscopic data, discussed below, clearly establish that they are of the second type.

The 32.1-MHz ^{11}B NMR spectra of all six compounds are very similar (Table II). Although each spectrum is heavily overlapped, valuable information can be obtained from the chemical shifts of both the clearly defined resonances and the overlapped resonances. A doublet of intensity 1 at ~+115 ppm and a doublet of intensity 1 or 2 at ~−21 ppm are present in all six spectra. The first resonance is highly characteristic of the 1,8,5,6-(η-C_5H_5)$_2Co_2B_5H_7$ cage system,[1a] while the second is characteristic of the parent carborane, 2,4-$C_2B_5H_7$.[10] A reasonable assumption as to the gross structure of these compounds can then be made on the basis of this information; that is, each compound is composed of an unmetalated 2,4-$C_2B_5H_6$ cage linked to a 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ unit. The heavily overlapped regions of the ^{11}B NMR spectra, ~+8 to −12 ppm, are also consistent with this assumption. Substitution at either the 2(7) or 3(9) boron positions on the 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ fragment renders all borons inequivalent (as well as the –CH and –C_5H_5 units), and it would therefore be expected, based on the known chemical shifts for 2,4-$C_2B_5H_7$ and 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$, that at least four doublets and two singlets would occur in this region. In addition, any alternative structures based on two coupled (η-C_5H_5)$CoC_2B_5H_6$ units may be ruled out due to the absence of a resonance in the ^{11}B NMR spectrum near +56 ppm, which is characteristic of the 3,1,7-(C_5H_5)$CoC_2B_5H_7$ system.[1a]

Careful examination of the ^{11}B-decoupled, 100-MHz ^1H NMR spectra (Figures 1 and 2, Table III) allows unambiguous structural assignments of the six isomers. The following general comments apply to the spectra of all six compounds.

The presence of –CH resonances of total intensity 2 in the region 5–6 ppm, which is indicative of the –CH resonance of 2,4-$C_2B_5H_7$, and the presence of –CH resonances of total intensity 2 in the region 4.0–3.3 ppm, which is characteristic of the –CH resonance of 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$, rules out the possibility of either carbon–carbon- or carbon–boron-bonded cages. Common to all six ^1H NMR spectra is also a peak of intensity 1 at ~+13.0 ppm. This peak is assignable to the 4-H–(B) position of the 1,8,5,6-(η-C_5H_5)$_2Co_2B_5H_6$ cage and, therefore, eliminates that position as a possible site of attachment. Consistent with this interpretation is the presence in the ^{11}B spectra of the low-field doublet of intensity 1 at ~115 ppm which is assigned to the 4-boron position. If substitution had occurred at this position, a singlet would have been observed. By the process of elimination, the only sites of substitution remaining are the 1′(7′), 3′, and 5′(6′) borons of the 2′,4′-$C_2B_5H_6$ cage and the 2(7) and 3(9) borons of the 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ unit. If all combinations are allowed, then six isomers should exist, which is in agreement with the experimental evidence.

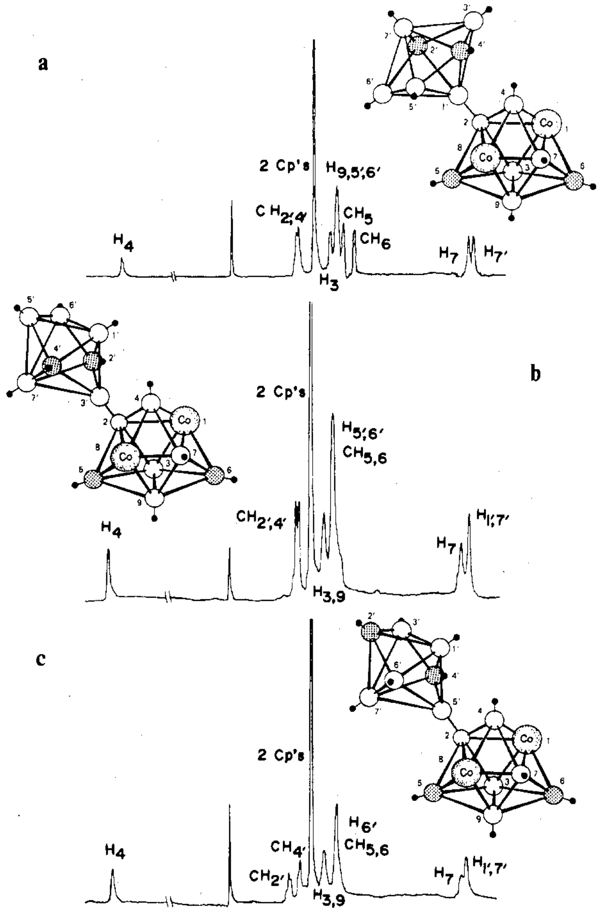


Figure 1. ^{11}B-decoupled 100-MHz ^1H NMR of compounds: a, 2-(1′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ (I); b, 2-(3′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ (II); c, 2-(5′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ (III). The cyclopentadienyl resonances are expanded off scale. The unassigned peak to the right of the break marks is due to residual C_6H_6.[21]

In agreement with the NMR data, the infrared spectra (Table IV) of compounds I–VI each contain three strong bands in the B–H stretching region near 2600, 2530, and 2480 cm^{-1}. The first band is indicative of 2,4-$C_2B_5H_7$ (2600 cm^{-1})[10] while the latter two bands are characteristic of 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$ (2545 and 2495 cm^{-1}).[1a]

The following comments concern the detailed structural assignment of each isomer.

