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Metal Atom Synthesis of Metallaboron Clusters. 1. Direct Synthesis of Cobaltaborane and Cobaltacarborane Complexes

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The application of the metal atom technique to the synthesis of metallaboron clusters was investigated. In particular, the reactions of cobalt atoms were examined with three different boron hydrides, pentaborane(9), hexaborane(10), and decaborane(14), in the presence of a variety of reactants. Reactions of cobalt vapor and cyclopentadiene with pentaborane(9) gave a number of new and structurally novel metallaborane clusters including $1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_5H_5$, $8\text{-}\sigma\text{-}(C_5H_9)\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_5H_4$ and $(\mu_3\text{-}CO)\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ as well as a series of previously reported polyhedral borane metal clusters. Analogous reactions with hexaborane(10) resulted in the isolation of the three previously reported cobaltaboranes $1,2\text{-}(\eta\text{-}C_5H_5)_2Co_2B_4H_6$, $2\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$, and $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$. Similarly, reactions with decaborane(14) gave $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$ along with the new isomer $6\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$. The metal atom technique has also been shown to allow the direct conversion of boron hydrides and alkynes into metallacarborane clusters. For example, the new metallacarborane $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$, along with the previously reported metallacarboranes $2,3\text{-}(CH_3)_2\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_4$ and $2,3\text{-}(CH_3)_2\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3$, was isolated in the reaction of cobalt atoms with cyclopentadiene, 2-butyne, and pentaborane(9). Similarly, the metallacarboranes $1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$, $6,7\text{-}(CH_3)_2\text{-}2,5,6,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$, and $6,7\text{-}(CH_3)_2\text{-}2,4,6,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ were all isolated in an analogous reaction employing hexaborane(10). In a separate experiment it was found that the latter compound could be thermally converted to the new isomer $4,9\text{-}(CH_3)_2\text{-}2,7,4,9\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$. The reaction of cobalt atoms with pentaborane(9) and diphenylacetylene gave a variety of metallacarboranes including $2,3\text{-}(C_6H_5)_2\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_5$ and $2,3\text{-}(C_6H_5)_2\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_3$, along with a unique four-carbon metallacarborane cluster, $4,5,7,8\text{-}(C_6H_5)_4\text{-}1,4,5,7,8\text{-}(\eta\text{-}C_5H_5)CoC_4B_3H_3$. Finally, it was found that in contrast to the results obtained with the smaller boron hyrides the reaction of cobalt atoms and cyclopentadiene with decarborane(14) and 2-butyne or diphenylacetylene did not result in the formation of metallacarborane products.

Introduction

Since its initial development by Timms and Skell, the metal atom technique[2a–c] has been widely employed in organometallic chemistry to generate new compounds which were unattainable by using more conventional techniques. Until recently, however, there has been little application to the synthesis of metal cluster compounds and, in particular, to the synthesis of metallaboron clusters. We have previously reported our preliminary results demonstrating the first such application of the metal atom reactions to the synthesis of metallaborane clusters,[3a] as well as the use of these techniques to effect the direct conversion of boron hydrides and alkynes into metallacarborane clusters.[3b] We have now extended these studies to include the reactions of cobalt atoms with three different boron hydrides: pentaborane(9), hexaborane(10), and decaborane(14). Full details of this work are reported here.

Experimental Section

Materials. Cobalt metal (99.9%, 50 mesh) was obtained from Alfa-Ventron Corp. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). Pentaborane(9) was obtained from laboratory stock, while Shore's method[4] was used to prepare hexaborane(10) from 1-bromopentaborane(9).[5] Decaborane(14) was obtained from Callery Chemical Co. and sublimed before use. All other reagents were commercially obtained, as indicated, and used as received.

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[6] was performed on 0.5-mm (20 × 20 cm) cellulose plates (Analtech) impregnated with Nujol. Column chromatography was carried out on silica gel (Merck, 70–270 mesh).

Physical Measurements. Boron-11 and proton Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were obtained on a JEOL PS-100 spectrometer equipped with the appropriate decoupling accessories. Boron-11 NMR spectra, at 115.5 MHz, were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ with a negative sign indicating an upfield shift and are presented in Table I. All proton chemical shifts (Table II) were measured relative to internal residual benzene from the lock solvent (99.9% C_6D_6) and then referenced to Me_4Si. Except as indicated high- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer which is interfaced to a Kratos DS50S data system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on either a Perkin-Elmer 521 or a Perkin-Elmer 337 spectrophotometer. All melting points are uncorrected.

General Procedure. The metal atom apparatus employed in these studies was based on a design published by Klabunde.[7] The reaction vessel is constructed from a 3-L reaction flask and a four-necked top (Knotes, K-162000 and K-6132000). Two of these necks are fitted with water-cooled copper electrodes which are equipped to hold an integral tungsten alumina evaporation crucible (Sylvania Emissive Products, CS-1008). The third neck contains an inlet tube which extends to within 3 in. of the crucible and allows substrate vapor to enter the reaction flask. The fourth neck is connected to a standard high-vacuum line. Power to the electrodes is supplied by two transformers connected in series with a range of 0–10 V and up to 100 A.

In a typical reaction, approximately 0.6 g of cobalt is placed in the evaporation crucible, and cobalt vapor is generated by electrical heating (7.2 V, 60 A). This vapor is then cocondensed over a 1–2-h period with the substrate vapor on the walls of the reactor which are maintained at −196 °C. A large excess of the desired substrates, typically 10 mL of each ligand, is used. In those reactions involving low volatile substrates, a large excess of the ligand (approximately

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(1) Alfred P. Sloan Foundation Fellow.

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Table I. ^{11}B NMR Data

compd[a]	δ[b] (J, Hz)	rel areas
1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_5H_5$ (I)	+136.8 (147)	1
	+124.4 (141)	1
	+104.0 (154)	2
	−12.8 (134)	1
8-σ-C_5H_9-1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_5H_4$ (II)	+137.4 (138)	1
	+123.4 (137)	1
	+101.2 (132)	2
	+3.3[c]	1
$(\mu_3\text{-}CO)$-1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ (III)	+89.9 (163)	
6-$(\eta\text{-}C_5H_5)CoB_9H_{13}$ (IV)	+21.1 (125)	2
	+17.6 (136)	2
	+7.2 (176)	1
	−2.0 (153)	2
	−16.0 (144)	1
	−26.3 (147)	1
2,5-$(CH_3)_2$-1,7,2,5-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ (V)	+73.2 (156)	1
	+55.4 (164)	1
	+1.0 (133)	1
	−1.9 (129)	1
	−13.4 (164)	1
2,3-$(C_6H_5)_2$-1,7,2,3-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3$ (VI)	+56.1 (132)	1
	+9.4 (136)	2
2,3-$(C_6H_5)_2$-1,2,3-$(\eta\text{-}C_5H_5)CoC_2B_3H_5$ (VII)	+3.7 (132)[d]	
4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta\text{-}C_5H_5)CoC_4B_3H_3$ (VIII)	+15.1 (189)	1
	−10.2 (171)	2
1,2-$(CH_3)_2$-3,1,2-$(\eta\text{-}C_5H_5)CoC_2B_5H_5$ (IV)	+64.9 (173)	1
	+17.2 (176)	1
	+4.9 (169)	1
	−6.9 (156)	2
6,7-$(CH_3)_2$-2,5,6,7-$(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$[e] (X)	+42.5 (140)	1
	+32.1 (147)	1
	+13.3 (161)	1
	+12.2 (140)	1
	+9.7 (152)	1
	−27.1 (145)	1
6,7-$(CH_3)_2$-2,4,6,7-$(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ (XI)	+58.1 (196)[f]	1
	−5.5 (180)[d]	3
	−11.5 (160)	2
4,9-$(CH_3)_2$-2,7,4,9-$(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ (XII)	+32.3 (151)	1
	+6.2 (151)	1
	−16.5 (156)	1

[a] All complexes were run in CH_2Cl_2 with internal C_6D_6 lock material. [b] Chemical shifts referenced to boron trifluoride etherate, with positive values indicating a shift to lower fields (less shielding) in conformity with the new sign convention adopted at the Third International Meeting on Boron Chemistry. [c] Singlet. [d] Overlapping resonance. [e] ^{11}B NMR spectrum at 115.5 MHz. [f] Poorly resolved resonance.

