Tetracarbon Metallocarboranes. 5.[1,2] A New Synthetic Route: Synthesis of $Co_2C_4B_6$ and CoC_4B_7 Nido Cage Systems by Fusion of Dicarbon Cobaltacarboranes in Ethanolic KOH. Crystal Structure of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$

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Abstract: The treatment of the dicarbon cobaltacarboranes *closo*-1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ (I), *nido*-1,2,3-$(\eta^5\text{-}C_5H_5)$-$CoC_2B_3H_7$ (II), or their *C,C'*-dimethyl derivatives (IA and IIA) with a 10% KOH/C_2H_5OH solution open to the atmosphere results in oxidative fusion of the dicarbon species to create tetracarbon 12-vertex cage systems containing a $Co_2C_4B_6$ or a CoC_4B_7 framework. From the parent species I or II, one obtains $(\eta^5\text{-}C_5H_5)CoC_4B_7H_{11}$ and three isomers of $(\eta^5\text{-}C_5H_5)_2$-$Co_2C_4B_6H_{10}$, which are the first parent tetracarbon metallocarboranes. Similar treatment of IA or IIA leads to a single tetracarbon product, $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$, which appears to be a *C*-tetramethyl derivative of one of the $(\eta^5\text{-}C_5H_5)_2$-$Co_2C_4B_6H_{10}$ isomers produced from I and II. An x-ray diffraction study of one of the $Co_2C_4B_6$ species disclosed an open 12-vertex cage system with the cobalt atoms in five- and six-coordinate vertices and all four cage carbons on the open face. The molecule is isostructural and isoelectronic with the previously reported $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$; it is also isoelectronic, but *not* isostructural, with the molecules $(CH_3)_4C_4B_8H_8$, $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6OC_2H_5$, and $R_2C_2B_{10}H_{11}^-$ (R = CH₃ or C₆H₅) which are all structurally established 28-electron, 12-vertex nido cage systems. The structures of the remaining tetracarbon products, the nature of the oxidative cage-fusion process, and the relationship of this work to earlier carborane fusion reactions are discussed. Crystal data for $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$: space group $P2_1/c$, $Z = 4$, $a = 13.606$ (10), $b = 8.970$ (3), $c = 13.050$ (4) Å, $\beta = 102.95$ (4)°, $V = 1552$ (2) Å³, $R = 0.046$ for the 1586 reflections for which $F_o^2 > 3\sigma$ (F_o^2).

Earlier publications from this laboratory described the synthesis[3] and structure determination[4] of the tetracarbon carborane $(CH_3)_4C_4B_8H_8$, and its subsequent conversion to tetracarbon metallocarboranes[5,6] by metal insertion reactions. This unusual carborane is produced in high yield from the reaction of $[(CH_3)_2C_2B_4H_4]_2Co^{III}H$ or $[(CH_3)_2C_2B_4H_4]_2$-$Fe^{II}H_2$ with air,[3,7] and involves oxidative fusion of two *metal-bound* carborane ligands:

$$2[(CH_3)_2C_2B_4H_4]^{2-} \xrightarrow{[O]} (CH_3)_4C_4B_8H_8$$
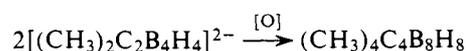
While the mechanistic details of the ligand-fusion process are not yet understood, it has considerable potential utility as a synthetic method; for example, the efficient direct conversion of small cages to large ones may ultimately lead to the construction of very large polyhedra ("supercages").[8]

We have sought to determine the extent to which cage fusion is a general process, and in doing so we turned to a previously studied reaction:[9] the synthesis of small metallocarboranes from $Na^+C_2B_4H_7^-$, $CoCl_2$, and $Na^+C_5H_5^-$ in tetrahydrofuran (THF) at room temperature. The three main cobaltacarborane products, isolated following workup in water and acetone, are *closo*-1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ (I), *nido*-1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ (II), and *closo*-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (III), a "triple-decked sandwich" complex. However, the quantities obtained are very sensitive to workup conditions; for example, the recovered yield of I is 10% when water is used but 63% when 1 M aqueous HCl is employed.[9b]

Examination of a wider range of conditions has led us to the discovery that when the cobaltacarborane products I and II or their *C,C'*-dimetyl derivatives are treated with *strong base*, oxidative fusion occurs and tetracarbon metallocarboranes are formed. We describe here the synthetic findings together with the crystallographic structure determination of one of the tetracarbon metallocarborane products.

Results and Discussion

Synthesis of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ Isomers and $(\eta^5\text{-}C_5H_5)CoC_4B_7H_{11}$. A. From $Na^+C_2B_4H_7^-$, $CoCl_2$, and $Na^+C_5H_5$. Initially, the carborane salt $Na^+C_2B_4H_7^-$ (obtained by bridge deprotonation of the carborane $2,3\text{-}C_2B_4H_8$ with NaH) was allowed to react in the usual manner[9b] with excess $CoCl_2$ and $Na^+C_5H_5^-$ in THF at 23 °C overnight. Instead of the normal workup in aqueous media, however, the solid products, after removal of solvent by distillation, were treated with 10% KOH in ethanol in air, after which the products were extracted with methylene chloride and purified by thick layer chromatography. The three expected dicarbon cobaltacarborane products (I, II, III) were found, though in much reduced yields compared to those obtained on workup in neutral or acid media;[9b] in addition, four new species were isolated, characterized as dark purple $(\eta^5\text{-}C_5H_5)CoC_4B_7H_{11}$ (IV) and three isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ (brown V, greenish brown VI, and dark greenish brown VII). The recovered yields of these new species were low (1–2% each), but the same compounds (and in one case a *C*-tetramethyl derivative) were later obtained in larger yield as described below.

In an attempt to optimize the formation of IV and the isomers V–VII, the base strength of the KOH–ethanol solution was varied between 5 and 15 wt % of KOH; the yields of all four species were highest when a 9–10% solution was employed, and fell off rapidly with higher or lower base concentrations.