2-(1′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_6$ (I). The ^{11}B NMR spectrum clearly established that the 2′,4′-$C_2B_5H_6$ cage is substituted at the 1′ position. The high-field doublet at −21.5 ppm is only of intensity 1 and is assigned to 7′ boron,

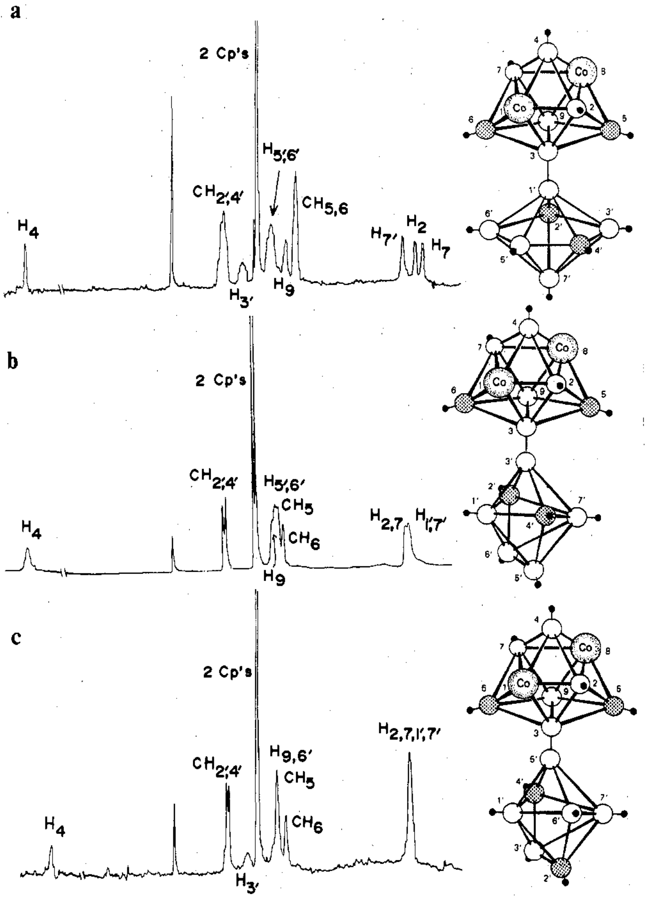


Figure 2. ^{11}B-decoupled 100-MHz ^{1}H NMR of compounds: a, 3-(1′-2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (IV); b, 3-(3′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (V); c, 3-(5′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (VI). The cyclopentadienyl resonances are expanded off scale. The unassigned peak to the right of the break marks is due to residual C_6H_6.[21]

while the singlet expected from the substituted 1′ boron is shifted downfield and overlaps with the 2(7) boron resonances of the metallacarborane cage, thus producing a broad peak of intensity 3 at −11.5 ppm. Apex-substituted derivatives of 2,4-$C_2B_5H_7$ frequently show such a downfield shift of the 1 boron.[10,11] The two upfield peaks, each of intensity 1, in the ^{1}H NMR spectrum (Figure 1a) are assigned to the protons attached to the 7- and 7′-boron positions and establish the 2-boron position as the point of substitution of the metallacarborane cage. As mentioned previously, substitution at the 2(7) or 3(9) position destroys the C_2 symmetry axis present in 1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_7$ and renders the metallacarborane fragment completely asymmetrical. Thus, the presence of two cyclopentadienyl resonances each of intensity 5 and two metallacarborane H–C resonances each of intensity 1 are consistent with the proposed structure. Free rotation about the boron–boron bond would maintain the symmetry of the $C_2B_5H_6$ cage, and, therefore, only one carborane H–C resonance of intensity 2 is observed.

2-(3′-(2′,4′-$C_2B_5H_6$)-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (II). The ^{11}B NMR spectrum shows an upfield doublet of intensity 2 at −21.5 ppm due to the equivalent 1′(7′) borons and indicates that substitution on the $C_2B_5H_6$ unit must occur at either the 3′ or 5′(6′) borons. The presence of only one carborane H–C resonance of intensity 2 in the ^{1}H NMR spectrum (Figure 1b) is consistent with substitution at the 3′ boron. This observation is by itself, however, not conclusive evidence for 3′ substitution, since it is known that many 5-substituted 2,4-$C_2B_5H_7$ derivatives do not give rise to two separate H–C resonances,[10,11a,c] but the isolation, discussed below, of 2-(5′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (III) which does show two distinct H–C carborane resonances does establish the 3′ boron as the point of attachment for compound II. Also observed in the ^{1}H NMR spectrum are two upfield peaks at −0.03 and −0.28 ppm in the ratio of 1:2 which can be assigned to the 7 and 1′(7′) H–B proton resonances, respectively. This firmly established the 2-position as the point of attachment to the metallacarborane cage. As expected, two cyclopentadienyl resonances are observed, and the metallacarborane H–C resonance which appears as a broad singlet in the 100-MHz ^{1}H NMR spectrum also resolves into the expected separate resonances at 3.91 and 3.96 ppm when recorded at 220 MHz.

