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Tetracarbon Metallacarboranes. 11.[1] 11-Vertex Nido Cages: Structures of Two Isomers of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$

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The structures of 2,7,8,10,11- and 9,7,8,10,11- $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$ were determined by single-crystal X-ray diffraction. Both compounds contain 11-vertex CoC_4B_6 cages having icosahedral-fragment (capped-pentagonal-antiprism) geometry with all four skeletal carbon atoms on the five-membered open face. In the 2,7,8,10,11 system (isomer I) the metal atom is located in the lower (CoB_4) belt adjacent to two cage carbon atoms, while in the 9,7,8,10,11 species (isomer II), the metal is on the open rim of the cage. Both complexes contain an idealized mirror plane, which in the case of isomer II is crystallographically imposed. The two isomers were obtained in equal amounts by reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with $(CH_3)_4C_4B_8H_8$ as previously reported, and the present investigation confirms the structures postulated earlier from NMR spectra. In contrast to many other four-carbon carborane and metallacarborane systems, there are no unusual distortions or anomalous features in the skeletal cage structures. However, the three framework C–C interactions are of nearly equal length in isomer II, which has a CoC_4 open face; in isomer I, the central C–C bond is substantially shorter than the other two, suggesting a localization of electron density in the central C–C link which probably involves a π-type interaction with cobalt. Crystal data for $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$, isomer I: mol wt 303, space group $P2_1/c$, $Z = 4$; $a = 14.638$ (3) Å; $b = 8.701$ (3) Å; $c = 13.483$ (7) Å; $\beta = 115.74$ (4)°; $V = 1547$ Å^3; $R = 0.041$ for 1309 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for isomer II: space group *Pnma*; $Z = 4$; $a = 13.252$ (3) Å; $b = 12.310$ (3) Å; $c = 9.521$ (2) Å; $V = 1553$ Å^3; $R = 0.044$ for 1009 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Insertion of transition metals into the carborane $(CH_3)_4C_4B_8H_8$ and its homologues $R_4C_4B_8H_8$ ($R = C_2H_5$ or $n\text{-}C_3H_7$) has generated a variety of four-carbon metallacarboranes exhibiting a wide range of structures.[1-5] If the carborane is first reduced to the $(CH_3)_4C_4B_8H_8^{2-}$ dianion,[6] metal insertion can be carried out under mild conditions with minimal loss of boron; the isolated products are typically 14-vertex $M_2C_4B_8$, 13-vertex MC_4B_8, or 12-vertex MC_4B_7 cage systems, where M is iron, cobalt, or nickel.

The insertion of cobalt directly into neutral $(CH_3)_4C_4B_8H_8$ requires more energetic conditions which tend to induce loss of boron from the cage. In the reaction[3] with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ the isolated products include two 11-vertex species having only six boron atoms:

$$(CH_3)_4C_4B_8H_8 + (\eta^5\text{-}C_5H_5)Co(CO)_2 \xrightarrow{h\nu} \underset{\substack{\text{isomer I, yellow (6\%)}\\ \text{isomer II, golden (6\%)}}}{(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6} + \underset{\text{isomer I, red-brown (10\%)}}{(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7}$$

The metallacarboranes obtained in this reaction were purified by plate chromatography in air and characterized from ^{11}B and ^1H NMR, IR, and mass spectra.[3] The structure of the CoC_4B_7 species, an open 12-vertex cage, is known from X-ray crystallographic studies[7] (two other structurally dissimilar isomers of this complex are also known).[1,5] However, the structures of the two CoC_4B_6 metallacarborane products could not be determined with certainty but were assigned[3] from NMR data under the assumption that the gross geometry in both cases was that of an 11-vertex nido cage, i.e., a capped pentagonal antiprism; it was also considered likely that, in each species, the four framework carbon atoms were located on the open rim of the cage. Although the NMR evidence suggested mirror symmetry for both isomers, there are several possible geometries meeting these conditions,[3] and in neither case could a unique structure be assigned. Because of this ambiguity, as well as the fact that no MC_4B_6 cage systems had previously been characterized, X-ray crystal structure determinations were conducted on both compounds.