B. Synthesis from $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ and $(\eta^5\text{-}C_5H_5)$-$CoC_2B_4H_6$. The results just described strongly implied that the tetracarbon products IV, V, VI, and VII were formed from the dicarbon monocobalt species I and II, which are the initial products of the $C_2B_4H_7^-$–$CoCl_2$–$C_5H_5^-$ reaction. This was proved to be the case by subjecting pure samples of $(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ (I) and $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ (II) to the ethanolic KOH treatment, which produced the identical tetracarbon metallocarboranes in somewhat higher yield (Table I). Moreover, as the yield data show, it seemed to make little difference which cobaltacarborane, I or II, was employed as
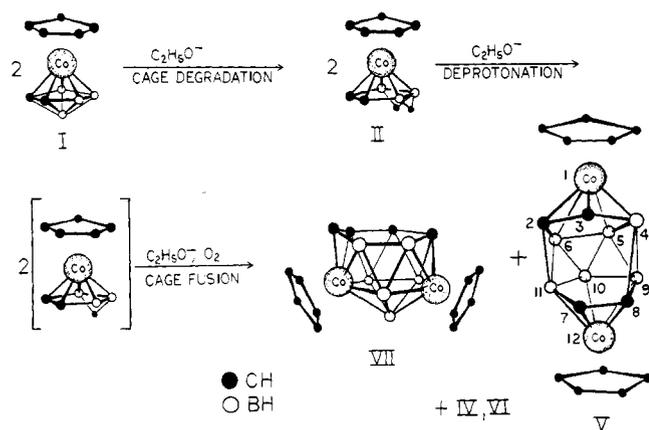
Figure. 1. Conversion of the parent dicarbon metallocarboranes I and II to the tetracarbon species IV–VII. The corresponding treatment of the C,C'-dimethyl derivative of I yields a single tetracarbon product, VIII (a C-tetramethyl derivative of V). The structure of V shown here is based on the established structure of VIII.

Table I. Yields[a] of Metallocarborane Products from Reactions with KOH/Ethanol

| | cobaltacarborane reagents[b] | | | | |
	I	II	IA 23 °C	IA 10 °C	IIA
Tetracarbon Metallocarboranes					
$(C_5H_5)CoC_4B_7H_{11}$ (IV)	3	5			
$(C_5H_5)_2Co_2C_4B_6H_{10}$ isomers (V, VI, VII)[c]	4	4			
$(C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ (VIII)			8	17	10
Other Products					
$1,7,2,3\text{-}(C_5H_5)_2Co_2C_2B_3H_5$ (III)	7	7			
$1,7,2,3\text{-}(C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (IIIA)			8	6	12
$1,2,4,5\text{-}(C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (IX)			2	2	2
$4\text{-}\sigma\text{-}C_2H_5O\text{-}1,7,2,3\text{-}(C_5H_5)_2Co_2(C\text{-}H_3)_2C_2B_3H_2$ (X)			1	1	1

[a] Average percent yield (based on cobaltacarborane consumed) from two or more experiments at 23 °C for each reaction. [b] I = $(C_5H_5)CoC_2B_4H_6$, II = $(C_5H_5)CoC_2B_3H_7$, IA = $(C_5H_5)Co(CH_3)_2C_2B_4H_4$, IIA = $(C_5H_5)Co(CH_3)_2C_2B_3H_5$. [c] Combined yield of three isomers.

starting material; the mixture of tetracarbon species produced was very nearly the same in each case. This observation is consistent with the fact, reported earlier,[9b] that the reaction of I in ethanolic KOH generates II (together with 1,7,2,3-$(\eta^5C_5H_5)_2Co_2C_2B_3H_5$, III). Consequently, the cage-fusion process which is responsible for the formation of the tetracarbon species operates primarily, if not entirely, on the nido system II. These conclusions were further supported in studies of the C,C'-dimethyl cobaltacarborane derivatives described below.

Synthesis of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$. It is frequently the case that reactions of *nido*-2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$ and its monoanion $(CH_3)_2C_2B_4H_5^-$ generate more stable products, and in higher yield, than do the corresponding reactions of the parent carborane.[10] Accordingly, studies of the cage fusion of the cobaltacarboranes I and II were extended to their C,C'-dimethyl derivatives $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ (IA) and $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ (IIA), both obtained from the reaction[9b] of $Na^+(CH_3)_2C_2B_4H_5^-$ with $CoCl_2$ and $Na^+C_5H_5^-$ in THF. As summarized in Table I, the treatment

of IA or IIA with 9–10% ethanolic KOH gave a C-tetramethyl tetracarbon cobaltacarborane, $(\eta^5\text{-}C_5H_5)_2Co_2\text{-}(CH_3)_4C_4B_6H_6$ (VIII), which is analogous to the parent $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ isomers generated from I and II. However, in contrast to the latter reaction, only one isomer of the tetramethyl species was produced; moreover, no methylated counterpart of $(\eta^5\text{-}C_5H_5)CoC_4B_7H_{11}$ (IV) was detected. These differences can be attributed to both steric and inductive (cage-stabilizing) effects of the methyl substituents; for example, the observation of a single tetracarbon metallocarborane product in the reactions of IA and IIA suggests that only one mechanistic pathway is operative, whereas in the reactions of the parent systems (I, II) there are evidently several competing processes (e.g., fusion at different locations on the cage frameworks) leading to a mixture of isomers V, VI, and VII.[11]

The other isolated products of the base treatment of IA and IIA were the known triple-decked sandwich 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (IIIA); an isomer of the latter system, 1,2,4,5-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (IX); and a trace of 4-σ-C_2H_5O-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_2$ (X), a *B*-ethoxy derivative of the triple-decked sandwich. The structure of X was assigned from its NMR spectra by comparison with those of the unsubstituted compound (IIIA),[9b] which has ^{11}B resonances at δ +50.4 [B(5)] and +9.0 [B(4,6)] and ^1H signals at δ +4.33 (C_5H_5) and +2.55 (CH_3). The singlet in the boron spectrum of X indicates attachment of the ethoxy group at a boron position, and the lack of symmetry in the central C_2B_3 ring identifies the substituted atom as B(4) [equivalent to B(6)]. Compounds IIIA[9b] and IX[7] have been reported previously, as have their parent species.[9b,12]

As was the case with the reactions of I and II with ethanolic KOH, nearly identical product mixtures were obtained from the closo species, IA, and the open-cage system, IIA (Table I). Again, the obvious inference is that IA is converted to IIA in an early stage of the reaction so that the cage fusion process involves primarily IIA whether or not one starts with that compound. This hypothesis was confirmed by examining the products of the KOH/ethanol treatment of IA at several stages; TLC analysis of aliquot portions of the reaction mixture revealed that IIA is formed very quickly (within 5 min) and persists for 20 min, but is absent after 30 min, by which time the reaction has reached completion. Thus, the tetracarbon products clearly are generated by fusion of two nido dicarbon moieties (II or IIA) (or, more precisely, by fusion of the anions derived from II or IIA by removal of a bridging proton[9b]). Figure 1 illustrates the sequence of events in schematic fashion for the formation of the tetracarbon products from the parent species I and II.

The choice of solvent is important in this system; replacement of ethanol with H_2O or THF gave unsatisfactory results in that no tetracarbon metallocarboranes were obtained. Although an extensive effort to optimize the formation of VIII was not made, we did observe that when the reaction was conducted at 10 °C (the lowest temperature at which it proceeded at a reasonable rate), the yield of VIII was 17%, twice that obtained at 23 °C. While this falls well short of the 70–80% yield of $(CH_3)_4C_4B_8H_8$ produced on air oxidation of $[(CH_3)_2C_2B_4H_4]_2FeH_2$,[3b] it is noteworthy that VIII is the primary isolable product at 10 °C and hence cage fusion is a major process, if not in fact the dominant one, in this reaction system.