3 g) is placed in the bottom of the reaction vessel before assembly. After metal deposition is complete, the matrix is allowed to warm gradually to room temperature, followed by removal of the volatiles in vacuo. The reactor is then vented with an inert gas, and the residue remaining in the vessel is extracted and filtered. The extract is then separated and purified by normal techniques discussed below. Typically only approximately 50% of the metal contained in the crucible is vaporized. Thus, the yields reported are calculated on the basis of only the metal vaporized and assume only 50% of the vapor reaches the reaction zone.

Reaction of Cobalt Vapor with B_5H_9 and C_5H_6. Cobalt vapor (~0.3 g) was cocondensed with 20 mL of pentaborane(9) and 20 mL of cyclopentadiene at −196 °C. After metal deposition was complete, the reactor was allowed to gradually warm to room temperature and stand for ~30 min. All volatile materials were then removed in vacuo, and the reactor, after an initial filling with nitrogen, was opened to air. The brown residue remaining in the reactor was extracted with tetrahydrofuran (THF), filtered through a course frit, and evaporated to dryness. This solid was then extracted with methylene chloride to give a solution which was filtered through a silica gel column. The material eluting from this column was found to be an extremely complex mixture of metallaborane complexes, most of which were present in only trace amounts. Separation by thin-layer chromatography on silica gel using a 40% benzene in carbon tetrachloride elution gave the following new compounds: I, 1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_5H_5$ [R_f = 0.70; green; 15 mg (4.1%); mp >300 °C. Anal. Calcd: C, 41.79; H, 4.68. Found: C, 41.65; H, 4.73. Mass measurement: calcd for $^{12}C_{15}{}^{1}H_{20}{}^{11}B_5{}^{59}Co_3$, 432.0027; found, 432.0014], II, 8-σ-C_5H_9-1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_5H_4$ [R_f = 0.86; yellow-green; 10 mg (2.4%); mp >300 °C; m/e 500], and III, $(\mu_3\text{-}CO)$-1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ [R_f = 0.27; orange; 10 mg (2.7%); mp 293 °C dec. Mass measurement: calcd for (M + 1) $^{12}C_{16}{}^{1}H_{18}{}^{16}O_1{}^{11}B_3{}^{59}Co_3$, 436.9712; found, 436.9732].[8] Several previously reported[9] clusters were also isolated: 1,2-$(\eta\text{-}C_5H_5)_2Co_2B_4H_6$ (7.5 mg (1.8%)), 3-σ-C_5H_9-1,2-$(\eta\text{-}C_5H_5)_2Co_2B_4H_5$ (5.0 mg (1.1%)), 4-σ-C_5H_9-1,2-$(\eta\text{-}C_5H_5)_2Co_2B_4H_5$ (4.0 mg (0.85%)), 1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_5$ (5.0 mg (1.45%)), 1,2,4,7-$(\eta\text{-}C_5H_5)_4Co_4B_4H_4$ (7.5 mg (0.25%)), and 1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_4H_4$ (2.5 mg (0.7%)). Each of these compounds was identified by comparison of their mass spectra and ^{11}B NMR data with known values.

In a separate experiment, the above reaction was repeated in the same manner with the exception that methylene chloride was used for extraction of the residue in the reactor. In this case, the products were essentially identical with those obtained earlier with the exception that no $(\mu_3\text{-}CO)$-1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ (III) was found.

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and CO. Cobalt vapor (~0.3 g) was cocondensed with 20 mL of pentaborane(9) and 20 mL of cyclopentadiene at −196 °C. After metal deposition was complete, the reactor was allowed to gradually warm to room temperature in the presence of carbon monoxide gas (340 mm). Workup of the products, in a similar manner to that described above, gave an improved yield of III, $(\mu_3\text{-}CO)$-1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ (23.8 mg (6.4%)).

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(8) Mass spectrum obtained at the University of Virginia under chemical ionization conditions.

(9) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); (b) V. R. Miller and R. N. Grimes, *ibid.*, **98**, 1600 (1976); (c) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).

Table II. 100-MHz ^{1}H NMR Data

compd[a]	δ[b] (rel area)	assignt
1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_5$ (I)	4.61 (5)	C_5H_5
	4.54 (10)	C_5H_5
8-σ-C_5H_9-1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_4$ (II)	4.66 (5)	C_5H_5
	4.55 (10)	C_5H_5
	1.21 (9)[c]	C_5H_9
(μ_3-CO)-1,2,3-(η-C_5H_5)$_3$$Co_3B_3H_3$ (III)	4.63 (15)	C_5H_5
	9.07 (3)	B-H
6-(η-C_5H_5)CoB_9H_{13} (IV)	5.60 (5)	C_5H_5
	−3.25 (2)	B-H-B
	−12.78 (2)	B-H-Co
2,5-$(CH_3)_2$-1,7,2,5-(η-C_5H_5)$_2$$Co_2C_2B_5H_5$ (V)	4.45 (5)	C_5H_5
	4.34 (5)	C_5H_5
	1.93 (3)	CH_3
	1.66 (3)	CH_3
	2.46 (1)	B-H
	7.56 (1)	B-H
	9.06 (1)	B-H
2,3-$(C_6H_5)_2$-1,7,2,3-(η-C_5H_5)$_2$$Co_2C_2B_3H_3$ (VI)	7.24[c] (10)	C_6H_5
	4.43 (10)	C_5H_5
	3.75 (2)	B-H
	6.66 (1)	B-H
2,3-$(C_6H_5)_2$-1,2,3-(η-C_5H_5)$CoC_2B_3H_5$ (VII)	6.96[c] (10)	C_6H_5
	4.64 (5)	C_5H_5
	3.81 (2)	B-H
	3.26 (1)	B-H
	−5.52 (2)	B-H-B
4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-(η-C_5H_5)$CoC_4B_3H_3$ (VIII)	7.04[c] (20)	C_6H_5
	4.92 (5)	C_5H_5
	5.36 (1)	B-H
	2.67 (2)	B-H
1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$ (IX)	4.68 (5)	C_5H_5
	2.50 (6)	CH_3
	4.46 (1)	B-H
	0.88 (2)	B-H
	1.27 (1)	B-H
	0.73 (1)	B-H
6,7-$(CH_3)_2$-2,5,6,7-(η-C_5H_5)$_2$$Co_2C_2B_6H_8$ (X)	4.84 (5)	C_5H_5
	4.73 (5)	C_5H_5
	2.42 (3)	CH_3
	1.63 (3)	CH_3
	5.34 (1)	B-H
	5.08 (1)	B-H
	3.71 (1)	B-H
	3.38 (1)	B-H
	2.67 (1)	B-H
	0.41 (1)	B-H
	−1.45 (1)	B-H-B
	−2.35 (1)	B-H-B
6,7-$(CH_3)_2$-2,4,6,7-(η-C_5H_5)$_2$$Co_2C_2B_6H_6$ (XI)	4.72 (10)	C_5H_5
	2.47 (6)	CH_3
	6.62 (1)	B-H
	1.56 (2)	B-H
	0.86[d] (3)	B-H
4,9-$(CH_3)_2$-2,7,4,9-(η-C_5H_5)$_2$$Co_2C_2B_6H_6$ (XII)	4.76 (10)	C_5H_5
	3.27 (6)	CH_3

[a] All complexes were run in CS_2 solution with C_6D_6 internal lock material. [b] Parts per million relative to $(CH_3)_4Si$ (TMS), with positive sign indicating a shift to lower field (less shielding). [c] Most intense peak of a multiplet. [d] Overlapping resonance.

Although many of the metallaborane clusters described above were also obtained in small amounts, no other products containing carbon monoxide were found.

Reaction of Cobalt Vapor with B_6H_{10} and C_5H_6. Cobalt vapor (~0.3 g) was cocondensed with 4.0 mL of hexaborane(10) and 10 mL of cyclopentadiene at −196 °C. Upon completion of the metal evaporation and ligand cocondensation, the reactor was warmed to room temperature and the reaction mixture stirred for 15 min. The reaction was worked up in the manner described above to give a material which was separated by TLC on silica gel by using a 40% benzene in carbon tetrachloride solution. Isolated from this reaction were the three previously reported cobaltaboranes 2-(η-C_5H_5)CoB_9H_{13}[10] ($R_f = 0.77$, 4 mg (0.7%)), 1,2-(η-C_5H_5)$_2$$Co_2B_4H_6$[9] ($R_f = 0.59$, 3 mg (0.2%)), and 5-($\eta$-$C_5H_5$)$CoB_9H_{13}$[9] ($R_f = 0.55$, 7 mg (1.2%)) which were identified by comparison of their ^{11}B NMR and mass spectra with known values.