2-(5′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (III). As in compound II, the ^{11}B NMR spectrum shows an upfield doublet of intensity 2 at −21.5 ppm due to the equivalent 1′(7′) borons and indicates that the substitution of the $C_2B_5H_6$ unit must occur at either the 3′ or 5′(6′) borons. The presence in the ^{1}H NMR spectrum (Figure 1c) of two carborane H–C resonances each of intensity 1 establishes substitution at the 5′ position, since this is the only position which renders the –CH groups of the $C_2B_5H_6$ cage nonequivalent. That substitution of the metallacarborane cage occurs at the 2 boron is again established by the observance of the 7 and 1′(7′) H–B proton resonances (−0.08 and −0.22 ppm, respectively) in a 1:2 ratio. Surprisingly, only one cyclopentadienyl resonance and only one H–C metallacarborane resonance, of intensity ratio 10:2, respectively, are observed.

3-(1′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (IV). The ^{11}B NMR spectrum of this compound is similar to that of compound I in that the upfield doublet at −20.5 ppm is of intensity 1 while the peak at −10.5 ppm is of intensity 3. As previously discussed for compound I, this indicates that the $C_2B_5H_6$ cage is substituted at the 1′ boron. Three upfield resonances each of intensity 1 are observed in the ^{1}H NMR spectrum (Figure 2a) and can be assigned to the inequivalent protons attached to the 2 and 7 borons on the metallacarborane cage and to the proton attached to the 7′ boron on the $C_2B_5H_6$ cage. Since both protons attached to 2 and 7 positions are now observed, then substitution on the metallacarborane cage must occur at the 3 boron. Consistent with this interpretation is the observance of a resonance of intensity 1 at 3.79 ppm which is assigned to the proton attached to the 9 boron. Also observed in the ^{1}H NMR spectrum are the expected two cyclopentadienyl resonances each of intensity 5 and a peak of intensity 2 at 5.67 ppm arising from the equivalent carborane H–C protons. The metallacarborane H–C resonance appears as a singlet at 3.51 ppm and could not be resolved into the two expected peaks.

3-(3′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (V). The doublet of intensity 2 at −20.8 ppm in the ^{11}B NMR spectrum again established that the substitution on the $C_2B_5H_6$ cage must occur at either the 3′ or 5′(6′) borons. The absence of a peak near 5.0 ppm in the ^{1}H NMR spectrum (Figure 2b), which can be assigned to the proton attached to the 3′ boron, indicates that this is the site of substitution of the $C_2B_5H_6$ cage. This peak is clearly visible in the spectra of compounds IV and VI. In addition, the presence of two peaks each of intensity 2 at 0.17 and 0.06 ppm confirms that substitution does not occur either at the 1′(7′)-position of the $C_2B_5H_6$ cage or at the 2(7)-position of the metallacarborane. Thus the 3-position of the metallacarborane cage is the assigned site of substitution. A shoulder at 4.32 ppm is assigned to the proton attached to the 9-position. The existence of two cyclopentadienyl resonances, one carborane H–C resonance of intensity 2, and two metallacarborane H–C resonances each of intensity 1 are also in agreement with the proposed structure.

3-(5′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ (VI). As discussed above, the doublet of intensity 2 at −20.9 ppm in the

^{11}B NMR spectrum established that substitution on the $C_2B_5H_6$ cage cannot occur at the 1′(7′) boron. Substitution at the 5′-position is indicated by the presence in the ^{1}H NMR (Figure 2c) of resonances at 5.01 and 0.19 ppm assigned to the protons attached to 3′ and 1′(7′) borons, respectively. Instead of two separate resonances, only one carborane H–C resonance of intensity 2 is observed; however, this is not unusual since, as previously mentioned, many other 5-substituted 2,4-$C_2B_5H_7$ derivatives do not show separate H–C resonances. The peak at 0.19 ppm of intensity 4 which consists of overlapped signals from the 1′(7′) and 2(7) protons again confirms that the metallacarborane cage is substituted at the 3 boron. The remaining peaks in the ^{1}H NMR spectrum can be assigned as given in Figure 2 and are consistent with the proposed structure.

In addition to the above six compounds, another adjacent cobalt isomer was obtained in smaller yields. Compound VII (green) was found to have a mass spectrum which was nearly identical with those of the red-brown complexes I–VI. In contrast to those compounds, however, the ^{11}B NMR spectrum (Table II) of VII contains a doublet of intensity 1 at +79.8 ppm and no resonance at +115 ppm. This new doublet is characteristic of the previously known cobaltacarborane cage 1,7,5,6-(η-C_5H_5)$_2$Co$C_2B_5H_7$[1c] (+80.3 ppm) which is also green. The remaining ^{11}B NMR spectrum is heavily overlapped, except for a doublet of intensity 1 at −20.8 ppm, which suggests a 1-substituted $C_2B_5H_6$ cage. The proton NMR consists of one carborane H–C resonance of intensity 2 at 5.50 ppm, two cyclopentadienyl resonances at 4.50 and 4.43 ppm, and two metallacarborane H–C resonances each of intensity 1 at 8.12 and 2.47 ppm. These latter two H–C resonances are also highly suggestive of a 1,7,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_7$ (8.63 and 2.86 ppm) cage system. Because of the small amount of compound which was isolated, a strong ^{11}B spin-decoupled ^{1}H NMR which could be interpreted with any confidence was not obtained. Thus a complete structural assignment was not possible; however, complex VII must be either 2-(1′-(2′,4′-$C_2B_5H_6$))-1,7,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_6$ or 3-(1′-(2′,4′-$C_2B_5H_6$))-1,7,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_6$.