Structural Characterization of Tetracarbon Cobaltacarboranes. The boron-11 and proton pulse Fourier transform NMR data on compounds IV, V, VI, VII, and VIII are listed in Tables II and III, while infrared spectra and high-resolution mass measurements are given in Tables IV and V. The ^{11}B and ^1H NMR spectra indicate that all boron and carbon atoms (except for the C-methyl compounds) contain terminal hydrogen

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

compd	solvent	δ, ppm^a (*J*, Hz)	rel area
(C₅H₅)CoC₄-B₇H₁₁ (IV)	CD₂Cl₂	15.8 (168), 8.9 (160), 2.5 (168), −4.5 (160), −8.5 (168), −11.5 (136)	1:1:2:1: 1:1
(C₅H₅)₂Co₂-C₄B₆H₁₀			
isomer V	CDCl₃	34.8 (145), −12.4 (150)	2:4
isomer VI	CDCl₃	69.1 (155), −15.8 (135)	2:4
isomer VII	CDCl₃	30.6 (130), 21.5 (165)^b, 15.4 (180), 12.5 (155),^{b} 9.9 (140), −7.8 (170)	1:1:1:1: 1:1
(C₅H₅)₂Co₂-(CH₃)₄C₄-B₆H₆ (VIII)	CDCl₃	30.9 (137), −12.8 (122)	2:4
σ-C₂H₅O-(C₅H₅)₂-Co₂(CH₃)₂-C₂B₃H₂ (X)	CDCl₃	43.7 (120), 24.8,^{c} 11.9 (128)	1:1:1

^{a} Parts per million relative to BF₃·OC₂H₅ with positive sign indicating shift to lower field (less shielding). ^{b} Estimated from overlapping resonances. ^{c} Singlet.

Table III. 100-MHz ^{1}H FT NMR Data (CDCl₃ Solution)

compd	δ,^{a} ppm (rel area)	assignment
IV^b	5.54	C₅H₅
V	5.24 (2)	CH
	5.05 (5)	C₅H₅
VI	6.73 (2)	CH
	5.02 (5)	C₅H₅
VII^b	4.97 (1)	C₅H₅
	4.95 (1)	C₅H₅
VIII	4.80 (5)	C₅H₅
	2.64 (3)	CH₃
	1.71 (3)	CH₃
X	4.33 (10)	C₅H₅
	4.08 (2)^c	CH₂CH₃
	2.78 (3)	CH₃
	2.49 (3)	CH₃
	1.47 (3)^d	CH₂CH₃

^{a} Parts per million relative to (CH₃)₄Si with positive sign indicating shift to lower field. ^{b} Cage CH resonances not observed. ^{c} Quartet. ^{d} Triplet.

atoms, thus effectively eliminating the possibility that some or all of these molecules might be linked-cage species such as $(\eta^5$-C₅H₅)₂Co₂C₂B₃H₄–C₂B₃H₆. (In VII, the four C–H signals were too weak to be observed but the structure was determined crystallographically, as described below).

Each of these products consequently is formulated as a 12-vertex single-cage system. From electron-counting rules,[13] all of them contain 28 skeletal bonding electrons (based on a two-electron contribution from each Co(C₅H₅) and BH unit and three from each CH), and are therefore $(2n + 4)$-electron cages for which nido (open) structures are predicted. It is apparent from the NMR spectra that V and VI have possible symmetry while IV and VII are completely asymmetric; beyond this, unambiguous structural assignments are not possible from the spectroscopic data. Consequently, a crystallographic study of VII was undertaken, revealing the geometry depicted in Figure 2. Tables VI–IX contain the relevant data from the structural analysis.

As shown, the molecule does contain a 12-vertex nido cage as expected. The gross geometry is that of a 13-vertex closo polyhedron[14] with one vertex eliminated to created a six-membered open face. The two cobalt atoms, interestingly, are located in different types of coordination sites; Co(2) is linked to six other framework atoms while Co(4) is only five-coordinate.
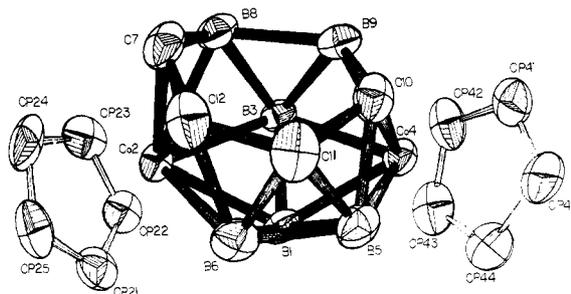
Figure 2. ORTEP drawing of the molecular structure of (η^5-C₅H₅)₂-Co₂C₄B₆H₁₀ (VII) with hydrogen atoms omitted. The enantiomer depicted here is different from that in Figures 1 and 3.

Table IV. Infrared Absorptions^a

IV	2960 (m), 2935 (s), 2860 (m), 2520 (vs), 1730 (m), 1460 (m), 1420 (m), 1375 (w), 1330 (m), 1175 (w), 1070 (m), 1020 (sh, s), 965 (w), 935 (w), 845 (sh, m), 825 (m)
V	2930 (m), 2860 (m), 2505 (br, s), 1650 (w), 1600 (w), 1370 (w), 1310 (w), 1185 (w), 1060 (m), 825 (br, s)
VI	2950 (m), 2920 (s), 2860 (m), 2520 (br, s), 1725 (s), 1460 (w), 1430 (w), 1285 (s), 1215 (s), 1130 (m), 1075 (m), 1005 (w), 965 (w), 860 (w), 840 (m), 800 (w)
VII	2950 (w), 2930 (m), 2860 (m), 2500 (s), 1725 (w), 1605 (w), 1460 (w), 1360 (w), 1200 (w), 1120 (w), 1070 (w), 1010 (m), 930 (w), 825 (s), 750 (m)
VIII	3040 (w), 2930 (m), 2845 (w), 2465 (vs), 1435 (m), 1420 (m), 1380 (w), 1360 (m), 1355 (sh, w), 1115 (sh, w), 1030 (w), 1010 (m), 985 (w), 825 (br, s)
X	2920 (s), 2840 (m), 1675 (w), 1590 (w), 1540 (m), 1460 (m), 1310 (w), 1145 (m), 825 (br, m), 810 (m), 805 (sh, w)

^{a} CH₂Cl₂ solution vs. CH₂Cl₂ in cm^{-1}.