Results and Discussion

Final positional and thermal parameters are given in Tables I and II, while bond lengths,, bond angles, and important mean planes are given in Tables III–VIII. Figure 1 depicts the cage geometries and numbering for the two isomers, and the molecular structure and unit cell packing are shown in Figures 2 and 3. The geometries of both cage systems are exactly as proposed earlier[3] on the basis of ^{11}B and ^1H pulse Fourier transform NMR data; this is partly fortuitous since, as noted above, the specific structures of isomers I and II could not be assigned unambiguously from NMR data alone. As had been previously assumed,[3] in each isomer the four skeletal $C\text{–}CH_3$ units are located on the open face of an 11-vertex icosahedral fragment. In isomer I the $(\eta^5\text{-}C_5H_5)Co$ moiety occupies vertex 2, below the open rim, while in isomer II it is on the rim together with the four carbons. Isomer II thus provides the first example of a nido-borane species in which boron is completely absent from the open face; the molecule can be described as a pyramidal B_6H_6 unit fused face-to-face to a CoC_4 metallacycle. In both structures there is a molecular mirror plane through the metal atom and the apex boron [B(1)], but only in isomer II is this symmetry crystallographically imposed.

The difference in cobalt atom placement in the two isomers has significant consequences in the skeletal C–C bonding, as reflected in the large difference in the "central" carbon–carbon vs. "end" carbon–carbon distances in isomer I. Thus, the C(7)–C(11) (central) bond length is only 1.457 (6) Å, in contrast to the C(7)–C(8) and C(10)–C(11) (end) distances which are 1.564 (8) and 1.559 (6) Å, respectively. In isomer II, by contrast, the two independent framework C–C bond lengths are virtually statistically identical: 1.530 (5) and 1.518 (4) Å for C(7)–C(7′) (corresponding to C(7)–C(11)) and C(7)–C(8), respectively. Moreover, these distances in isomer II are very close to the *average* of the cage C–C lengths in isomer I (1.527 Å). These observations are quite consistent with extensively delocalized bonding in the C_4Co open rim in isomer II (supporting the "cobaltacycle" model suggested