Trace Products. Several minor products were also obtained from this reaction which were shown to contain isomeric mixtures of three- and four-cobalt clusters. While the quantities obtained were insufficient to permit separation and complete characterization, the spectroscopic data does provide some structural details. For example, the mass spectrum of the fourth band (R_f 0.35) contained a cutoff at m/e 542 which is consistent with a three-cobalt system. Although the proton NMR showed it to be a mixture of compounds, the ^{11}B NMR spectrum suggested the gross structure. The presence of a doublet at +49.8 ppm of intensity 1 and a doublet of intensity 2 at +20.8 ppm is indicative of the known 2,3,8,1,6-(η-C_5H_5)$_3$Co$_3B_5H_7$[1c] (+50.0 and +20.3 ppm) while a peak of intensity 2 at −21.1 ppm is characteristic of the apex borons of 2,4-$C_2B_5H_7$. This evidence strongly indicates that this material consists of the various boron–boron-bonded isomers of 2′,4′-$C_2B_5H_6$-2,3,8,1,6-(η-C_5H_5)$_3$Co$_3C_2B_5H_6$.

The three lower bands (red-brown, R_f 0.32, brown, R_f 0.14, and green, R_f 0.09) were each found to be complex isomer mixtures by ^{1}H NMR, but once again the gross structures are indicated by mass spectroscopy and ^{11}B NMR. The mass spectra of all three bands were nearly identical, with each containing a cutoff at m/e 666, corresponding to the formula (η-C_5H_5)$_4$Co$_4$($C_2B_5H_6$)$_2$. The ^{11}B NMR of the red-brown band contained a doublet at +115.0 ppm and was very similar to the spectra for compounds I–VI, except for the absence of the upfield doublet characteristic of 2,4-$C_2B_5H_7$. The only structure consistent with this information is two linked 1,8,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_6$ cages. The ^{11}B NMR of the brown band was unusual in that it contained two downfield peaks at +114.0 and +80.3 ppm, characteristic of red 1,8,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_7$ and green 1,7,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_7$, respectively. Thus the probable structure is the red-green coupled compound. The green band contained a doublet at +78.9 ppm which as discussed above is characteristic of green 1,7,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_7$. This together with the absence of a doublet near −20.0 ppm suggests that this material is composed of two coupled 1,7,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_6$ cages.

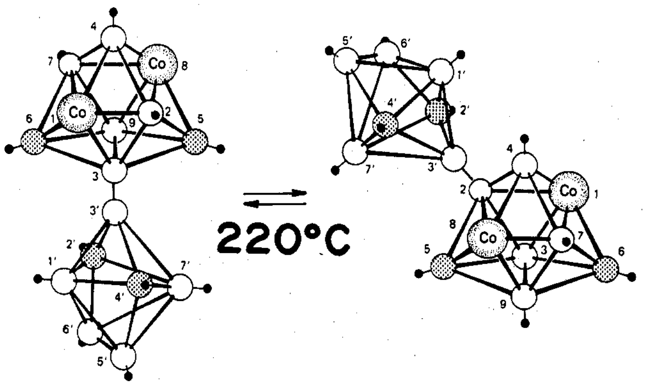
Several general features of this reaction are apparent. First, the major products of the reaction contain two cobalts with only small amounts of three- and four-cobalt compounds and with no monocobalt complexes being formed. These results differ from the previous studies of the reaction of 2,4-$C_2B_5H_7$ and (η-C_5H_5)Co(CO)$_2$ (hot/cold reactor) which gave both mono- and dicobalt species as primary products.[1c] The absence of monocobalt compounds in the present reaction can be attributed to the severe conditions employed for metal insertion, and it may be possible to produce an even wider range of complexes by varying these conditions and the ratio of reactants.

A second and perhaps the most interesting feature of the reaction was that almost all products contained metals in only one cage. Apparently, the incorporation of one metal into the cage framework renders that cage more susceptible to further metal insertion, relative to the unmetalated cage. These findings are consistent with an observation previously made by Grimes[12] that the presence of one or more cobalt centers in a single cage system promotes further addition of cobalt to that cage. Only in the case of the tetracobalt complexes were compounds found which contained metals in both cages; however, these were obtained in only trace amounts.

Thirdly, it is also noted that in no case was the $C_2B_5H_6$ cage found bounded to the apex 4-boron position of the cobaltacarborane cage. This can be attributed to steric hinderance, since in order for bonding to occur at this position the 2,4-$C_2B_5H_6$ cage would have to be directly stiuated between the two cyclopentadienyl rings associated with the cobalt atoms. This is clearly an unfavorable situation, and hence attack of the (η-C_5H_5)Co units upon the coupled carborane must occur in such a way as to avoid this arrangement.

Thermal Rearrangements. In the course of our investigations of the thermal stabilities of compounds I–VII we discovered that these compounds undergo three different types of rearrangements at selected elevated temperatures which provide considerable insight into the relative ease of various dynamic processes in polyhedral borane cages.