Table V. High-Resolution Mass Measurements^a

compd	formula	mass calcd	obsd
IV	^{12}C₉^{1}H₁₇^{11}B₇^{59}Co$^+$	261.1314	261.1308
VI^b	^{12}C₁₄^{1}H₂₁^{11}B₆-^{59}Co₂$^+$	373.0866	373.0864
VIII	^{12}C₁₈^{1}H₂₉^{11}B₆-^{59}Co₂$^+$	429.1492	429.1490
X	^{12}C₁₆^{1}H₂₄^{11}B₃-^{59}Co₂^{16}O$^+$	383.0770	383.0775

^{a} Mass of P + 1 ion (protonated parent ion) obtained in methane or argon–water under chemical ionizing conditions. ^{b} Isomeric with V and VII.

The locations of the four cage carbon atoms were established from (1) the characteristically short C–C bond lengths [1.423 (8) to 1.530 (8) Å] which are distinguishable from the longer C–B and B–B interactions; (2) the fact that replacement of the carbon scattering factors with those of boron for atoms C(7), C(10), C(11), and C(12) produced a higher residual (*R*) factor; and (3) the slightly larger isotropic temperature factor which is produced, as expected, when these atoms are treated as carbons rather than borons.

The fact that all four carbon atoms occupy contiguous positions on the open face is particularly noteworthy. The cage framework in (η^5-C₅H₅)Fe(CH₃)₄C₄B₇H₈ (Figure 3a) has an isoelectronic and isostructural relationship to VII, yet only three of its four framework carbons are on the open face, the remaining one being as far from the open face as possible. We

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Co(2)	0.323 61 (6)	−0.0700 (1)	0.291 50 (7)	0.004 80 (4)	0.0147 (1)	0.005 31 (5)	0.0016 (2)	0.002 92 (8)	0.0029 (2)
Co(4)	0.166 62 (6)	0.2208 (1)	0.130 45 (7)	0.004 21 (4)	0.0146 (1)	0.006 22 (6)	0.0014 (2)	0.001 39 (9)	0.0020 (2)
C(7)	0.4429 (5)	0.0445 (10)	0.2628 (6)	0.0039 (4)	0.024 (2)	0.0095 (6)	0.001 (1)	0.0032 (7)	0.009 (2)
C(10)	0.3003 (5)	0.1911 (9)	0.0838 (5)	0.0064 (4)	0.018 (1)	0.0058 (4)	0.002 (1)	0.0048 (7)	0.006 (1)
C(11)	0.3378 (5)	0.0321 (10)	0.0740 (5)	0.0086 (5)	0.022 (2)	0 0057 (4)	0.006 (1)	0.0080 (7)	0.002 (1)
C(12)	0.4054 (5)	−0.0335 (9)	0.1672 (6)	0.0073 (4)	0.019 (1)	0.0096 (5)	0.008 (1)	0.0089 (7)	0.005 (2)
CP(21)	0.2515 (6)	−0.2598 (9)	0.3292 (6)	0.0100 (6)	0.016 (1)	0.0098 (6)	−0.003 (2)	0.0060 (9)	0.006 (2)
CP(22)	0.2438 (5)	−0.1454 (10)	0.3968 (6)	0.0085 (5)	0.022 (1)	0.0073 (5)	−0.001 (2)	0.0065 (8)	0.006 (2)
CP(23)	0.3399 (7)	−0.0977 (100	0.4507 (6)	0.0148 (7)	0.022 (2)	0.0051 (5)	−0.007 (2)	0.0032 (10)	0.006 (2)
CP(24)	0.4122 (6)	−0.1915 (11)	0.4133 (7)	0.0075 (6)	0.032 (2)	0.0126 (7)	0.003 (2)	−0.0000 (11)	0.030 (2)
CP(25)	0.3555 (7)	−0.2915 (10)	0.3373 (7)	0.0144 (8)	0.017 (1)	0.0109 (7)	0.009 (2)	0.0071 (12)	0.012 (2)
CP(41)	0.1149 (6)	0.4381 (9)	0.0986 (7)	0.0069 (5)	0.017 (1)	0.0134 (8)	0.009 (1)	0.0014 (10)	0.008 (2)
CP(42)	0.0876 (5)	0.3858 (10)	0.1904 (7)	0.0086 (5)	0.019 (1)	0.0125 (7)	0.014 (1)	0.0097 (9)	0.009 (2)
CP(43)	0.0263 (5)	0.2564 (11)	0.1605 (7)	0.0057 (4)	0.030 (2)	0.0147 (8)	0.012 (1)	0.0087 (9)	0.011 (2)
CP(44)	0.0169 (5)	0.2335 (11)	0.0485 (9)	0.0031 (4)	0.026 (2)	0.0204 (11)	0.005 (1)	−0.0038 (11)	0.010 (2)
CP(45)	0.0749 (6)	0.3459 (11)	0.0109 (7)	0.0065 (5)	0.023 (2)	0.0121 (7)	0.009 (2)	−0.0032 (10)	0.006 (2)
B(1)	0.1874 (5)	0.002 (1)	0.1842 (6)	0.0050 (4)	0.016 (1)	0.0052 (5)	0.000 (1)	0.0005 (8)	−0.005 (1)
B(3)	0.2512 (5)	0.152 (1)	0.2704 (6)	0.0039 (4)	0.013 (1)	0.0063 (5)	−0.000 (1)	0.0022 (7)	−0.003 (1)
B(5)	0.2099 (6)	0.046 (1)	0.0563 (6)	0.0072 (5)	0.020 (2)	0.0047 (5)	−0.002 (2)	0.0011 (9)	0.001 (2)
B(6)	0.2726 (7)	−0.098 (1)	0.1266 (6)	0.0088 (6)	0.016 (2)	0.0054 (5)	−0.002 (2)	0.0036 (9)	−0.005 (2)
B(8)	0.3855 (6)	0.155 (1)	0.3030 (7)	0.0046 (4)	0.021 (2)	0.0069 (6)	−0.005 (1)	0.0010 (8)	0.003 (2)
B(9)	0.3135 (6)	0.266 (1)	0.1934 (7)	0.0049 (4)	0.015 (1)	0.0079 (6)	−0.003 (1)	0.0021 (8)	−0.004 (2)
H(1)	0.1200	−0.0580	0.1821	5.0000					
H(3)	0.2248	0.1833	0.3375	5.0000					
H(5)	0.1657	0.0243	−0.0192	5.0000					
H(6)	0.2625	−0.2093	0.0977	5.0000					
H(7)	0.5106	0.0268	0.2975	5.0000					
H(8)	0.4256	0.2174	0.3685	5.0000					
H(9)	0.3325	0.3795	0.2130	5.0000					
H(10)	0.3000	0.2511	0.0244	5.0000					
H(11)	0.3549	0.0009	0.0111	5.0000					
H(12)	0.4352	−0.1199	0.1448	5.0000					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
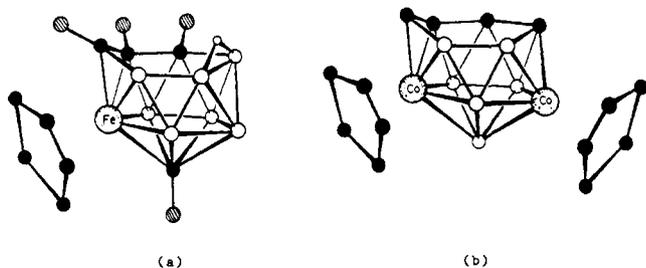
Figure 3. Comparison of the structures of $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$[5] (a) and $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$, isomer VII (b).