Trace amounts of a compound with a mass spectral cutoff at *m/e* 348 corresponding to a formula (η-C_5H_5)$_2$$Co_2B_8H_{12}$ were also obtained but in insufficient amounts to allow complete characterization.

Reaction of Cobalt Vapor with $B_{10}H_{14}$ and C_5H_6. Before metal deposition was begun, decaborane(14) (4.0 g) was sublimed onto the walls of the reactor. Then cobalt vapor (0.3 g) and 20 mL of cyclopentadiene were cocondensed on this coating at −196 °C. After metal evaporation was complete, the reactor was allowed to warm to room temperature and stirred for 30 min. The volatile materials were removed in vacuo, and the reactor was vented with an atmosphere of prepurified nitrogen. It was then opened to air and the residue extracted with THF. This extract was filtered on a coarse-frit funnel and evaporated to dryness. Excess decaborane(14) was removed by vacuum sublimation, and the remaining residue was separated by TLC on silica gel by using chloroform as the eluant into two major products: 5-(η-C_5H_5)CoB_9H_{13}[9] ($R_f = 0.77$; red-orange; 50 mg (8.3%)) and a

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(10) R. Wilczynski and L. G. Sneddon, *Inorg. Chem.*, **18**, 864 (1979).

new isomer of the same cage system, IV, $6\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$ [R_f = 0.72; violet; 42 mg (7.0%); mp 178–181 °C dec. Mass measurement: calcd for $^{12}C_5{}^1H_{18}{}^{11}B_9{}^{59}Co_1$, 236.1578; found, 236.1589].

Trace amounts of a compound with a mass spectral cutoff at *m/e* 246, corresponding to the formula $(\eta\text{-}C_5H_5)CoB_{10}H_{12}$, were also obtained but in insufficient amounts to allow complete characterization.

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and 2-Butyne. Cobalt vapor (0.3 g) was cocondensed with a mixture of 20 mL of pentaborane(9), 20 mL of cyclopentadiene, and 20 mL of 2-butyne (Chem. Samples Co.) at −196 °C. The reaction was worked up in a manner similar to that described above to give a residue which was separated by TLC on silica gel by using 40% benzene in carbon tetrachloride as the elution solvent to give V, $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ [R_f = 0.80; green; 4.8 mg (1.7%); mp 136–137 °C. Mass measurement: calcd for $^{12}C_{14}{}^1H_{21}{}^{11}B_5{}^{59}Co_2$, 362.0773; found, 362.0823], $2,3\text{-}(CH_3)_2\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3$ (5.2 mg (1.0%)), and $2,3\text{-}(CH_3)_2\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_4$ (14.5 mg (5.4%)). The latter two compounds have been previously reported[11] and were identified by comparison of their mass spectra and ^{11}B and ^1H NMR spectra with their literature values.

Thermal Isomerization of $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$. A 2.0-mg sample of V (green) was heated at 190 °C in an evacuated Pyrex tube for 14 h. Analysis of the resultant sample by TLC on silica gel using a 10% benzene in pentane solution as the elution mixture gave a single orange compound (R_f = 0.72) which was subsequently identified by its ^{11}B and ^1H NMR spectra and mass spectrum to be the known[12] isomer of compound V, $5,6\text{-}(CH_3)_2\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ (1.8 mg).

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and Diphenylacetylene. Cobalt vapor (0.3 g) was cocondensed with a mixture of 20 mL of pentaborane(9) and 20 mL of cyclopentadiene at −196 °C. After metal deposition was complete, the reactor was warmed and the condensate allowed to melt and flow to the bottom of the reactor where it was mixed with 4.0 g of diphenylacetylene (Eastman). This mixture was stirred for 30 min, the volatiles then were removed in vacuo, and the residue was extracted with methylene chloride and filtered. Separation of the products by TLC on silica gel using a 20% benzene in hexanes solution gave VI, $2,3\text{-}(C_6H_5)_2\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3$ [R_f = 0.17; red; 17 mg (2.9%); mp 291–292 °C. Mass measurement: calcd for $^{12}C_{24}{}^1H_{23}{}^{11}B_3{}^{59}Co_2$, 462.0743; found, 462.0746] and VII, $2,3\text{-}(C_6H_5)_2\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_5$ [R_f = 0.59; yellow; 12 mg (1.4%); mp 156–158 °C. Mass measurement: calcd for $^{12}C_{19}{}^1H_{20}{}^{11}B_3{}^{59}Co_1$, 340.1176; found, 340.1195]. Two additional bands were also collected (R_f = 0.33, 0.26) and subjected to further separations by using reversed-phase TLC Nujol-impregnated cellulose plates with use of a 2% water in methanol solution as the elution solvent. This allowed the isolation of an additional metallacarborane, VIII, $4,5,7,8\text{-}(C_6H_5)_4\text{-}1,4,5,7,8\text{-}(\eta\text{-}C_5H_5)CoC_4B_3H_3$ [R_f = 0.69; red; 1 mg (0.01%). Mass measurements: calcd for $^{12}C_{33}{}^1H_{28}{}^{11}B_3{}^{59}C_1$, 516.1802; found, 516.1833]. Also obtained were two other compounds, but the quantities isolated were insufficient to permit complete characterization. The mass spectra of these compounds correspond to $(\eta\text{-}C_5H_5)_2Co_2(C_6H_5)_2C_2B_3H_3$ (green; R_f = 0.65) and $(\eta\text{-}C_5H_5)Co(C_6H_5)_2C_2B_3H_5$ (green; R_f = 0.43).

Reaction of Cobalt Vapor with B_6H_{10}, C_5H_6, and 2-Butyne. Cobalt vapor (0.3 g) was cocondensed with 7 mL of hexaborane(10), 10 mL of 2-butyne, and 12 mL of cyclopentadiene at −196 °C. Upon completion of the metal evaporation the reactor was warmed to room temperature and the reaction mixture stirred for 15 min. The reaction was worked up in the manner described above to give a material which was separated by TLC on silica gel by using a 40% benzene in hexanes solution. The following metallacarborane products were obtained: IX, $1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$ [R_f = 0.42; red-brown; 23.0 mg (3.9%); mp 183–184 °C. Mass measurement: calcd for $^{12}C_9{}^1H_{16}{}^{11}B_5{}^{59}Co_1$, 238.1049; found, 238.1059], X, $6,7\text{-}(CH_3)_2\text{-}2,5,6,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$ [R_f = 0.29; green; 23.0 mg (4.8%); mp 201–203 °C dec. Mass measurement: calcd for $^{12}C_{14}{}^1H_{24}{}^{11}B_6{}^{59}Co_2$, 376.1101; found, 376.1106], and XI, $6,7\text{-}(CH_3)_2\text{-}2,4,6,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ [R_f = 0.22; black-brown; 19.9 mg (4.2%); mp 278 °C dec. Mass measurement: calcd for $^{12}C_{14}{}^1H_{22}{}^{11}B_6{}^{59}Co_2$, 374.0944; found, 374.0941]. In addition, several known clusters were also obtained: $2\text{-}(\eta\text{-}C_5H_5)CoB_4H_8$[9] (9.8 mg (2.2%)) and trace amounts of $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ and $1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_5H_5$. Each of these compounds was identified by comparisons of their mass spectra and ^{11}B and ^1H NMR data with known values.

Thermal Isomerization of $1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$ (IX). A 2.0-mg sample of IX (red-brown) was heated at 215 °C in an evacuated tube for 17 h. Separation by TLC on silica gel of the resulting orange product in 20% benzene in carbon tetrachloride solution gave 1.8 mg of the previously known[12] isomer $1,7\text{-}(CH_3)_2\text{-}3,1,7\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$.