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(C_5H_5)Co(CH_3)_4C_4B_6H_6$, Isomer I[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	−0.16494 (5)	0.1822 (1)	0.04049 (6)	3.04 (2)	3.12 (3)	3.12 (2)	0.15 (4)	1.48 (2)	−0.13 (4)
C(P1)	−0.0370 (4)	0.2403 (8)	0.1799 (5)	4.5 (3)	5.5 (4)	3.4 (3)	−1.0 (3)	0.4 (2)	−0.2 (3)
C(P2)	−0.1039 (4)	0.3639 (8)	0.1478 (5)	4.7 (2)	5.5 (4)	5.5 (3)	−1.8 (3)	2.7 (2)	−2.9 (3)
C(P3)	−0.1225 (5)	0.4074 (8)	0.0439 (5)	5.7 (3)	3.4 (3)	4.9 (3)	−1.1 (3)	1.3 (2)	−0.0 (3)
C(P4)	−0.0627 (4)	0.3115 (9)	0.0095 (4)	4.7 (2)	5.8 (4)	4.6 (2)	−2.4 (3)	2.7 (2)	−1.5 (3)
C(P5)	−0.0121 (4)	0.2105 (8)	0.0916 (5)	3.2 (2)	5.3 (4)	6.7 (3)	−0.0 (3)	1.9 (2)	−0.8 (3)
C(7)	−0.3118 (3)	0.1511 (7)	0.0219 (4)	3.4 (2)	3.2 (3)	3.0 (2)	0.6 (2)	2.0 (1)	−0.1 (2)
C(8)	−0.3919 (4)	0.0812 (8)	−0.0885 (4)	2.8 (2)	4.2 (3)	3.5 (2)	0.4 (2)	1.6 (2)	0.6 (2)
C(10)	−0.2731 (4)	−0.1278 (6)	0.0355 (4)	3.7 (2)	2.7 (3)	3.4 (2)	0.5 (2)	1.9 (1)	0.1 (2)
C(11)	−0.2447 (3)	0.0325 (7)	0.0923 (4)	2.9 (2)	3.6 (3)	2.4 (2)	0.2 (2)	1.5 (1)	0.1 (2)
C(M7)	−0.3513 (4)	0.2784 (7)	0.0692 (5)	4.1 (2)	3.8 (4)	5.6 (3)	0.4 (2)	2.6 (2)	−0.5 (3)
C(M8)	−0.4982 (4)	0.1479 (9)	−0.1428 (5)	3.0 (2)	7.5 (5)	5.2 (3)	0.8 (3)	0.9 (2)	2.0 (3)
C(M10)	−0.2596 (4)	−0.2705 (7)	0.1055 (5)	5.3 (3)	3.2 (3)	5.3 (3)	0.7 (3)	2.3 (2)	1.0 (3)
C(M11)	−0.2105 (4)	0.0313 (8)	0.2167 (4)	4.5 (2)	5.2 (4)	3.2 (2)	0.1 (3)	1.8 (2)	−0.1 (3)
B(1)	−0.2087 (5)	0.0417 (9)	−0.0969 (5)	3.7 (2)	4.4 (4)	2.9 (2)	0.3 (3)	1.9 (2)	−0.2 (3)
B(3)	−0.2975 (4)	0.1807 (9)	−0.1044 (5)	4.2 (2)	3.1 (3)	2.9 (2)	0.3 (3)	1.8 (2)	0.8 (3)
B(4)	−0.3406 (5)	0.0052 (10)	−0.1675 (5)	3.8 (3)	5.3 (4)	2.6 (3)	−0.6 (3)	1.0 (2)	0.1 (3)
B(5)	−0.2593 (5)	−0.1389 (8)	−0.0835 (5)	5.0 (3)	3.3 (4)	3.7 (2)	−0.5 (3)	2.7 (2)	−1.1 (3)
B(6)	−0.1658 (5)	−0.0527 (8)	0.0330 (5)	3.6 (2)	3.5 (3)	3.3 (2)	1.0 (3)	1.9 (2)	0.2 (3)
B(9)	−0.3740 (5)	−0.0999 (10)	−0.0739 (5)	3.9 (3)	5.1 (4)	3.1 (3)	−0.9 (3)	1.4 (2)	−1.0 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(P1)	−0.019 (3)	0.190 (7)	0.245 (4)	5 (1)	H(72)	−0.372 (4)	0.374 (7)	0.020 (4)	6 (2)
H(P2)	−0.133 (3)	0.397 (6)	0.189 (4)	5 (1)	H(73)	−0.408 (4)	0.247 (7)	0.085 (4)	6 (2)
H(P3)	−0.168 (4)	0.483 (8)	−0.007 (4)	7 (2)	H(81)	−0.498 (4)	0.249 (8)	−0.144 (4)	7 (2)
H(P4)	−0.070 (3)	0.308 (6)	−0.064 (4)	4 (1)	H(82)	−0.525 (4)	0.131 (7)	−0.213 (4)	7 (2)
H(P5)	0.030 (4)	0.134 (7)	0.092 (4)	7 (2)	H(83)	−0.541 (4)	0.112 (8)	−0.115 (5)	8 (2)
H(1)	−0.164 (3)	0.042 (6)	−0.144 (3)	3 (1)	H(101)	−0.192 (4)	−0.296 (7)	0.150 (4)	6 (2)
H(3)	−0.320 (3)	0.292 (6)	−0.143 (3)	3 (1)	H(102)	−0.287 (4)	−0.359 (7)	0.054 (4)	6 (2)
H(4)	−0.384 (3)	0.005 (6)	−0.255 (3)	4 (1)	H(103)	−0.303 (4)	−0.262 (7)	0.150 (4)	7 (2)
H(5)	−0.242 (3)	−0.253 (6)	−0.106 (3)	3 (1)	H(111)	−0.267 (3)	−0.005 (7)	0.229 (4)	5 (2)
H(6)	−0.099 (3)	−0.105 (5)	0.080 (3)	2 (1)	H(112)	−0.148 (3)	−0.031 (6)	0.252 (4)	5 (1)
H(9)	−0.437 (3)	−0.182 (6)	−0.106 (4)	5 (1)	H(113)	−0.194 (4)	0.130 (7)	0.252 (4)	6 (2)
H(71)	−0.303 (3)	0.312 (6)	0.134 (3)	3 (1)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}l^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)/2]$. [b] For all hydrogen atoms, standard isotropic B values are reported.