note, however, that the iron compound was prepared via an entirely different route,[5] i.e., by reaction of the $(CH_3)_4$-$C_4B_8H_8{}^{2-}$ ion with $FeCl_2$ and $Na^+C_5H_5{}^-$. The gross cage geometries of the two compounds are quite similar, as illustrated in Figure 3, where both cages are shown in the same enantiomorphic form. In each molecule the unique carbon atom C(7) occupies a three-coordinate vertex which is well outside the plane of the remaining five atoms on the open face; in VII, C(7) is 0.402 Å from this plane, and in $(\eta^5\text{-}C_5H_5)$-$Fe(CH_3)_4C_4B_7H_8$ it is 0.507, Å removed.

The six framework atoms bonded to Co(2) are not quite coplanar (Table IX), with C(7) and C(12) nearly 0.2 Å out of plane, but the calculated least-squares plane through these atoms is nearly parallel (within 4.7°) to the cyclopentadienyl ring CP(21)-CP(25). Similarly, Co(4) is sandwiched between the rings B(1)-B(3)-B(9)-C(10)-B(5) and CP(41)-CP(45) whose planes are within 3.5° of being parallel.

The resolution of the molecular structure of VII might have been expected to shed light on the structures of its isomers V

Table VII. Selected Interatomic Distances (Å)

Co(2)-Co(4)	3.711 (2)	C(10)-C(11)	1.530 (8)
Co(2)-B(1)	2.156 (5)	C(11)-C(12)	1.473 (8)
Co(2)-B(3)	2.209 (6)	C(7)-C(10)	2.987 (7)
Co(2)-B(6)	2.123 (6)	B(8)-C(11)	3.115 (8)
Co(2)-C(7)	2.025 (5)	B(9)-C(12)	3.017 (9)
Co(2)-B(8)	2.179 (7)	Co(2)-CP(21)	2.078 (6)
Co(2)-C(12)	2.189 (5)	Co(2)-CP(22)	2.048 (5)
Co(4)-B(1)	2.083 (7)	Co(2)-CP(23)	2.055 (6)
Co(4)-B(3)	2.025 (6)	Co(2)-CP(24)	2.076 (5)
Co(4)-B(5)	1.999 (7)	Co(2)-CP(25)	2.093 (7)
Co(4)-B(9)	2.024 (5)	Co(4)-CP(41)	2.083 (6)
Co(4)-C(10)	2.060 (5)	Co(4)-CP(42)	2.083 (6)
B(1)-B(3)	1.841 (8)	Co(4)-CP(43)	2.058 (5)
B(1)-B(5)	1.808 (8)	Co(4)-CP(44)	2.081 (5)
B(1)-B(6)	1.763 (8)	Co(4)-CP(45)	2.093 (6)
B(3)-B(8)	1.780 (7)	CP(21)-CP(22)	1.373 (8)
B(3)-B(9)	1.778 (8)	CP(22)-CP(23)	1.406 (8)
B(5)-B(6)	1.703 (9)	CP(23)-CP(24)	1.459 (10)
B(5)-C(10)	1.770 (8)	CP(24)-CP(25)	1.429 (10)
B(5)-C(11)	1.708 (8)	CP(25)-CP(21)	1.424 (9)
B(6)-C(11)	1.704 (9)	CP(41)-CP(42)	1.413 (8)
B(6)-C(12)	1.859 (9)	CP(42)-CP(43)	1.431 (9)
C(7)-B(8)	1.432 (9)	CP(43)-CP(44)	1.452 (10)
C(7)-C(12)	1.423 (8)	CP(44)-CP(45)	1.434 (9)
B(8)-B(9)	1.836 (9)	CP(45)-CP(41)	1.418 (9)
B(9)-C(10)	1.555 (8)		

and VI and the monocobalt compound IV. However, to deduce the relationship between these species is not a simple matter. Recent work in our laboratory has disclosed several cases of electronically equivalent species (even isomers) which have turned out to have different gross geometries. For example, crystallographic analysis of four isomers[6,15] of the 14-vertex

Table VIII. Selected Bond Angles (deg)