Thermolysis of $6,7\text{-}(CH_3)_2\text{-}2,5,6,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$ (X). A 2.0-mg sample of X (green) was heated at 215 °C in an evacuated Pyrex tube for 9 h. Separation of the brown-black residue by TLC on silica gel using a 20% benzene in carbon tetrachloride solution gave a new complex, XII, $4,9\text{-}(CH_3)_2\text{-}2,7,4,9\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ [R_f = 0.36; red-brown; 0.8 mg. Mass measurement: calcd for $^{12}C_{14}{}^1H_{22}{}^{11}B_6{}^{59}Co_2$, 374.0944; found, 374.0903].

Thermal Isomeration of $6,7\text{-}(CH_3)_2\text{-}2,4,6,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ (XI). A 2.0-mg sample of XI (black-brown) was heated at 215 °C in an evacuated Pyrex tube for 9 h. Separation of the black residue by TLC on silica gel using a 20% benzene in carbon tetrachloride solution gave 1.6 mg of the new isomer $4,9\text{-}(CH_3)_2\text{-}2,7,4,9\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ (XII), which was identified by its ^1H and ^{11}B NMR spectra.

Reaction of Cobalt Vapor with $B_{10}H_{14}$, C_5H_6, and 2-Butyne. Before metal deposition was begun, decaborane(14) (4.0 g) was sublimed onto the walls of the metal atom reactor. Then cobalt vapor (0.3 g), 15 mL of cyclopentadiene, and 15 mL of 2-butyne were cocondensed on this coating at −196 °C. After metal evaporation and ligand cocondensation was complete, the reactor was allowed to warm to room temperature and stand for 30 min. The excess volatile reactants were removed in vacuo, the reactor was opened to the air, and the residue was extracted with THF. This extract was filtered and evaporated to dryness. Excess decaborane(14) was removed by vacuum sublimation, and the remaining residue was separated by TLC on silica gel by using chloroform as the eluant. This separation gave $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$[9] [$R_f$ = 0.76; 20.8 mg (3.5%)] and the isomer $6\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$ [R_f = 0.70; violet; 15.4 mg (2.6%)].

Reaction of Cobalt Vapor with $B_{10}H_{14}$, C_5H_6, and Diphenylacetylene. Before metal deposition was begun, decaborane(14) (4.0 g) and diphenylacetylene (4.0 g) were sublimed onto the walls of the metal atom reactor. Then cobalt vapor (0.3 mg) and 25 mL of cyclopentadiene cocondensed on this coating at −196 °C. After metal evaporation and ligand cocondensation was complete, the reactor was allowed to warm to room temperature and stirred for 45 min. The excess volatile reactants were removed in vacuo, the reactor was opened to air, and the residue was extracted with methylene chloride. This extract was filtered through a coarse frit and evaporated to dryness. Excess decaborane(14) and diphenylacetylene were removed by vacuum sublimation, and the remaining residue was separated by TLC on silica gel by using hexanes as the elution solvent. Only one boron-containing product was isolated and identified as $1,2\text{-}(C_6H_5)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ [R_f = 0.65; 10.4 mg] along with small amounts of several organic and organometallic complexes: $C_6(C_6H_5)_6$ (6.5 mg), $C_8(C_6H_5)_8$ (2.1 mg), and $1\text{-}(\eta\text{-}C_5H_5)CoC_4(C_6H_5)_4$ (2.0 mg (0.2%)).

Results

In order to ascertain the advantages of the metal atom technique for the synthesis of metallaboron clusters, the reactions of cobalt atoms were examined with three different boron hydrides, pentaborane(9), hexaborane(10), and decaborane(14), in the presence of a variety of reagents. In all cases, structures of the new metallaborane products were deduced from ^{11}B and ^1H NMR data, infrared spectra (Tables I–III) as well as unit resolution mass spectra, elemental analysis, and/or exact mass measurements, and, in three cases, single-crystal X-ray determinations. The results of these reactions are discussed below.

Synthesis of Metallaborane Clusters. The initial study of metal vapor reactions with boron hydrides involved the reaction of cobalt atoms with pentaborane(9) and cyclopentadiene. This reaction was easily the most complex reaction studied,

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(11) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974).

(12) (a) $1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2B_5H_7$: V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 2830 (1973). (b) In addition, one other isomer of this cage system, $1,7,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$, has also been reported: V. R. Miller, R. N. Grimes, L. G. Sneddon, and D. C. Beer, *ibid.*, **96**, 3090 (1974).

Table III. Infrared Data

compd	IR absorptions, cm^{-1}
1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_5$^{a,d} (I)	2965 (w), 2940 (m), 2860 (w), 2490 (s), 2460 (sh), 2415 (w), 1730 (m), 1650 (w), 1415 (m), 860 (s), 645 (br), 575 (br)
8-σ-C_5H_9-1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_4$^{a,d} (II)	2940 (s), 2865 (m), 2490 (s), 2335 (w), 1735 (m), 1435 (m), 1340 (w), 1255 (m), 1248 (sh), 1150 (m), 1135 (sh), 1000 (m), 780 (sh), 720 (br)
(μ_3-CO)-1,2,3-(η-C_5H_5)$_3$$Co_3B_3H_3$^{a,d} (III)	2965 (m), 2920 (m), 2910 (sh), 2495 (s), 2460 (sh), 2365 (w), 2340 (sh), 1695 (vs), 1420 (m), 1265 (m), 850 (m), 765 (sh), 730 (s, br)
6-(η-C_5H_5)CoB_9H_{13}^{b,e} (IV)	2960 (sh), 2935 (m), 2865 (w), 2590 (sh), 2555 (sh), 2530 (s), 1615 (m), 1300 (br), 1240 (br), 1018 (sh), 1000 (m), 845 (m), 820 (w)
2,5-$(CH_3)_2$-1,7,2,5-(η-C_5H_5)$_2$$Co_2C_2B_5H_5$^{f,d} (V)	2980 (w), 2930 (m), 2860 (w), 2510 (vs), 1410 (m), 1280 (m), 1260 (m), 1110 (m), 1000 (m), 950 (m), 885 (sh), 875 (m), 830 (m), 810 (s), 800 (sh), 765 (w), 740 (m), 470 (w)
2,3-$(C_6H_5)_2$-1,7,2,3-(η-C_5H_5)$_2$$Co_2C_2B_3H_3$^{c,d} (VI)	3083 (w), 3064 (w), 3038 (w), 3025 (sh), 2505 (vs), 2245 (w), 1805 (w), 1738 (m), 1670 (w), 1100 (w), 1015 (w), 997 (m), 955 (w), 910 (w), 789 (s), 753 (s), 733 (sh), 686 (s), 599 (w), 536 (w)
2,3-$(C_6H_5)_2$-1,2,3-(η-C_5H_5)$CoC_2B_3H_5$^{c,d} (VII)	3080 (m), 3050 (m), 3020 (m), 2920 (w), 2535 (vs), 1953 (sh), 1940 (w), 1885 (sh), 1870 (m), 1255 (w), 1165 (w), 1142 (sh), 1100 (w), 1058 (m), 1018 (m), 1001 (m), 994 (m), 913 (s), 818 (s), 775 (s), 748 (s), 730 (sh), 685 (s), 575 (m), 555 (m), 540 (sh), 533 (w), 495 (w), 485 (sh), 438 (w), 430 (w)
1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$^{c,e} (IX)	2975 (m), 2960 (m), 2920 (s), 2855 (m), 2540 (vs), 1825 (w), 1750 (w), 1380 (m), 1269 (w), 1118 (m), 1092 (w), 1060 (m), 1012 (m), 1000 (m), 985 (sh), 928 (m), 875 (m), 840 (s), 819 (s), 802 (sh), 783 (sh), 765 (m), 712 (m, br), 645 (m, br), 593 (w), 525 (w), 460 (m)
6,7-$(CH_3)_2$-2,5,6,7-(η-C_5H_5)$_2$$Co_2C_2B_6H_8$^{c,d} (X)	2973 (sh), 2955 (sh), 2920 (m), 2860 (sh), 2560 (sh), 2520 (vs), 2460 (m), 2380 (m), 2115 (br, w), 1345 (w), 1335 (sh), 1250 (m), 1110 (w), 1055 (w), 1040 (w), 1004 (sh), 990 (s), 955 (m), 830 (sh), 815 (s), 800 (sh), 738 (s)
6,7-$(CH_3)_2$-2,4,6,7-(η-C_5H_5)$_2$$Co_2C_2B_6H_6$^{c,d} (XI)	2948 (sh), 2922 (s), 2860 (m), 2550 (s, sh), 2510 (vs), 2448 (m), 1253 (w), 1055 (w), 1005 (w), 954 (m), 930 (w), 829 (sh), 816 (s), 796 (m)
4,9-$(CH_3)_2$-2,7,4,9-(η-C_5H_5)$_2$$Co_2C_2B_6H_6$^{c,d} (XII)	2950 (sh), 2920 (s), 2855 (m), 2808 (sh), 2505 (vs), 2478 (sh), 1004 (w), 958 (m), 932 (w), 807 (s), 780 (sh)

[a] Carbon tetrachloride solution. [b] Methylene chloride solution. [c] Carbon disulfide solution. [d] Perkin-Elmer 521. [e] Perkin-Elmer 337. [f] KBr Pellet.