above) and with a relatively more localized bond between C(7) and C(11) in isomer I. This shortened C–C bond may participate in a π interaction between the C(7)–C(11) link and the cobalt adjacent to it;[8] similar localized carbon–carbon bonding has been proposed in other metallacarboranes (especially those involving C_2B_3 or C_2B_4 ligands face coordinated to metals), on the basis of short (1.4–1.5 Å) C–C distances[10a] and NMR observations.[10b]

The two cage systems are formally assigned 26 skeletal valence electrons based on contributions of two from each BH and $Co(C_5H_5)$ unit and three from each C–CH_3 group and hence are $(2n + 4)$-electron polyhedra (n is the number of skeletal atoms, in this case 11). The observed structures are thus in full agreement with the skeletal electron-count theory,[11] which predicts nido geometry (i.e., a closed polyhedron minus

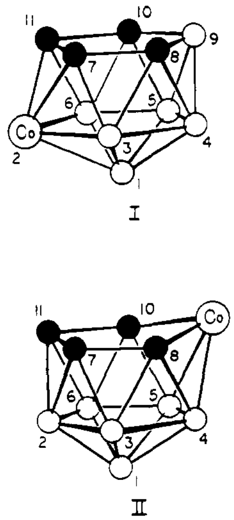

Figure 1. Cage geometry and numbering for isomers I and II: ○, BH; ●, CCH_3.

one vertex) for $(2n + 4)$-electron systems. These isomers are analogous to the prototype 11-vertex nido boron cluster, the $B_{11}H_{11}^{4-}$ (ollide) ion, which has not been detected as a free species though it does exist in complexes[12] such as $(\eta$-$C_5H_5)NiB_{11}H_{11}^-$. This geometry is also exhibited by the $C_2B_9H_{11}^{2-}$ (dicarbollide) ion and by numerous metallaboranes and metallacarboranes, all of which are formal 26-electron cages. X-ray crystal structures have been reported for some