B(1)–Co(2)–B(3)	49.9 (2)	B(3)–B(9)–Co(4)	64.0 (2)
B(1)–Co(2)–B(6)	48.7 (2)	Co(4)–B(9)–C(10)	68.9 (3)
B(3)–Co(2)–B(8)	47.9 (2)	Co(4)–C(10)–B(5)	62.4 (3)
B(6)–Co(2)–C(12)	51.1 (2)	Co(4)–C(10)–B(9)	66.4 (3)
C(7)–Co(2)–B(8)	39.6 (2)	B(5)–C(10)–C(11)	61.8 (4)
C(7)–Co(2)–C(12)	39.2 (2)	B(5)–C(11)–B(6)	59.9 (4)
B(1)–Co(4)–B(3)	53.2 (2)	B(5)–C(11)–C(10)	66.0 (4)
B(1)–Co(4)–B(5)	52.5 (2)	B(6)–C(11)–C(12)	71.2 (4)
B(3)–Co(4)–B(9)	52.1 (2)	Co(2)–C(12)–B(6)	62.6 (2)
B(5)–Co(4)–C(10)	51.7 (2)	Co(2)–C(12)–C(7)	64.2 (3)
B(9)–Co(4)–C(10)	44.7 (2)	B(6)–C(12)–C(11)	60.2 (4)
Co(2)–B(1)–B(3)	66.6 (2)	C(12)–C(7)–B(8)	123.0 (5)
B(3)–B(1)–Co(4)	61.8 (3)	C(7)–B(8)–B(9)	109.3 (5)
Co(4)–B(1)–B(5)	61.3 (3)	B(8)–B(9)–C(10)	114.4 (5)
B(5)–B(1)–B(6)	56.9 (4)	B(9)–C(10)–C(11)	120.6 (5)
B(6)–B(1)–Co(2)	64.7 (3)	C(10)–C(11)–C(12)	117.5 (5)
B(1)–B(3)–Co(2)	63.6 (3)	C(11)–C(12)–C(7)	124.2 (5)
Co(2)–B(3)–B(8)	65.2 (3)	CP(21)–Co(2)–CP(22)	38.9 (2)
B(8)–B(3)–B(9)	62.1 (3)	CP(22)–Co(2)–CP(23)	40.1 (2)
B(9)–B(3)–Co(4)	63.9 (3)	CP(23)–Co(2)–CP(24)	41.4 (3)
Co(4)–B(3)–B(1)	65.0 (3)	CP(24)–Co(2)–CP(25)	40.1 (3)
B(1)–B(5)–Co(4)	66.1 (3)	CP(25)–Co(2)–CP(21)	39.9 (2)
Co(4)–B(5)–C(10)	66.0 (3)	CP(41)–Co(4)–CP(42)	39.6 (2)
C(10)–B(5)–C(11)	52.1 (3)	CP(42)–Co(4)–CP(43)	40.4 (3)
C(11)–B(5)–B(6)	59.9 (4)	CP(43)–Co(4)–CP(44)	41.1 (3)
B(6)–B(5)–B(1)	60.2 (3)	CP(44)–Co(4)–CP(45)	40.2 (3)
B(1)–B(6)–Co(2)	66.6 (3)	CP(45)–Co(4)–CP(41)	39.7 (3)
Co(2)–B(6)–C(12)	66.3 (3)	CP(25)–CP(21)–CP(22)	108.6 (6)
C(12)–B(6)–C(11)	48.6 (3)	CP(21)–CP(22)–CP(23)	110.7 (6)
C(11)–B(6)–B(5)	60.2 (4)	CP(22)–CP(23)–CP(24)	106.2 (6)
B(5)–B(6)–B(1)	62.9 (4)	CP(23)–CP(24)–CP(25)	107.1 (6)
Co(2)–C(7)–B(8)	76.0 (3)	CP(24)–CP(25)–CP(21)	107.4 (6)
Co(2)–C(7)–C(12)	76.6 (3)	CP(45)–CP(41)–CP(42)	111.4 (7)
Co(2)–B(8)–C(7)	64.4 (3)	CP(41)–CP(42)–CP(43)	106.6 (7)
Co(2)–B(8)–B(3)	66.9 (3)	CP(42)–CP(43)–CP(44)	107.7 (6)
B(3)–B(8)–B(9)	58.9 (3)	CP(43)–CP(44)–CP(45)	108.3 (7)
B(3)–B(9)–B(8)	59.0 (3)	CP(44)–CP(45)–CP(41)	105.9 (7)

Table IX. Selected Molecular Planes

atom	deviation, Å	atom	deviation, Å
Plane 1: B(1), B(3), B(6), C(7), B(8), C(12) $-0.1109x - 0.6832y + 0.7218z = 1.3669$			
B(1)	−0.090	B(8)	0.019
B(3)	0.106	C(12)	0.184
B(6)	−0.028	Co(2)	−1.344
C(7)	−0.193		
Plane 2: B(1), B(3), B(5), B(9), C(10) $0.7585x - 0.5992y + 0.2562z = 2.0633$			
B(1)	−0.052	B(9)	0.057
B(3)	0.005	C(10)	−0.096
B(5)	0.086	Co(4)	1.395
Plane 3: B(8), B(9), C(10), C(11), C(12) $0.8884x + 0.4365y - 0.1421z = 3.9672$			
B(8)	−0.036	C(11)	−0.084
B(9)	0.012	C(12)	0.066
C(10)	0.042	C(7)	0.402
Plane 4: CP(21), CP(22), CP(23), CP(24), CP(25) $-0.1897x - 0.6620y + 0.7251z = 4.1123$			
CP(21)	0.000	CP(24)	−0.002
CP(22)	−0.002	CP(25)	0.001
CP(23)	0.003	Co(2)	1.682
Plane 5: CP(41), CP(42), CP(43), CP(44), CP(45) $-0.7881x + 0.5797y - 0.2072z = 1.0052$			
CP(41)	0.009	CP(44)	0.012
CP(42)	−0.001	CP(45)	−0.013
CP(43)	−0.007	Co(4)	−1.687

	Angles between Planes		
Planes	Angle, deg	Planes	Angle, deg
1,2	59.3	2,4	64.0
1,3	60.0	2,5	3.5
1,4	4.7	3,4	55.9
1,5	62.7	3,5	65.3
2,3	67.9	4,5	67.4

system $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ revealed three different types of polyhedra, including one closo and two nido structures. Even more relevant to the present case is the structure of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6\text{-}OC_2H_5$, which has a 28-electron, 12-vertex cage system analogous to VII, yet exhibits markedly different geometry.[16] The species $(CH_3)_4C_4B_8H_8$,[4] $(CH_3)_2\text{-}B_{10}H_{11}^-$,[18] and $(C_6H_5)_2C_2B_{10}H_{11}^-$,[19] all of which are also 28-electron, 12-vertex polyhedra, exhibit still different cage structures. The problem posed by the divergence of these 12-vertex nido systems has been considered elsewhere,[1] and other cases of structural dissimilarity in electronically analogous cage systems have been reported also.[20]

Obviously, then, it cannot safely be assumed that IV, V, VI, and VII have a common gross geometry based on the same polyhedron, even though V, VI, and VII are isomers and IV differs only by formal replacement of a BH with a $(\eta^5\text{-}C_5H_5)$ unit. Indeed, it now appears that isomer V is structurally quite distinct from VII, as shown in Figure 1. The structure depicted for V was determined from an x-ray investigation[21] of the tetramethyl species VIII, which is evidently a C-tetramethyl derivative of V as indicated by the close similarity of the ^{11}B NMR spectra. The structure of VIII (V) is closely similar to that of the complex $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6\text{-}OC_2H_5$,[16] mentioned above. Both molecules can be viewed as derivatives of $(CH_3)_4C_4B_8H_8^4$ in which one and two BH units, respectively, have been replaced by $Co(C_5H_5)$ groups; however, in each metal species the central C–C distance C(3)–C(7) is distinctly nonbonding (~2.8 Å), in contrast to $(CH_3)_4C_4B_8H_8$ in which it is a bonding interaction (1.53 Å). The cage structure of VIII (and V) contains a C_2 axis bisecting the B(5)–B(10) bond, and is consistent with the ^{11}B and ^1H data provided that the area-4 ^{11}B resonance is assigned to two superimposed area-2 peaks [probably arising from B(5,10) and B(6,9)].