At 220 °C each compound undergoes a single rearrangement which established equilibrium mixtures of pairs of specific isomers. In particular, we found that if compound II, 2-(3′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_6$, was heated in an evacuated tube at 220 °C for 2 h, the resulting material contained a mixture of both II and 3-(3′-(2′,4′-$C_2B_5H_6$))-1,8,5,6-(η-C_5H_5)$_2$Co$_2C_2B_5H_6$, V (both red). That is, a reversible migration of the 2′,4′-$C_2B_5H_6$ cage from the 2- to the 3-position on the cobaltacarborane cage had occurred (see Figure 3). The equilibrium constant for this reaction was measured as ~2.2, thus indicating that the 2-position is favored. This is the first example of a measurable equilibrium existing between sites of substitution of a boron-substituted metallacarborane. The mechanism of this rearrangement is not easily explainable in terms of previously proposed mechanisms. An intermolecular-exchange mechanism can be ruled out by the absence of any compounds such as ($C_2B_5H_6$)$_2$ or (η-C_5H_5)$_4$Co$_4$($C_2B_5H_6$)$_2$, which would be expected to be formed if a cleavage of the boron–boron bond followed by recombination was occurring. An intramolecular mechanism which has been favored by several groups to explain rear-



V II

Figure 3. Isomeric mixture of metallacarboranes resulting from reversible rearrangements observed at 220 °C.[21]

rangements in other carboranes and metallacarboranes involves rotations of triangular faces of a polyhedron.[13] Indeed, this type of mechanism can account for the observed isomerization of the carborane cage between the 2- and 3-positions of the metallacarborane. For example, a 120° rotation of triangle Co(1)–B(2)–B(3) (Figure 3) coupled with an opposite direction 120° rotation of triangle Co(8)–B(7)–B(9) does accomplish this rearrangement. We, however, do not feel that this is the correct mechanism for the following reason. A rotation of just one of the triangular faces results in a movement of the cobalt atoms to adjacent positions 1 and 7. Since Miller and Grimes[13a] have shown that the adjacent cobalt isomer of the parent compound $(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ is slightly more stable at 220 °C than the nonadjacent cobalt isomer, a second triangular rotation which separates the cobalt atoms should not be a favored process. Thus, if the carborane cage migration were proceeding by this rotation mechanism, it would be expected, at the very least, to observe a mixture of both adjacent cobalt and nonadjacent cobalt isomers; however, only nonadjacent cobalt compounds are observed at 220 °C. In a separate experiment, complex VII, a green adjacent cobalt isomer, was also heated to 220 °C. Again, the only rearrangement observed was the migration of the carborane cage with no evidence for rearrangement of the metallacarborane cage to give nonadjacent cobalt isomers. Thus, this evidence and the results from the rearrangement studies at higher temperatures, which are discussed below, indicate that the reversible migration of the carborane cage observed at 220 °C does not involve a skeletal rearrangement of the metallacarborane cage but must instead occur by some sort of direct shift of the carborane cage between the two metallacarborane boron positions. Such a shift might occur by means of a three-center transition state in which the carborane cage boron adopts a bridging position and enters into three-center bonding with the 2 and 3 metallacarborane borons. This would allow the carborane cage to migrate between the two adjacent borons on the metallacarborane cage without requiring a rearrangement of the metallacarborane cage. This type of bonding arrangement has previously been demonstrated in another coupled-cage compound, $B_{20}H_{18}{}^{2-}$, where the two B_{10} cages were shown to be linked via two three-center B–B–B bonds.[14] Furthermore, Hawthorne has proposed that the isomerization of the boron–boron-bonded isomers of $B_{20}H_{18}{}^{4-}$ in acid solution may also occur through a transition state containing similar three-center bonding.[15]

A second rearrangement process, in addition to the one previously observed at 220 °C, was found when compound II was heated at 340 °C. At this temperature reversible migration of the cobalt atoms between adjacent and nonadjacent positions in the metallacarborane cage occurred to generate an equilibrium mixture of four compounds: the two red isomers, II and V, plus the corresponding green isomers 2-(3′-(2′,4′-$C_2B_5H_6$))-1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ and 3-(3′-(2′,4′-$C_2B_5H_6$))-1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$. Analogous results were obtained when other individual isomers were heated at this temperature. This reversible cobalt migration is similar to the one previously observed for the parent compounds 1,8,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ and 1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ at 340 °C[18a] and can be adequately explained by the rotation of triangles mechanism which was eliminated for the 220 °C rearrangement. This provides futher evidence that skeletal metallacarborane cage rearrangement is unimportant at 220 °C.

Finally, it was observed that when individual samples of the complexes I–VI were heated at an even hotter temperature, 400 °C, a third reversible rearrangement occurred to produce a mixture of 12 compounds (six red, six green). This new rearrangement involves the migration of the metallacarborane fragment to the other boron positions of the carborane cage. This was not unexpected, since it has already been demonstrated that the individual isomers of the parent coupled carborane, $(2,4\text{-}C_2B_4H_6)_2$, will rearrange at 400 °C to establish equilibrium mixtures of all six coupled compounds.[5] In addition, Onak has reported that at 300 °C the various boron-substituted methyl derivatives of 2,4-$C_2B_5H_7$ will also rearrange to form an equilibrium mixture of the three possible boron-substituted isomers.[16] Onak has proposed that the rearrangement of the methyl compounds does not involve a dissociative methyl migration from boron to boron but instead accompanies its attached boron as the cage undergoes skeletal shifts. This could also explain the rearrangements observed in the coupled-cage complexes, but, given the observations described above concerning the isomerization reaction at 220 °C, a direct shift mechanism must still be considered a possibility.