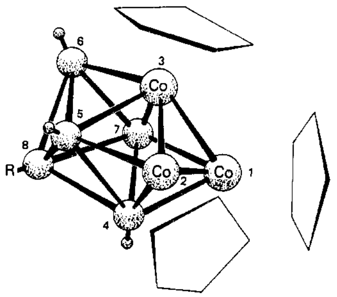

Figure 1. Proposed dodecahedral structure for 1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_5$ (I) and 8-σ-C_5H_9-1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_4$ (II).

giving ~30 different products with only nine of these obtained in quantities sufficient for complete characterization: 1,2-(η-C_5H_5)$_2$$Co_2B_4H_6$, 3-$\sigma$-($C_5H_9$)-1,2-($\eta$-$C_5H_5$)$_2$$Co_2B_4H_5$, 4-$\sigma$-($C_5H_9$)-1,2-($\eta$-$C_5H_5$)$_2$$Co_2B_4H_5$, 1,2,3-($\eta$-$C_5H_5$)$_3$$Co_3B_3H_5$, 1,2,4,7-($\eta$-$C_5H_5$)$_4$$Co_4B_4H_4$, 1,2,3-($\eta$-$C_5H_5$)$_3$$Co_3B_4H_4$, 1,2,3-($\eta$-$C_5H_5$)$_3$$Co_3B_5H_5$ (I), 8-σ-(C_5H_9)-1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_4$ (II), (μ_3-CO)-1,2,3(η-C_5H_5)$_3$$Co_3B_3H_3$ (III).

As indicated, the reaction yielded a very complex mixture of products including a number of cage-fragmented metallaborane clusters which have been previously isolated by Grimes.[9] The major products of the reaction were, however, three new metallaborane products. Two of these were found to be five-boron clusters: 1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_5$ (I) and its cyclopentyl derivative 8-σ-(C_5H_9)-1,2,3-(η-C_5H_5)$_3$$Co_3B_5H_4$ (II). The dodecahedral structure shown in Figure 1, which retains the basic pentaborane framework, is consistent with the spectroscopic data obtained for each compound. For example, both compounds show in their ^{11}B NMR data the expected four resonances with three of these shifted to lower field, as would be expected due to their proximity to the metals. Likewise, the ^1H NMR spectrum of each compound shows the expected 2:1 cyclopentadienyl resonances and in the case of II a multiplet at 1.21 ppm of intensity 9 which can be assigned to the cyclopentyl group.

Both compounds I and II are examples of 2*n* electron cluster systems (eight framework atoms and 16 skeletal electrons) and would be expected according to electron counting rules[13] to adopt a distorted structure such as a capped pentagonal pyramid rather than the closo dodecahedral structure shown in Figure 1. A capped structure which is consistent with the spectroscopic data can, indeed, be proposed; however, this structure is not favored since it would require one cobalt to occupy only a three-coordinate position. Furthermore, the adoption of a closo dodecahedral structure rather than the predicted capped structure is not without precedent. For example, Grimes has recently confirmed,[14] by a crystallographic investigation, that the compound (η-C_5H_5)$_4$$Co_4B_4H_4$ (also an eight-vertex 2*n* electron system) adopts a dodecahedral rather than a capped structure. Clearly, other factors such as the adoption of a higher coordination number for the cobalt atoms in I and II may be of more importance than the skeletal electron count in the determination of cage geometry.

The third new cluster obtained in the reaction with pentaborane(9) was the unique cluster (μ_3-CO)-1,2,3-(η-C_5H_5)$_3$$Co_3B_3H_3$ (III). The indicated composition of III is consistent with exact mass determination,[8] and in addition, the mass spectrum shows an initial fragmentation corresponding to the loss of carbon monoxide. Both the ^{11}B and ^1H NMR data indicate the presence of a threefold axis in the molecule. Thus, the ^{11}B NMR spectrum consists of only one doublet, while the ^{11}B spin-decoupled proton NMR consists of two peaks in a ratio of 5:1, indicating equivalent cyclopentadienyl and equivalent B–H groups, respectively. The IR spectrum shows a very strong band at 1695 cm^{-1}, indicating a carbon monoxide bridging three metals. A structure which is consistent with these data and with the skeletal electron counting rules (2*n* + 2 system) is the octahedrally shaped cluster shown in Figure 2, and this structure has recently been confirmed[15] by a single-crystal X-ray structural determination.

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(13) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).
(14) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **18**, 257 (1979).

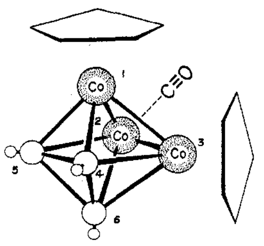

Figure 2. Structure of $(\mu_3\text{-CO})\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ (III).

The compound has a cage structure similar to those of two previously reported isoelectronic (in a cluster sense) compounds, $(\eta\text{-}C_5H_5)_3Co_3B_3H_5$[16] and $(\eta\text{-}C_5H_5)_3Co_3B_4H_4$,[16] but is unique in that it is the first metallaborane that contains a carbonyl bridging three metals inserted into the cage framework.

The formation of $(\mu_3\text{-CO})\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_3H_3$ is unusual in that it was formed in the absence of carbon monoxide as a reactant. The source of the carbonyl group is still unproven; however, it may have resulted either from the reactions of metal oxide impurities found in the powdered cobalt used for metal atom vaporization[17] or from the decomposition of the tetrahydrofuran used as solvent for extraction. The latter explanation appears to be favored because, when this reaction was repeated, this time by extraction of the residue with methylene chloride, no such carbonyl containing complex was isolated. Regardless of the source of carbon monoxide in the above reaction, it has been found that the yield of this cluster can be increased substantially when the reaction matrix is warmed into an atmosphere of carbon monoxide gas.

On the basis of the results obtained in the pentaborane(9) reaction, it was expected that the reaction of cobalt atoms with cyclopentadiene and hexaborane(10) would yield six-boron metallaborane clusters. It was found, however, that, although the reaction yielded a great number of products, no six-boron species were obtained. Only three products were obtained in sufficient quantities to permit characterization. Those were found to be the previously reported $2\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$,[10] $1,2\text{-}(\eta\text{-}C_5H_5)_2Co_2B_4H_6$,[9] and $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$.[9] Likewise, the reaction of cobalt atoms and cyclopentadiene with decaborane(14) did not yield any 10-boron clusters in isolable quantities but instead gave $5\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$[9] and $6\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$ (IV). Compound IV was previously unknown and is the third isomer of this cage system to be reported. Its composition was established by exact mass studies, and the proposed structure is supported by the spectroscopic data. The ^{11}B NMR spectrum at 32.1 MHz showed six doublets of intensity 2:2:1:2:1:1, while the boron-decoupled ^1H NMR at 100 MHz showed a cyclopentadienyl resonance of intensity 5, along with two separate broad resonances of intensity 2 each at higher fields. One of these broad resonances was located slightly above Me_4Si, indicating a pair of equivalent boron–boron-bridging hydrogen atoms, while the other resonance was located at much higher field (δ −12.78), suggesting two equivalent boron–cobalt-bridging hydrogen atoms. These NMR data indicate that IV must be the symmetrical isomer $6\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$ (Figure 3). The complex is the cobalt analogue of the species $(CO)_3MB_9H_{12}R$ prepared by Gaines,[18] where M = Mn or Re and R = THF or $(C_2H_5)_3N(CH_2)_4O$.