The cage geometries of the remaining dicobalt isomer (VI) and the monocobalt species (IV) have not been established. The question of their structural relationship to V and VII, and the mechanism of formation of all these species via oxidative cage fusion, will be discussed together with the details of the structure determination of VIII in a separate article.[21]

Summary

We have now reported three substantially different types of reaction systems in which the formation of large cages from small cages via oxidative fusion is observed: (1) the conversion

of $[(CH_3)_2C_2B_4H_4]_2FeH_2$[3] and $[(CH_3)_2C_2B_4H_4]_2CoH$[7] to $(CH_3)_4C_4B_8H_8$; (2) the synthesis of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4$-$C_4B_7H_6\text{-}OC_2H_5$[17] from $[(CH_3)_2C_2B_4H_4]_2FeH_2$, $CoCl_2$, and C_5H_6 in ethanolic KOH; and (3) the formation of species containing CoC_4B_7 and $Co_2C_4B_6$ cage systems from $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$, $(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$, and their C-methyl derivatives by reaction with ethanolic KOH, as described here. Still other reactions involving cage fusion have been observed in the course of our work and are currently under investigation.

The overall picture suggested by these findings is that oxidative cage fusion is a process of general occurrence in carborane and metallocarborane chemistry. Indeed, certain long-known reactions in the boron hydride area, such as the preparation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ from $B_3H_8^-$ ion,[22] may also be loosely described as oxidative fusions (numerous other examples can be cited); however, such reactions are very different from the carborane fusions, in which transition metals play a major role. It is important to note that the formation of the polyborane $B_nH_n^{2-}$ anions from BH_4^- and $B_3H_8^-$ requires elevated temperature, in contrast to the carborane fusion reactions, which occur at or below room temperature. Of course, oxidative *couplings* of borane cages (e.g., the conversion of $B_{10}H_{10}^{2-}$ ion to the linked cage $B_{20}H_{18}^{2-}$ ion,[23] the electrochemical formation[24] of $(CB_9H_9)_2^{2-}$ from $CB_9H_{10}^-$, and the joining of two $C_2B_9H_{12}^-$ units to produce $(C_2B_9H_{11})_2^{2-}$[25]) are also known, but are distinct from fusion in that the products are dimeric rather than single cage systems.

A secondary aspect of the present study, but not an inconsequential one, is that the new products IV, V, VI and VII are the first tetracarbon metallocarboranes without attached substituents; all of the tetracarbon species we have reported heretofore have contained a methyl group on each cage carbon atom. Thus the new compounds allow examination of some important aspects of the chemistry of the tetracarbon systems—such as metalation and introduction of functional groups at carbon—which were precluded in the C-tetramethyl derivatives. Studies in this area will be reported at a later date.

Experimental Section

Materials. The metallocarboranes $1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$, $1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$, $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$, and $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ were prepared and purified as described elsewhere.[9b] All other reagents were commercially obtained (reagent grade) and used as received.

Spectra and Chromatography. ^{11}B and ^1H pulse Fourier transform NMR spectra were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer, and high-resolution mass measurements were conducted on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high-resolution measurements were performed under chemical ionizing conditions in methane or argon-water. Thin and preparative layer chromatography was conducted in air on precoated plates of silica gel F-254 (Brinkmann Instruments, Inc.).

Preparation of $(\eta^5\text{-}C_5H_5)CoC_4B_7H_{11}$ **(IV) and** $(\eta^5\text{-}C_5H_5)_2$-$Co_2C_4B_6H_{10}$ **Isomers (V, VI, VII). A. From** $Na^+C_2B_4H_7^-$, $CoCl_2$, **and** $Na^+C_5H_5^-$. A 4.1-mmol sample of $Na^+C_2B_4H_7^-$[26] was allowed to react with 12.0 mmol of $CoCl_2$ (anhydrous) and 12.0 mmol of $Na^+C_5H_5^-$ in THF at 23 °C for ~10 h. After removal of solvent via vacuum distillation, 30 mL of 10% KOH in ethanol was added to the reaction residue and the mixture was magnetically stirred for about 1 h in air. After addition of 20 mL of water to the reaction mixture followed by extraction with methylene chloride, the extracts were collected from a separation funnel. The collected extracts were dried over anhydrous MgSO$_4$, and the solvent was distilled off under reduced pressure to yield a dark brown reaction residue. This material was redissolve in methylene chloride and filtered through a sintered glass filter funnel which was packed with a 1-cm layer of 70-230 mesh silica gel, and eluted with methylene chloride. Four 10-15-mL frac-

tions were collected and the solvent was removed. The resulting residue was applied to several TLC plates and eluted with a 1:1 hexane-methylene chloride mixture. Several previously reported compounds, $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (III, 12 mg), $1,2,3\text{-}(\eta^5\text{-}C_5H_5)$-$CoC_2B_4H_6$ (I, 2 mg), and $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ (II, 4 mg), were collected. A dark purple band was characterized as $(\eta^5\text{-}C_5H_5)$-$CoC_4B_7H_{11}$ (IV, R_f 0.13, 12 mg). A brown band was characterized as $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ (V, R_f 0.56, 2 mg); a greenish brown band was VI, isomeric with V, R_f 0.46, 8 mg; a dark greenish-brown band was VII, isomeric with V and VI, R_f 0.42, 4 mg. Compounds V, VI, and VII had very similar mass spectra with high mass cutoffs at m/e 372 corresponding to $^{59}Co_2^{12}C_{14}^{11}B_6^{1}H_{20}^+$ and a parent ion intensity pattern characteristic of a six-boron species having a normal $^{11}B/^{10}B$ isotope distribution. Other characterization data are presented in Tables II-V.

When a similar experiment was conducted using 5 or 15% KOH-ethanol solutions in place of the 10% reagent, the yields of the tetracarbon species IV, V, VI, and VII were reduced by 80-90%.

B. From $1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ **(II) or** $1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ (I). The treatment of each of these compounds with ethanolic KOH followed the same procedure as that described below for the reactions of $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ (IIA) or $1,2,3\text{-}(\eta^5\text{-}C_5H_5)$-$Co(CH_3)_2C_2B_4H_4$ (IA). Average yields of the isolated products are given in Table I.

Preparation of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ **from** $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ **(IIA) or** $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ **(IA).** All experiments were conducted either at room temperature or at 10 °C, and followed a sequence similar to that described here for the treatment of IA with ethoxide ion at 10 °C. The same products were obtained from IA as from IIA, except for an unidentified trace compound having a mass spectroscopic cutoff at m/e 354 which was obtained only from IA.