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(8) A reviewer has taken issue with this suggestion on the grounds that the Dewar–Chatt–Duncanson (DCD) model for metal–alkene/alkyne bonding predicts lengthening, rather than shortening, of the C–C bond due to donation of electron density from the metal into a C–C π^* orbital. While this is an interesting point, it seems inapplicable in this case because (1) the structural and electronic dissimilarities between metal–alkene/alkyne complexes and metallacarborane cage systems are so great as to invalidate comparison on such a simple basis, (2) the DCD model applies only to low-valent, late-transition series metals[9] (which Co(III) clearly is not), and (3) shortening of the C(7)–C(11) bond in I relative to II *must* be associated with the placement of cobalt in the cage, this being the only structural difference in the two isomers. The conclusion that a local Co–C_2 interaction is involved seems plausible, if not inescapable.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(C_5H_5)Co(CH_3)_4C_4B_6H_6$, Isomer II[a,b]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.10572 (9)	0.2500 (0)	0.0581 (1)	3.10 (4)	4.10 (4)	2.43 (3)	0.0000 (0)	−0.07 (5)	0.0000 (0)
C(P1)	0.2277 (5)	0.1938 (5)	−0.0585 (7)	4.7 (3)	6.2 (3)	3.5 (2)	0.6 (3)	1.2 (3)	−0.4 (3)
C(P2)	0.1322 (5)	0.1584 (6)	−0.1186 (7)	5.4 (3)	8.1 (4)	3.7 (2)	−1.3 (3)	0.5 (3)	−2.4 (3)
C(P3)	0.0811 (7)	0.2500 (0)	−0.1582 (9)	4.3 (4)	12.1 (8)	2.0 (3)	0.0 (0)	−0.6 (3)	0.0 (0)
C(7)	0.1101 (4)	0.1877 (4)	0.3552 (5)	2.9 (2)	3.5 (2)	2.8 (2)	−0.3 (2)	−0.2 (2)	0.3 (2)
C(8)	0.0952 (4)	0.1386 (4)	0.2101 (6)	3.1 (2)	2.9 (2)	3.4 (2)	−0.2 (2)	−0.0 (2)	−0.0 (2)
C(M7)	0.1773 (5)	0.1286 (6)	0.4602 (7)	4.5 (3)	5.9 (3)	4.0 (3)	0.6 (3)	−0.2 (3)	1.5 (3)
C(M8)	0.1394 (5)	0.0274 (5)	0.1856 (8)	5.7 (3)	3.6 (3)	6.4 (4)	0.8 (3)	−0.3 (3)	−0.7 (3)
B(1)	−0.0800 (7)	0.2500 (0)	0.2783 (11)	2.8 (4)	6.9 (6)	3.4 (4)	0.0 (0)	0.0 (3)	0.0 (0)
B(2)	0.0006 (7)	0.2500 (0)	0.4225 (10)	2.3 (3)	6.6 (6)	2.6 (4)	0.0 (0)	0.3 (3)	0.0 (0)
B(3)	−0.0096 (5)	0.1344 (6)	0.3193 (8)	3.4 (3)	4.5 (3)	4.2 (3)	−1.2 (3)	0.1 (3)	0.8 (3)
B(4)	−0.0174 (5)	0.1762 (6)	0.1426 (7)	3.1 (3)	4.8 (3)	3.6 (3)	−1.0 (3)	−0.3 (3)	0.0 (3)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(P1)	0.285 (4)	0.147 (5)	−0.027 (6)	6 (2)	H(M71)	0.174 (4)	0.160 (5)	0.541 (6)	5 (2)
H(P2)	0.111 (4)	0.084 (5)	−0.124 (6)	5 (1)	H(M72)	0.245 (4)	0.118 (5)	0.430 (7)	6 (2)
H(P3)	0.016 (7)	0.250 (0)	−0.199 (10)	7 (3)	H(M73)	0.154 (4)	0.052 (5)	0.476 (6)	6 (2)
H(1)	−0.160 (6)	0.250 (0)	0.308 (8)	5 (2)	H(M81)	0.114 (4)	−0.002 (4)	0.095 (5)	4 (1)
H(2)	−0.023 (6)	0.250 (0)	0.531 (8)	4 (2)	H(M82)	0.122 (4)	−0.028 (5)	0.264 (6)	5 (1)
H(3)	−0.027 (4)	0.053 (4)	0.347 (5)	4 (1)	H(M83)	0.206 (4)	0.028 (5)	0.179 (6)	5 (1)
H(4)	0.442 (4)	0.119 (4)	0.434 (6)	4 (1)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}l^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)/2]$. [b] For all hydrogen atoms, standard isotropic *B* values are reported.