Therefore, in summary, it is found that at 400 °C three different reversible rearrangements are taking place concurrently: (1) a carborane cage migration between the 2- and 3-positions of the metallacarborane cage, (2) a skeletal rearrangement in the metallacarborane cage to produce adjacent and nonadjacent cobalt isomers, and (3) a metallacarborane migration between the boron positions of the $C_2B_5H_6$ cage. These rearrangements would then be expected to produce the equilibrium mixture of 12 compounds (six red, six green) at 400 °C, which is observed experimentally.

Cobaltacarboranes from $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$. The mercury-sensitized photolysis of *nido*-2,3-$(CH_3)_2C_2B_4H_6$ yields a thermally unstable oil which is thought to be mainly a mixture of the four boron–boron-bonded coupled carboranes: 4,4′-$[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$, 5,5′-$[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$, 4,5′-$[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$, and 4,6′-$[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$.[5] The studies described above of the insertion of metals into the *closo*-carboranes $(2,4\text{-}C_2B_5H_6)_2$ resulted in the formation of complexes containing metals in only one cage as the primary products. For this reason the coupled carboranes derived from *nido*-2,3-$(CH_3)_2C_2B_4H_6$ are of particular interest, since they each contain two coupled open (nido) cages and might be expected to readily form complexes in which metals would be incorporated into both cages.

The reaction method chosen was identical with that developed by Grimes for the synthesis of the monocobalt clusters 1,2,3-$(\eta\text{-}C_5H_5)CoC_2B_4H_6$ and 1,2,3-$(\eta\text{-}C_5H_5)CoC_2B_3H_7$ and the novel dicobalt triply decked compound 1,7,2,3-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ from *nido*-2,3-$C_2B_4H_8$.[7a,b] Thus it appeared that the use of the coupled *nido*-carboranes might lead to more than simple metal insertion and, in fact, might lead to the formation of a coupled, triply decked compound.

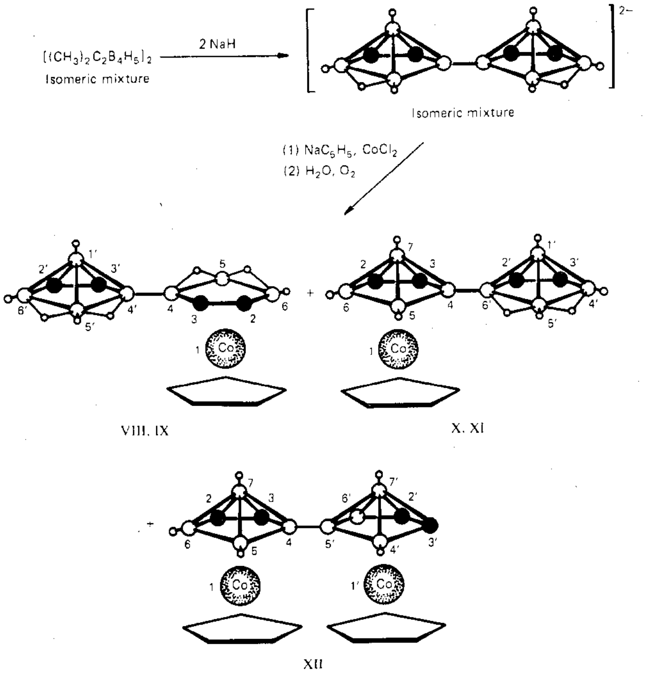


Figure 4. Reaction scheme for the synthesis of sandwich complexes derived from an isomeric mixture of the coupled carborane [2,3-$(CH_3)_2C_2B_4H_5]_2$. Only one possible structure is indicated for each of the isomer pairs VIII, IX and X, XI. The specific structures could not be determined. The open circles are boron atoms, the large solid circles are C–CH_3 groups, and the small open circles are hydrogen atoms.

Deprotonation of the coupled carborane [2,3-$(CH_3)_2C_2B_4H_5]_2$ with 2 equiv of sodium hydride in tetrahydrofuran, to presumably form the dianionic species [2,3-$(CH_3)_2C_2B_4H_4^-]_2$,[17] followed by the addition of sodium cyclopentadienide and anhydrous cobaltous chloride gives a variety of metal-containing products upon oxidative workup (see Figure 4). Separation of the products by preparative thin layer chromatography gives three distinct sets of compounds, each of which consists of several isomers, as described below.

Complexes VIII and IX. From the first set of compounds, two complexes were isolated which gave identical mass spectra, each consisting of a sharp cutoff at *m/e* 318 with an intense fragment at *m/e* 124 due to $(^{59}Co^{12}C_5{}^1H_5)^+$. A monocobalt compound in which a (η-C_5H_5)Co$(CH_3)_2C_2B_3H_4$ cage is bonded to a $(CH_3)_2C_2B_4H_5$ cage would be consistent with these spectra. The boron-11 NMR spectrum of each compound contains an upfield doublet of intensity 1 near −45.0 ppm. This resonance is characteristic of an apical boron position in 2,3-$(CH_3)_2C_2B_4H_6$ (−47.7 ppm)[18] and may therefore be assigned to the apex 1′-boron position in the unmetalated 2′,3′-$(CH_3)_2C_2B_4H_5$ cage (see Figure 4). The presence of this upfield doublet also eliminates the 1′-boron position as a site of substition in complexes VIII and IX. The remainder of the spectra are heavily overlapped from +3 to −6 ppm, and complete interpretation is difficult if not impossible; however, the occurrence of these resonances in this region is not unexpected and is consistent with the formulation of a 2′,3′-$(CH_3)_2C_2B_4H_5$ unit linked to a 2,3-$(CH_3)_2$-1,2,3-(η-C_5H_5)Co$C_2B_3H_4$ cage since the ^{11}B resonances of 1,2,3-(η-C_5H_5)Co$C_2B_3H_7$[6a] (the dimethyl derivative has not been characterized) and the basal resonances in 2,3-$(CH_3)_2C_2B_4H_6$[18] occur at −1.8 and −3.7 ppm and at −7.2 ppm, respectively.