A 9.0% solution of KOH in ethanol (13.0 mmol of OH$^-$), prepared by dissolving 0.7277 g of KOH pellets in 7.362 g of C_2H_5OH, was added to a pure sample of IA (429 mg, 1.92 mmol), resulting in a rapid darkening in color. The reaction mixture was stirred in air at 10 °C and aliquots were extracted for TLC analysis after 5, 10, 20, and 30 min. The 5-min analysis disclosed the presence of IIA, which persisted through 20 min but did not appear in the 30-min analysis. After 30 min the reaction was quenched with 12 mL of 1 M aqueous HCl. The resulting dark brown suspension was extracted with 200 mL of CH_2Cl_2, dried over MgSO$_4$, and stripped of solvent. Subsequent purification by TLC (50% hexane-50% CH_2Cl_2) gave green $1,2,4,5$-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (IX), R_f 0.73, 8 mg (2% yield); orange $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (IIIA), R_f 0.53, 20 mg (6%); brown $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ (VIII), R_f 0.46, 72 mg (17%); and red-brown $4\text{-}\sigma\text{-}C_2H_5O\text{-}1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2$-$(CH_3)_2C_2B_3H_2$ (X), R_f 0.17, 4 mg (1%). Traces of other products were observed mass spectroscopically, and m/e cutoffs and probable compositions are as follows: 360 (seven-boron pattern), $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$; 488 (six-boron pattern), $(\eta^5\text{-}C_5H_5)_2Co_2[(CH_3)_2C_2B_3H_3]_2CoH$; 354 (three- or four-boron pattern), unidentified.

The reaction temperature influences yields of products, as summarized in Table I. At temperatures below 5 °C the reaction rate is extremely slow.

The use of alternative base reagents was examined to a limited extent. Treatment of IIA with 10% KOH in H_2O gave very little reaction in 40 min at 25 °C, probably owing to low solubility of the metallocarborane substrate. Treatment of IA with 10% KOH in THF at 25 °C gave IIA in 40% yield, but the latter material was not observed to react further.

X-Ray Crystallographic Study of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ **(VII).** A dark green, flat plate with maximum dimensions of 0.43 × 0.24 × 0.10 mm was grown by the vapor diffusion of pentane into a methylene chloride solution of VII. From precession photographs it was determined that this crystal was of high quality and suitable for data collection. Crystal data: $Co_2C_{14}B_6H_{20}$, mol wt 371.05; space group $P2_1/c$; $Z = 4$; $a = 13.606$ (10), $b = 8.970$ (3), $c = 13.050$ (4) Å, $\beta = 102.95$ (4)°; $V = 1552$ (2) Å^3; μ(Mo Kα) = 22.17 cm^{-1}; $\rho_c = 1.598$ g cm^{-3}; $F(000) = 752$. For this crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then employed in the program INDEX to obtain an orientation matrix for data collection and also provide approximate cell constants. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω scan

technique and found to be acceptable. Systematic absences for $k = 2n + 1$ on $0k0$ and $l = 2n + 1$ on $h0l$ uniquely determine the space group to be $P2_1/c$ (no. 14).

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo $K\alpha$ radiation from a highly oriented graphite crystal monochromator. The θ-2θ scan technique was used to record the unique intensities for all reflections for which $1° < 2\theta < 49.00°$. Scan widths (SW) were calculated from the formula SW = $A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in the width of each peak due to $K\alpha_1$ and $K\alpha_2$ splitting. The values of A and B, respectively, were 0.6 and 0.3°. This calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) was then calculated as NC = TOT -2 (BG1 + BG2) where TOT is the estimated peak intensity. Reflection data were considered insignificant if the intensities registered less than ten counts above background on a rapid prescan, such reflections being rejected automatically by the computer. The intensities of four standard reflections were monitored at 100-reflection intervals and showed no systematic trends. The raw intensity data were corrected for Lorentz-polarization effects and their standard deviations were calculated in the usual manner from counting statistics ($\rho = 0.03$).[27] This resulted in 1794 reflections of which 1586 had $F_o^2 > 3 \sigma (F_o^2)$. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the solution and refinement of the structural parameters.

Solution and Refinement of the Structure. A three-dimensional Patterson map was used to locate the positions of the two cobalt atoms. Refinement of their coordinates and isotropic thermal parameters reduced R to 0.28 where R is defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. An electron density map was then phased with the two cobalt atoms, yielding the positions of the remaining 20 nonhydrogen atoms. Isotropic refinement of all atoms, with boron scattering factors employed for each atom other than cobalt, reduced R to 0.117. At this point a detailed examination was made of the bond lengths and angles within the cage in an attempt to locate the carbons. Assuming that bond lengths in general increase in the order C–C < C–B < B–B, aided by comparison with a closely related structure, $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4\text{-}C_4B_7H_8$,[5] we concluded that the four carbons are adjacent and located on the six-membered open face of the cage (vide supra). Further isotropic refinement with correct scattering factors for the boron and carbon atoms further reduced the residual to 0.114. Additional confirmation that the carbon atoms were correctly identified was the fact that the isotropic temperature factors of each of these atoms increased as expected when their scattering factors were changed from boron to carbon. The average increase was 1.29 Å^2 with a range of 1.24–1.37 Å^2.

At this point an absorption correction was made (transmission factors: minimum 0.66, maximum 0.91). Further isotropic refinement reduced R to 0.098. All atoms were then refined anisotropically to an R value of 0.056.

A new electron density difference map yielded nine of the ten hydrogens associated with the cage carbon and boron atoms. Several cycles of refinement during which the hydrogen positional parameters (B fixed at 5.0 Å^2) were allowed to vary, followed by another map, served to locate the last hydrogen. Unfortunately, however, several of the hydrogen atoms refined to unacceptably long distances from the atom to which they were bonded. Consequently, all hydrogens were reset to reasonable distances (B–H, 1.05 Å; C–H, 0.05 Å)[28] and their positional as well as thermal parameters were held fixed. (It should be noted that when they were permitted to vary during refinement, all B–H distances were greater than 1.05 Å and all C–H lengths were less than 0.95 Å, tending to further confirm the choice of carbon and boron atoms in the cage.)

Additional refinement reduced R to its final value of 0.046. In the last cycle of refinement the largest parameter shift was less than 0.01 times its estimated standard deviation. The weighted R factor, defined as $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, was 0.055. The estimated standard deviation of an observation of unit weight was 2.15. A final difference electron density map was featureless.

Least-squares refinement was based on F, and the function minimized was $w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[29] and those for hydrogen from Stewart.[30] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[31] values for $\Delta F'$ and $\Delta F''$. The computing system and programs used are described elsewhere.[32] After the final cycle of refinement, a structure factor calculation including those reflections for which $F_o^2 < 3\sigma(F_o^2)$ gave an R of 0.053 indicating that the structure determination would not be improved by accurately recollecting these reflections. A table of structure factors is available, as is a list of the shortest intermolecular contacts (see paragraph at end of paper regarding supplementary material). There are no abnormally short intermolecular distances.

Supplementary Material Available: Listing of observed and calculated structure factors and a table of intermolecular contacts (8 pages). Ordering information is given on any current masthead page.

References and Notes

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