Table III. Bond Distances (Å) in $(C_5H_5)Co(CH_3)_4C_4B_6H_6$, Isomer I

	Cage Framework		
Co–B(1)	2.075 (6)	B(4)–C(8)	1.683 (7)
Co–B(3)	2.071 (5)	B(4)–B(9)	1.789 (8)
Co–B(6)	2.046 (6)	B(5)–B(6)	1.742 (8)
Co–C(7)	2.071 (4)	B(5)–B(9)	1.771 (8)
Co–C(11)	2.063 (4)	B(5)–C(10)	1.705 (7)
B(1)–B(3)	1.746 (8)	B(6)–C(10)	1.715 (7)
B(1)–B(4)	1.772 (8)	B(6)–C(11)	1.824 (7)
B(1)–B(5)	1.780 (8)	C(7)–C(8)	1.564 (6)
B(1)–B(6)	1.783 (8)	C(7)–C(11)	1.457 (6)
B(3)–B(4)	1.728 (9)	C(8)–B(9)	1.596 (8)
B(3)–C(7)	1.822 (7)	B(9)–C(10)	1.588 (7)
B(3)–C(8)	1.721 (7)	C(10)–C(11)	1.559 (6)
B(4)–B(5)	1.760 (9)		
	$Co(C_5H_5)$ Group		
Co–C(P1)	2.059 (5)	C(P4)–C(P5)	1.354 (7)
Co–C(P2)	2.066 (5)	C(P5)–C(P1)	1.412 (7)
Co–C(P3)	2.051 (6)	C(P1)–H(P1)	0.92 (2)
Co–C(P4)	2.055 (5)	C(P2)–H(P2)	0.88 (2)
Co–C(P5)	2.049 (5)	C(P3)–H(P3)	0.97 (2)
C(P1)–C(P2)	1.391 (8)	C(P4)–H(P4)	0.95 (2)
C(P2)–C(P3)	1.360 (7)	C(P5)–H(P5)	0.91 (2)
C(P3)–C(P4)	1.424 (7)	⟨C–H⟩(C_5H_5)	0.93
	$C–CH_3$ Groups		
C(M7)–C(7)	1.512 (6)	C(M8)–H(82)	0.86 (2)
C(M8)–C(8)	1.517 (6)	C(M8)–H(83)	0.92 (2)
C(M10)–C(10)	1.519 (6)	C(M10)–H(101)	0.96 (2)
C(M11)–C(11)	1.527 (6)	C(M10)–H(102)	0.99 (2)
C(M7)–H(71)	0.90 (2)	C(M10)–H(103)	1.05 (2)
C(M7)–H(72)	1.03 (2)	C(M11)–H(111)	0.96 (2)
C(M7)–H(73)	0.98 (2)	C(M11)–H(112)	0.98 (2)
C(M8)–H(81)	0.88 (2)	C(M11)–H(113)	0.96 (2)
		⟨C–H⟩(CH_3)	0.96
	B–H		
B(1)–H(1)	1.10 (2)	B(5)–H(5)	1.10 (2)
B(3)–H(3)	1.08 (2)	B(6)–H(6)	1.01 (2)
B(4)–H(4)	1.07 (2)	B(9)–H(9)	1.10 (2)
		⟨B–H⟩	1.08
	Nonbonded Distances on Open Face		
C(7)–B(9)	2.499 (7)	C(8)–C(11)	2.491 (6)
C(7)–C(10)	2.481 (6)	B(9)–C(11)	2.499 (7)
C(8)–C(10)	2.570 (6)		

Table IV. Bond Distances (Å) in $(C_5H_5)Co(CH_3)_4C_4B_6H_6$, Isomer II[a]

	Cage Framework		
Co–C(8)	1.999 (3)	C(8)–B(4)	1.679 (5)
Co–B(4)	2.026 (4)	B(1)–B(2)	1.747 (7)
C(7)–C(7′)	1.530 (5)	B(1)–B(3)	1.753 (5)
C(7)–C(8)	1.518 (4)	B(1)–B(4)	1.786 (6)
C(7)–B(2)	1.751 (5)	B(2)–B(3)	1.735 (5)
C(7)–B(3)	1.742 (5)	B(3)–B(4)	1.763 (5)
C(8)–B(3)	1.728 (5)	B(4)–B(4′)	1.817 (8)
	$Co(C_5H_5)$ Group		
Co–C(P1)	2.074 (3)	C(P2)–C(P3)	1.372 (6)
Co–C(P2)	2.062 (4)	C(P1)–H(P1)	0.90 (2)
Co–C(P3)	2.096 (5)	C(P2)–H(P2)	0.91 (2)
C(P1)–C(P1′)	1.373 (8)	C(P3)–H(P3)	0.76 (2)
C(P1)–C(P2)	1.438 (5)	⟨C–H⟩(C_5H_5)	0.86
	$C–CH_3$ Groups		
C(M7)–C(7)	1.521 (5)	C(M7)–H(73)	0.94 (2)
C(M8)–C(8)	1.513 (5)	C(M8)–H(71)	0.96 (2)
C(M7)–H(71)	1.04 (2)	C(M8)–H(72)	1.09 (2)
C(M7)–H(72)	0.87 (2)	C(M8)–H(73)	0.98 (2)
		⟨C–H⟩(CH_3)	0.98
	B–H		
B(1)–H(1)	1.01 (2)	B(3)–H(3)	1.07 (2)
B(2)–H(2)	1.08 (2)	B(4)–H(4)	1.08 (2)
		⟨B–H⟩	1.06
	Nonbonded Distances on Open Face		
Co–C(7)	2.933 (3)	C(7)–C(8′)	2.548 (4)
C(8)–C(8′)	2.736 (4)		