The 220-MHz ^1H NMR spectrum of VIII consists of a cyclopentadienyl resonance of intensity 5 at 4.75 ppm and four resonances at 2.19, 2.03, 1.80, and 1.77 ppm each of intensity 3 which may be assigned to four nonequivalent methyl groups. In addition, the boron-11 spin-decoupled 100-MHz ^1H NMR reveals two upfield peaks, each of intensity 1, at −6.14 and −6.42 ppm which are assigned to the bridge hydrogens on the cobaltacarborane unit. This is in agreement with the previous observation of the bridge hydrogen resonance of 1,2,3-(η-C_5H_5)Co$C_2B_3H_7$ at −6.0 ppm.[7a] The bridge hydrogens on the carborane cage are overlapped and occur at −0.57 ppm (2,3-$(CH_3)_2C_2B_4H_6$, H_μ peak at −2.4 ppm).[19] These spectra indicate a completely asymmetric molecule, but several linkages are possible: 4–4′, 4–5′, 4–6′, and 5–4′. Because of the very small structural differences and the very complex ^{11}B NMR spectrum, one structure cannot be favored over another.

The 220-MHz ^1H NMR spectrum of IX consists of a cyclopentadienyl resonance of intensity 5 and only two methyl resonances at 1.96 and 1.80 ppm, each of intensity 6. The boron-11 spin-decoupled 100-MHz ^1H NMR spectrum shows two upfield peaks each of intensity 1 at −5.63 and −6.36 ppm which may be assigned to nonequivalent bridge hydrogens on the 2,3-$(CH_3)_2$-1,2,3-(η-C_5H_5)Co$C_2B_3H_4$ unit. That these were, in fact, two different resonances and not a doublet caused by some sort of proton–proton coupling was verified by observing these resonances at both 100 and 220 MHz. The two bridge hydrogens on the carborane cage were observed at −0.48 and −0.68 ppm. Thus, the data concerning the bridge-hydrogen resonances again indicate an asymmetrical structure; however, if this is true, then a coincidental overlapping of the methyl resonances to give only the two peaks observed, instead of the four peaks expected, must be occurring. Although this is unusual, it is not unreasonable considering the very subtle differences in each methyl environment. In fact, complexes XIII, X, and XI also showed equivalent methyl groups at 100 MHz, and only at higher field strengths (220 MHz) were the nonequivalent methyl resonances resolved.

As was the case for compound VIII, the boron-11 NMR spectrum of IX is so heavily overlapped that little information regarding linkage sites could be obtained. All that can be confidently stated is that both XIII and IX are both composed of a 2,3-$(CH_3)_2C_2B_4H_5$ cage bound to a 2,3-$(CH_3)_2$-1,2,3-(η-C_5H_5)Co$C_2B_3H_4$ cage through a boron–boron bond to give an asymmetric molecule. Four isomers are possible: 4–4′, 4–5′, 4–6′, and 5–4′.

Although a coupled, triply decked compound was not isolated, the formation of complexes VIII and IX which have an apex boron removed from the metallacarborane fragment suggests that with the proper choice of reaction conditions such a compound may be produced.

Complexes X and XI. Three compounds having identical mass spectra were found in the second set of compounds. Each complex had a sharp cutoff at *m/e* 328 with an intense fragment at *m/e* 124 due to the $(^{59}Co^{12}C_5{}^1H_5)^+$ group. A complex in which a (η-C_5H_5)Co$(CH_3)_2C_2B_4H_3$ cage is bonded to a *nido*-2,3-$(CH_3)_2C_2B_4H_5$ cage would be consistent with this mass spectrum. Only two compounds, X and XI, were characterized, the third compound being present in insufficient amounts to allow complete characterization.

The ^{11}B NMR spectra of X and XI are very similar, each consisting of an upfield doublet of intensity 1 at ∼−44.0 ppm and a heavily overlapped region between +14 and −5 ppm. The 220-MHz ^1H NMR spectrum of each compound shows one cyclopentadienyl resonance and four separate methyl resonances. The bridge hydrogens of X appear as one peak at −1.51 ppm while the bridge hydrogens of XI appear at −0.47 ppm. These spectra are consistent with a 2,3-$(CH_3)_2C_2B_4H_5$ cage bonded to a 2,3-$(CH_3)_2$-1,2,3-(η-C_5H_5)Co$C_2B_4H_3$ cage in such a manner as to make the resultant molecule asymmetric. Bonding to the apical 1′-boron position in the 2′,3′-$(CH_3)_2C_2B_4H_5$ cage can be ruled out, since the resonance at ∼−44.0 ppm in the ^{11}B NMR spectra is a doublet for both X and XI. Although substitution at the apical 7-boron position of the cobaltacarborane cage cannot be completely ruled out, it seems unlikely in view of the fact that substitution is not favored at the carborane apical position. Thus, only four structures are possible which will render all the methyl groups nonequivalent: 4–4′, 4–5′, 4–6′, and 5–4′. Again, because of the complexity of the ^{11}B NMR spectra exact structural assignments cannot be made for X and XI.