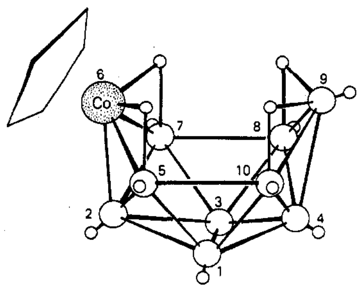

Figure 3. Proposed structure of $6\text{-}(\eta\text{-}C_5H_5)CoB_9H_{13}$ (IV).

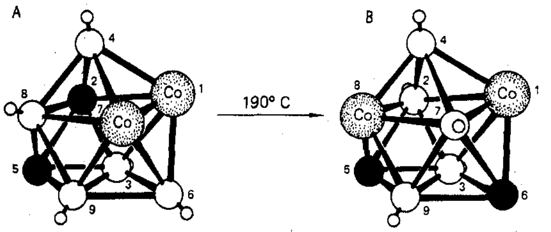

Figure 4. Proposed structure and thermal rearrangement of $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2B_5H_5$ (V).

Synthesis of Metallacarborane Clusters. The discovery of compound III, $\mu_3\text{-CO-}1,2,3\text{-}(\eta\text{-}C_5H_5)_3Co_3B_3H_3$, indicated that metal atom reactions could be used to incorporate other molecules into polyhedral boron clusters. It was therefore decided to investigate the feasibility of the use of the metal atom technique to effect the direct synthesis of metallacarborane clusters.

The initial reaction involved the cocondensation of cobalt atoms with pentaborane(9), cyclopentadiene, and 2-butyne and yielded as products three metallacarboranes: $2,3\text{-}(CH_3)_2\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3$, $2,3\text{-}(CH_3)_2\text{-}1,2,3\text{-}(\eta\text{-}C_5H_5)\text{-}CoC_2B_4H_4$, and $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ (V).

The three- and four-boron cobaltacarborane clusters were identified by comparison of their mass spectra and ^{11}B and ^1H NMR data with literature values as the methyl analogues of previously reported cage systems.[11] Compound V was assigned the indicated formula on the basis of exact mass measurements on the parent ion. This air-stable, green crystalline complex is an example of a $2n + 2$ electron system (nine framework atoms and 20 electrons) and according to electron counting rules[13] would be predicted to adopt a closo tricapped trigonal-prism structure. The ^1H NMR spectrum of this complex shows two cyclopentadiene resonances each of intensity 5 and two methyl resonances each of intensity 3. The ^{11}B NMR spectrum at 32.1 MHz shows five separate doublets of equal intensity. Thus, both the ^{11}B and ^1H NMR spectra indicate the absence of any plane of symmetry in the molecule. Furthermore, the observance of two doublets at very low field in the ^{11}B NMR spectrum is consistent with the presence of two different four-coordinate boron atoms attached to two metal atoms.[12,19] Therefore, if the cobalt atoms are assumed to occupy five-coordinate positions in the cage and the carbon atoms remain adjacent, then only the structure indicated in Figure 4A is in agreement with the above data. Thus the new metallacarborane is $2,5\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$. This complex is a new isomer of the previously reported[12] $Co_2C_2B_5$ cage system in which the carbon atoms are in adjacent positions in the polyhedral cage. It was later found that this new adjacent carbon isomer could be quantitatively isomerized to the previously known[3,12] $5,6\text{-}(CH_3)_2\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ complex (Figure 4B) at high temperatures. This fact provides further evidence for the proposed adjacent carbon structure.

The metal atom reactions of pentaborane(9) were also investigated with diphenylacetylene. Several new clusters were

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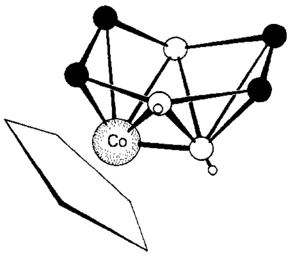

Figure 5. Structure of 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta\text{-}C_5H_5)CoC_4B_3H_3$ (VIII) (phenyl rings attached to carbon atoms omitted).

isolated from this reaction, including 2,3-$(C_6H_5)_2$-1,7,2,3-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_3$ (VI), 2,3-$(C_6H_5)_2$-1,2,3-$(\eta\text{-}C_5H_5)CoC_2B_3H_5$ (VII), and 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta\text{-}C_5H_5)CoC_4B_3H_3$ (VIII). The indicated formulas were again established on the basis of exact mass measurements. The ^{11}B NMR and ^1H NMR data for VI indicate that it is the diphenyl C-substituted derivative of the parent triply decked sandwich compound 1,7,2,3-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$,[11] while the NMR data for VII indicate it to be the diphenyl C-substituted analogue of the parent metallocarborane 1,2,3-$(\eta\text{-}C_5H_5)CoC_2B_3H_7$.

The formula for compound VIII indicated that it was a unique example of a four-carbon metallacarborane cluster. Such a compound would be a $2n + 4$ electron system (eight framework atoms, 20 skeletal electrons) and should adopt a nido cage geometry (tricapped trigonal prism missing one equatorial vertex); however, it has previously been observed that other such systems deviate from this predicted geometry. For example, B_8H_{12},[20] $C_2B_6H_{10}$,[21] and $(CH_3)_4C_4B_4H_4$[22] are each proposed to adopt arachno $(2n + 6)$ structures, while $(\eta\text{-}C_5H_5)_4Ni_4B_4H_4$[23] and $(\eta\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_4H_4$ have closo $(2n + 2)$ dodecahedral structures. Only in the case of $(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$[24] has the predicted nido geometry been observed. Thus on the basis of these observations it might also be expected that the four-carbon metallacarborane complex would deviate from the predicted nido structure and adopt either a closo or arachno framework. The spectroscopic data are consistent with any of these cage geometries. The 32.1-MHz ^{11}B NMR spectrum of this compound shows two doublets of intensity 2:1. A weak 100-MHz ^1H NMR spectrum shows one sharp cyclopentadienyl resonance of intensity 5 and a broad phenyl resonance of intensity 20. The boron-decoupled ^1H NMR spectrum shows two B–H resonances of intensity 2:1. A possible arachno structure which is consistent with this spectroscopic evidence is shown in Figure 5. The molecule contains the required mirror plane, giving two equivalent boron atoms, as well as situating the cobalt atom in the preferred five-coordinate position. Because of the small amounts of this complex obtained, it was impossible to obtain spectroscopic evidence of sufficient quality to definitely assign a structure to this complex. It was, however, possible to grow single crystals of the compound, enabling a single-crystal X-ray structure determination which confirmed the structure shown in Figure 5. Full details of the structural determination appear in the following paper.[25]

The reaction of cobalt atoms with hexaborane(10), cyclopentadiene, and 2-butyne gave three new metallacarborane clusters along with several previously isolated metallaborane products: 1,2-$(CH_3)_2$-3,1,2-$(\eta\text{-}C_5H_5)CoC_2B_5H_5$ (IX), 6,7-$(CH_3)_2$-2,5,6,7-$(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$ (X), 6,7-$(CH_3)_2$-2,4,6,7-$(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_6$ (XI), 2-$(\eta\text{-}C_5H_5)CoB_4H_8$,[9] 2,5-$(CH_3)_2$-1,7,2,5-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$, 1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_5H_5$.

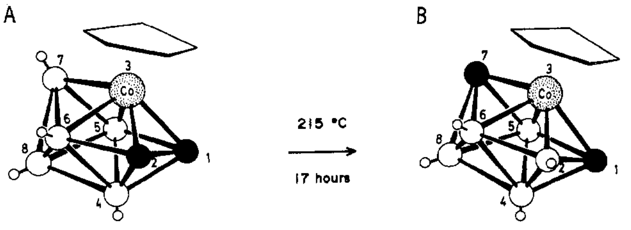

Figure 6. Structure and thermal rearrangement of 1,2-$(CH_3)_2$-3,1,2-$(\eta\text{-}C_5H_5)CoC_2B_5H_5$ (IX).