[a] Primed atoms are related by mirror symmetry to the unprimed atoms of the same numbers.

of these, including several MC_2B_8 systems where M is cobalt,[13] silver,[14] or platinum,[15] as well as the metallaboranes $M(B_{10}H_{12})_2^{2-}$ (M = Ni,[16] Zn[17]) and $[(C_2H_5)_2P]_2HPtSB_9H_{10}$.[18] The same skeletal cage structure has been proposed for a number of other 26-electron, 11-vertex species including

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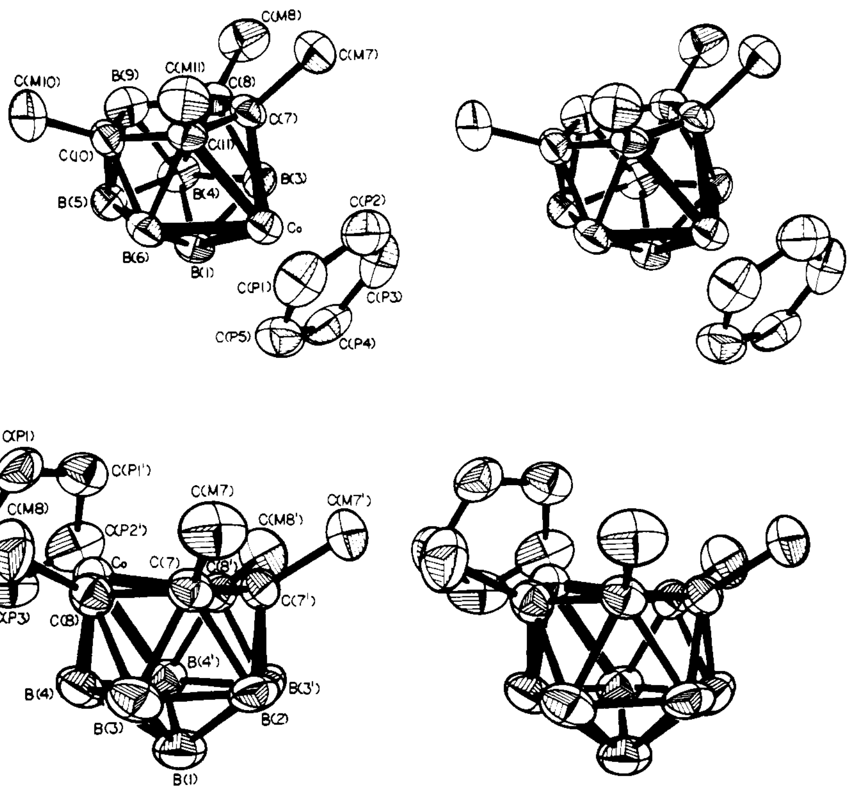

Figure 2. Stereoviews of molecular structures of isomer I (top) and isomer II (bottom). Hydrogen atoms are omitted for clarity. In isomer II, a crystallographic mirror plane bisects the molecule through Co, B(1), B(2), and C(P3).