Complex XII. The final set of products all had mass spectra showing a cutoff at m/e 450 and containing intense peaks at m/e 189 $[(^{59}\mathrm{Co}_2(^{12}\mathrm{C}_5{}^1\mathrm{H}_5)_2)^+]$ and m/e 124 $[(^{59}\mathrm{Co}(^{12}\mathrm{C}_5{}^1\mathrm{H}_5))^+]$. The peak at m/e 189 is indicative of a multimetal system. Only one compound, XII, from this set could be isolated and characterized; however, at least two other isomers were present but could not be isolated in pure form.

The ^{11}B NMR spectrum of XII consists of a broad peak centered at +7.3 ppm with a shoulder on the upfield side. Notably absent from the spectrum is the upfield doublet near −45 ppm which was assigned, in the complexes discussed above, to the apical boron in an unmetalated 2,3-$(\mathrm{CH}_3)_2\mathrm{C}_2\mathrm{B}_4\mathrm{H}_5$ unit. This indicates that cobalts must be inserted into both cages. Indeed, the observance of only one broad resonance in the ^{11}B NMR spectrum is consistent with this interpretation, since the apical boron resonance in 2,3-$(\mathrm{CH}_3)_2$-1,2,3-$(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{CoC}_2\mathrm{B}_4\mathrm{H}_4$ is shifted downfield and overlaps with the basal boron resonances.[3a]

The 220-MHz ^{1}H NMR spectrum consists of two separate cyclopentadienyl resonances and four separate methyl resonances, again indicating an asymmetrical structure. If it is assumed that substitution at the apical boron positions does not occur, then only one structure is possible which will have nonequivalent cyclopentadienyl rings and four nonequivalent methyls: 4,5′-[2,3-$(\mathrm{CH}_3)_2$-1,2,3-$(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{CoB}_4\mathrm{H}_3]_2$. This compound is the first reported example of a coupled metallacarborane.

Metallacarboranes have often been suggested as being analogues of metallocenes, and in this sense XII can be considered a carborane equivalent of a fulvalene–metal complex such as dicobaltacene. While there are certain obvious structural similarities there are also distinct differences, such as, the enhanced oxidative and hydrolytic stability of the metallacarborane system. Likewise, the monometal complexes VIII–XI also show considerable air and water stability, which is perhaps surprising since each of these compounds has an unmetalated *nido*-carborane cage, $(\mathrm{CH}_3)_2\mathrm{C}_2\mathrm{B}_4\mathrm{H}_5$, attached to the metallacarborane fragment.

Transition-metal–fulvalene complexes have received considerable interest in recent years due to the possibility that these complexes may exhibit unusual mixed-valence properties.[20] The use of coupled-cage carboranes may allow the synthesis of a wide range of complexes, such as XII, which are not only structurally related to metal–fulvalene complexes but might also exhibit similar electronic properties.

In summary, the studies described above indicate the potential for the formation of a number of new and unusual multicage, multimetal cage systems when linked-cage carboranes are employed as reagents. Further work is now in progress on both the development of improved synthetic techniques for the formation of these complexes and in the extension of these studies to new systems.

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Registry No. I, 70480-08-9; II, 67228-54-0; III, 67228-53-9; IV, 67228-58-4; V, 67228-57-3; VI, 67228-56-2; XII, 70480-09-0; XIII, 50803-47-9; 2-(3′-(2′,4′-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6$))-1,7,5,6-$(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{Co}_2\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6$, 70519-08-3; 3-(3′-(2′,4′-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6$))-1,7,5,6-$(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{Co}_2\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6$, 70480-10-3; 1,1′-[2,4-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6]_2$, 70480-11-4; 1,3′-[2,4-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6]_2$, 70480-12-5; 1,6′-[2,4-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6]_2$, 70494-91-6; 3,3′-[2,4-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6]_2$, 59419-84-0; 3,5′-[2,4-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6]_2$, 70513-48-3; 5,5′-[2,4-$\mathrm{C}_2\mathrm{B}_5\mathrm{H}_6]_2$, 70480-13-6; 4,4′-[2,3-$(\mathrm{CH}_3)_2\mathrm{C}_2\mathrm{B}_4\mathrm{H}_5]_2$, 70519-05-0; 5,5′-[2,3-$(\mathrm{CH}_3)_2\mathrm{C}_2\mathrm{B}_4\mathrm{H}_5]_2$, 70519-07-2; 4,5′-[2,3-$(\mathrm{CH}_3)_2\mathrm{C}_2\mathrm{B}_4\mathrm{H}_5]_2$, 70519-06-1; 4,6′-[2,3-$(\mathrm{CH}_3)_2\mathrm{C}_2\mathrm{B}_4\mathrm{H}_5]_2$, 70519-05-0; $(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{Co(CO)}_2$, 12078-25-0.

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