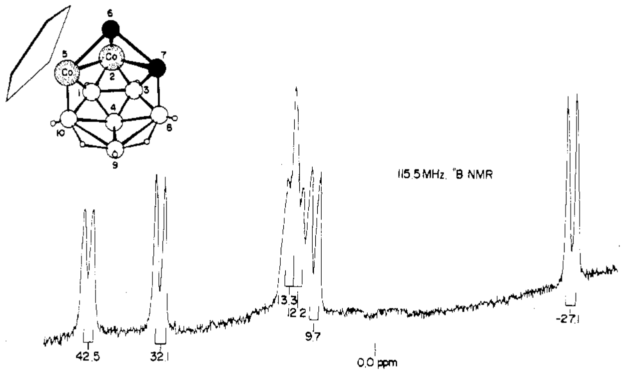

Figure 7. Proposed structure and 115.5-MHz ^{11}B NMR spectrum of 6,7-$(CH_3)_2$-2,5,6,7-$(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$ (X).

The first compound isolated in this reaction was an air-stable reddish crystalline material whose mass spectrum and exact mass measurements were consistent with the fomula $(\eta\text{-}C_5H_5)Co(CH_3)_2C_2B_5H_5$. A compound of this formula would be predicted to adopt a closed dodecahedral structure. An arrangement of atoms within this dodecahedral structure which is consistent with the spectroscopic data is presented in Figure 6. The ^{11}B NMR spectrum indicates the presence of a mirror plane in the molecule placing two boron atoms in equivalent positions (B(5), B(6)) and three boron atoms in nonequivalent positions. The 100-MHz ^1H NMR spectrum confirms the presence of this mirror plane by indicating the equivalence of the terminal methyl groups attached to the two cage carbon atoms. A single cyclopentadienyl resonance and the appropriate B–H resonances (with ^{11}B decoupling) confirm the proposed structure for 1,2-$(CH_3)_2$-3,1,2-$(\eta\text{-}C_5H_5)CoC_2B_5H_5$. This compound is a new isomer of the previously reported[12] metallacarborane 1,7-$(CH_3)_2$-3,1,7-$(\eta\text{-}C_5H_5)CoC_2B_5H_5$, and it was later observed that the new isomer could be quantitatively isomerized to the known nonadjacent carbon isomer (Figure 6B). The proposed structure has also been recently confirmed by a single-crystal X-ray structure determination.[26]

The major product of the hexaborane(10) reaction gave mass spectral evidence indicating the formula $(\eta\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_6H_8$. This air-stable green crystalline material is a $2n + 4$ electron system (10 framework atoms and 24 skeletal electrons), with a predicted open-cage nido (octadecahedron missing one vertex) structure. The 115.5-MHz ^{11}B NMR spectrum showed resolution of six nonequivalent B–H resonances, indicating that the compound does not contain a mirror plane. The 100-MHz ^1H NMR spectrum with boron decoupling likewise shows six separate B–H resonances, two separate boron–boron bridge hydrogens and two cyclopentadienyl and two methyl resonances. An arrangement

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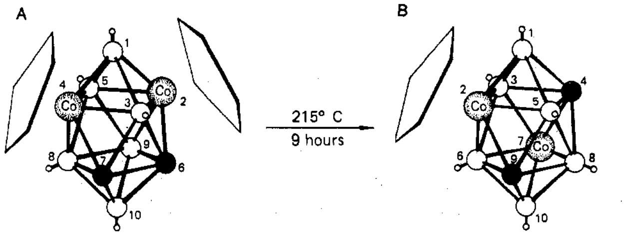

Figure 8. Proposed structures and thermal rearrangement of 6,7-$(CH_3)_2$-2,4,6,7-(η-$C_5H_5)_2Co_2C_2B_6H_6$ (XI) to 4,9-$(CH_3)_2$-2,7,4,9-(η-$C_5H_5)_2Co_2C_2B_6$ (XII).

of atoms in the proposed open-cage structure which is consistent with these spectroscopic data is shown in Figure 7. This new metallacarborane cage system is thus isoelectronic and isostructural with decaborane(14).

The third new cluster, XI, isolated in this reaction with hexaborane(10), gave a mass measurement consistent with the formula (η-$C_5H_5)_2Co_2(CH_3)_2C_2B_6H_6$. Two isomers of this cage system have previously been reported[12a,27] and proposed to have structures based on a closo 10-atom (bicapped Archimedian antiprism) geometry. An arrangement of atoms for XI with this geometry which is consistent with the spectroscopic data is shown in Figure 8A. In support of this proposed structure the 32.1-MHz ^{11}B NMR data showed the presence of a mirror plane in the molecule, placing two of the six boron atoms in equivalent positions. In addition, the poorly resolved doublet of intensity 1 at low field observed in the ^{11}B NMR spectrum is highly indicative[12a] of a four-coordinate B–H group which is attached to two metal atoms. The ^1H NMR data also indicated the presence of the mirror plane since a single cyclopentadienyl resonance and single methyl resonance of intensity 10:6 were observed along with the appropriate B–H resonances.

In a separate experiment, it was shown that 6,7-$(CH_3)_2$-2,4,6,7-(η-$C_5H_5)_2Co_2C_2B_6H_6$ (XI) could be thermally converted to a fourth isomer, XII, 4,9-$(CH_3)_2$-2,7,4,9-(η-$C_5H_5)_2Co_2C_2B_6H_6$ (Figure 8B). The process involves migration of both the cobalt and carbon atoms in the framework. The structure of XII was proposed on the basis of its exact mass measurements and its NMR spectra, which shows equivalent cyclopentadienyl and methyl resonances in the proton NMR spectrum and three pairs of equivalent B–H resonances in the boron NMR spectrum. It was also found that the pyrolysis of X at 215 °C also yields compounds XII as the primary product. This latter reaction involves both cage closure and isomerization of the cobalt and carbon atoms.

The metal atom reaction with decarborane(14) was performed in hopes of isolating new 10-boron metallacarborane products; however, the reaction gave only the two metallaborane clusters 5-(η-$C_5H_5)CoB_9H_{13}$[9] and 6-(η-C_5H_5)-CoB_9H_{13}, and no new large cage metallacarboranes were isolated. Analogous reactions with diphenylacetylene, which also failed to yield any metallacarborane products, however did result in the formation of diphenyl-*o*-carborane in small amounts.

Discussion

At the outset of this work, it was felt that the highly reactive nature of the transition-metal atoms generated by the use of metal atom techniques could be used for the production of metal clusters and, in particular, metallaboron clusters. The work described in the Results clearly demonstrated that this is the case since a variety of new metallaborane and metallacarborane species have been obtained by using these technqiues.

The initial studies were aimed at the production of new metallaborane clusters. The application of the metal atom technique to the synthesis of these types of compounds seemed ideal since this technique employs mild reaction conditions which will promote metal cluster–ligand interactions. The first study of metal vapor reactions with boron hydrides involved the reaction of cobalt atoms with pentaborane(9) and cyclopentadiene. This reaction was selected because Grimes et al. had previously studied[9] a comparable reaction involving the reaction of NaB_5H_8 and NaC_5H_5 with $CoCl_2$ in THF at low temperature. This reaction produced a number of multimetal species, but most contained only three or four boron atoms, indicating extensive cage fragmentation of the parent boron hydride, and no products were obtained containing the parent five-boron framework. An analogous metal atom reaction was therefore undertaken to allow a comparison of cluster products isolated by using the metal atom technique. Among the products isolated were a number of three- and four-boron multimetal cage complexes, including, 1,2-(η-$C_5H_5)_2Co_2B_4H_6$, 1,2,4,7-(η-$C_5H_5)_4Co_4B_4H_4$, 1,2,3-(η-$C_5H_5)_3Co_3B_4H_4$, and 1,2,3-(η-$C_5H_5)_3Co_3B_3H_5$, which were originally isolated in the solution reaction; however, these known complexes were isolated in low yields. The major products of the metal atom reaction were the two five-boron clusters I, 1,2,3-(η-$C_5H_5)_3Co_3B_5H_5$, and II, 8-σ-(C_5H_9)-1,2,3-(η-$C_5H_5)_3Co_3B_5H_4$. It should be noted that the proposed structures for these two new clusters, as described in the Results (Figure 1), both retain the square-based-pyramid structure of pentaborane(9) in the boron portion of the molecule, demonstrating the synthetic advantage of the mild conditions employed in the metal atom technique.

Considering the results from the pentaborane(9) reaction, it was somewhat surprising that analogous reactions with hexaborane(10) did not yield any six-boron metallaborane clusters but instead gave as major products 2-(η-C_5H_5)-CoB_9H_{13}[10] and 5-(η-$C_5H_5)CoB_9H_{13}$.[9] This behavior may be due to the relative instability of hexaborane(10) as compared to pentaborane(9). Thus, the larger cage metalloboranes must have formed by a recombination of metallaborane and/or borane fragments generated in the matrix.

The isolation and characterization of a third new cluster in the pentaborane(9) reaction, III, μ_3-CO-1,2,3-(η-$C_5H_5)_3Co_3B_3H_3$, proved to be a significant discovery. Since the starting reactants were carbon monoxide free, it was assumed that the carbonyl group in the complex in the original reaction may have come from some degradation reaction between the extraction solvent (THF) and the reaction residue. This was later confirmed by repeating the reaction and extracting the residue with methylene chloride. When this was done, no such complex was isolated. Likewise, when the reaction was repeated and the Co–C_5H_6–B_5H_9 matrix was warmed to room temperature in an atmosphere of carbon monoxide gas, increased yields of this new complex were obtained. The isolation of this complex was important for two reasons. First, it demonstrated that there are reactive metal fragments remaining in the reaction residue long after matrix warm-up, and, second, it indicated that it might be possible to incorporate other types of heteroatoms or molecules into metallaboron cage system by using metal atom techniques.

These conclusions suggested that the inclusion of alkynes in the metal atom reactions with boron hydrides might be a direct synthetic route to metallacarborane complexes and, indeed, the reactions of either pentaborane(9) or hexaborane(10) with dimethyl- or diphenylacetylene yielded a variety of metallacarborane clusters.

The production of these complexes is significant for several reasons. First, it shows that the metal atom technique is a method which can be used to effect the direct conversion of

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boron hydrides and alkynes into metallacarborane clusters at low temperature without the prior synthesis of the carborane cage; that is, the metal atoms or reactive fragments derived from these atoms are being used as sites for cage construction. In only a few previous instances,[9c,22,28] has a carborane or metallacarborane been synthesized by direct reaction of an alkyne and parent borane at a metal site. Second, the low-temperature reaction conditions have led to only adjacent carbon isomers. This is in direct contrast to what is often observed in conventional synthesis of small cage metallacarborane clusters, which, because of the high temperatures employed in either the synthesis of the carboranes themselves or the synthesis of the metal complexes, can readily isomerize to give nonadjacent isomers. Thus many of the adjacent carbon isomers produced in the metal atom reactions are inaccessible by other synthetic technqiues. Third, although some cage fragmentation products were observed, the major products usually contained the same number of boron atoms as the starting boron hydride molecule, again demonstrating the synthetic advantages of the mild conditions employed in the metal atom reaction. Finally, several of the new metallacarboranes produced were shown to be structurally novel. In this regard, the compound which is probably of most interest was the unique four-carbon metallacarborane cluster 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta$-$C_5H_5)CoC_4B_3H_3$ (VIII). The isolation of this complex, which contains more carbon than boron cage atoms, indicates that with appropriate conditions metal atom techniques may be used to incorporate an even greater number of carbon or other heteroatoms into these cages to form new hybrid clusters.

In contrast to the results obtained with pentaborane(9) and hexaborane(10), it was found that the metal atom reactions of decaborane(14) were less fruitful. For example, although the reactions of decaborane(14) and cyclopentadiene with cobalt atoms did result in the formation of both 6-$(\eta$-$C_5H_5)CoB_9H_{13}$ and 5-$(\eta$-$C_5H_5)CoB_9H_{13}$[9] in reasonable yields, inclusions of either dimethyl- or diphenylacetylene in the reaction did not result in the formation of metallacarborane products. It is important to note, however, that in the latter reaction diphenyl-*o*-carborane was obtained in small amounts, suggesting that it may be eventually possible to develop metal atom assisted synthesis of carboranes.

It is apparent that the chief disadvantage of the reactions reported herein is their complex nature which often leads to the formation of many products and low individual yields. Thus, while the metal atom technique must be considered a forefront method for the formation of new types of cage systems, further developments will be needed before these techniques can be applied to preparative scale syntheses of the complexes described.

Acknowledgment. We thank the National Science Foundation (Grant CHE-77-06793) and the University of Pennsylvania Materials Research Laboratory (Grant DMR-76-00678) for the support of this research.

Registry No. I, 74978-05-5; II, 63179-56-6; III, 75125-07-4; IV, 74978-06-6; V, 67579-06-0; VI, 74978-07-7; VII, 74965-08-5; VIII, 74964-99-1; IX, 74978-08-8; X, 74987-43-2; XI, 74977-73-4; XII, 74965-00-7; 1,2-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$, 17805-19-5; 6-$(\eta$-$C_5H_5)CoB_9H_{13}$, 74978-06-6; 1-$(\eta$-$C_5H_5)CoC_4(C_6H_5)_4$, 1278-02-0; 1,2-$(\eta$-$C_5H_5)_2Co_2B_4H_6$, 50924-50-0; 3-σ-C_5H_9-1,2-$(\eta$-$C_5H_5)_2Co_2B_4H_5$, 43062-02-8; 4-σ-C_5H_9-1,2-$(\eta$-$C_5H_5)_2Co_2B_4H_5$, 43062-03-9; 1,2,3-$(\eta$-$C_5H_5)_3Co_3B_3H_5$, 59217-07-1; 1,2,4,7-$(\eta$-$C_5H_5)_4Co_4B_4H_4$, 59370-82-0; 1,2,3-$(\eta$-$C_5H_5)_3Co_3B_4H_4$, 59458-52-5; 2-$(\eta$-$C_5H_5)CoB_9H_{13}$, 68457-40-9; 5-$(\eta$-$C_5H_5)CoB_9H_{13}$, 43062-04-0; 2,3-$(CH_3)_2$-1,7,2,3-$(\eta$-$C_5H_5)_2Co_2C_2B_3H_3$, 51108-06-6; 2,3-$(CH_3)_2$-1,2,3-$(\eta$-$C_5H_5)CoC_2B_4H_4$, 50932-66-6; 5,6-$(CH_3)_2$-1,8,5,6-$(\eta$-$C_5H_5)_2Co_2C_2B_5H_5$, 67579-07-1; 2-$(\eta$-$C_5H_5)CoB_4H_8$, 43062-00-6; 1,7-$(CH_3)_2$-3,1,7-$(\eta$-$C_5H_5)CoC_2B_5H_5$, 74965-09-6; B_5H_9, 19624-22-7; B_6H_{10}, 23777-80-2; $B_{10}H_{14}$, 17702-41-9; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5.

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Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter,
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Crystal and Molecular Structure of 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta$-$C_5H_5)CoC_4B_3H_3$: A Four-Carbon Metallacarborane Complex Containing More Carbon Than Boron Cage Atoms

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The crystal and molecular structure of 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta$-$C_5H_5)CoC_4B_3H_3$, an unusual four-carbon metallacarborane complex containing more carbon than boron cage atoms, has been determined from single-crystal X-ray diffraction data. The cage framework is best described as a bicapped square antiprism missing two vertices (one cap and one equatorial position). This structure is not predicted by simple electron counting rules but is consistent with the structures observed for certain other eight-atom 20-skeletal-electron systems. Crystal data: space group $P2_1/c$, $Z = 4$, $a = 14.997$ (5) Å, $b = 10.472$ (6) Å, $c = 17.576$ (8) Å, $\beta = 109.83$ (1)°, $V = 2596$ Å^3. The structure was refined by full-matrix least-squares methods to final R of 0.042 and R_w of 0.039 for the 2278 reflections which had $F_o^2 > 3\sigma(F_o^2)$.

In the previous paper[2] it was demonstrated that metal atom techniques can be used to produce several types of structurally novel metalloboron clusters. One complex of particular interest, which was isolated from the reaction of pentaborane(9), cyclopentadiene, and diphenylacetylene with cobalt atoms, was the compound 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta$-$C_5H_5)CoC_4B_3H_5$. This complex is an unusual example of a four-carbon metallacarborane containing more carbon than boron cage atoms. Furthermore, it is an eight-atom $2n + 4$ cluster system (eight cage atoms, 20 skeletal electrons) and is thus of additional interest since such cluster systems have previously been proposed to deviate from the structures expected on the basis of

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[1] Alfred P. Sloan Foundation Fellow.

[2] G. J. Zimmerman, L. W. Hall, and L. G. Sneddon, *Inorg. Chem.*, preceding paper in this issue.

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