Table V. Selected Bond Angles (Deg) in Isomer I

Atoms on Open Face			
C(8)-C(7)-C(11)	111.1 (4)	B(4)-B(9)-H(9)	120 (2)
C(8)-C(7)-C(M7)	114.8 (4)	B(5)-B(9)-H(9)	120 (2)
C(11)-C(7)-C(M7)	121.2 (4)	B(9)-C(10)-C(11)	105.2 (4)
Co-C(7)-C(M7)	114.9 (3)	B(9)-C(10)-C(M10)	121.3 (5)
B(3)-C(7)-C(M7)	120.7 (4)	C(11)-C(10)-C(M10)	119.4 (4)
C(7)-C(8)-B(9)	104.6 (4)	B(5)-C(10)-C(M10)	120.1 (4)
C(7)-C(8)-C(M8)	119.9 (4)	B(6)-C(10)-C(M10)	116.8 (4)
B(3)-C(8)-C(M8)	117.2 (4)	C(10)-C(11)-C(7)	110.7 (4)
B(4)-C(8)-C(M8)	119.4 (4)	B(6)-C(11)-C(M11)	120.7 (4)
B(9)-C(8)-C(M8)	121.1 (5)	C(10)-C(11)-C(M11)	115.1 (4)
C(8)-B(9)-C(10)	107.6 (4)	Co-C(11)-C(M11)	114.3 (3)
C(8)-B(9)-H(9)	122 (2)	C(7)-C(11)-C(M11)	121.8 (4)
C(10)-B(9)-H(9)	123 (2)		
Cyclopentadienyl Ring			
C(P5)-C(P1)-C(P2)	106.5 (5)	C(P3)-C(P4)-C(P5)	108.1 (5)
C(P1)-C(P2)-C(P3)	109.6 (5)	C(P4)-C(P5)-C(P1)	108.6 (5)
C(P2)-C(P3)-C(P4)	107.2 (5)	⟨C-C-C⟩	108.0 (2)
Methyl Groups			
C(7)-C(M7)-H(71)	112 (2)	C(10)-C(M10)-H(101)	118 (2)
C(7)-C(M7)-H(72)	112 (2)	C(10)-C(M10)-H(102)	107 (2)
C(7)-C(M7)-H(73)	113 (2)	C(10)-C(M10)-H(103)	110 (2)
⟨H-C(M7)-H⟩	106 (2)	⟨H-C(M10)-H⟩	107 (2)
C(8)-C(M8)-H(81)	112 (2)	C(11)-C(M11)-H(111)	107 (2)
C(8)-C(M8)-H(82)	111 (2)	C(11)-C(M11)-H(112)	108 (2)
C(8)-C(M8)-H(83)	115 (2)	C(11)-C(M11)-H(113)	116 (2)
⟨H-C(M8)-H⟩	106 (2)	⟨H-C(M11)-H⟩	108 (2)

Table VI. Selected Bond Angles (Deg) in Isomer II

Atoms on Open Face			
C(7')-C(7)-C(8)	113.4 (2)	C(7)-C(8)-C(M8)	116.8 (3)
C(7')-C(7)-C(M7)	118.1 (2)	Co-C(8)-C(M8)	118.4 (3)
C(8)-C(7)-C(M7)	119.2 (3)	B(3)-C(8)-C(M8)	112.5 (3)
B(2)-C(7)-C(M7)	116.6 (3)	B(4)-C(8)-C(M8)	122.5 (3)
B(3)-C(7)-C(M7)	118.8 (3)	C(8)-Co-C(8')	86.4 (2)
C(7)-C(8)-Co	112.3 (2)		
Cyclopentadienyl Ring			
C(P1')-C(P1)-C(P2)	107.5 (3)	C(P2)-C(P3)-C(P2')	109.4 (6)
C(P1)-C(P2)-C(P3)	107.7 (5)	⟨C-C-C⟩	108.2 (3)
Methyl Groups			
C(7)-C(M7)-H(71)	113 (2)	C(8)-C(M8)-H(81)	111 (2)
C(7)-C(M7)-H(72)	117 (2)	C(8)-C(M8)-H(82)	112 (2)
C(7)-C(M7)-H(73)	111 (2)	C(8)-C(M8)-H(83)	110 (2)
⟨H-C-H⟩	108 (2)	⟨H-C-H⟩	104 (2)

$(\eta^5\text{-}C_5H_5)CoC_2B_8H_{12}$,[19] the $(CH_3)_2InB_{10}H_{12}^-$ ion,[20] and $SeSB_9H_9$.[21]

In the present CoC_4B_6 isomeric systems, there are no marked distortions from the geometry of a capped pentagonal antiprism, other than those attributable to the large covalent radius of cobalt relative to boron and carbon. The open C_4B rim in isomer I is nearly planar, as is the "lower belt" Co–B(3)–B(4)–B(5)–B(6) (Table VII). In both isomers, the carborane face coordinated to the metal atom is essentially planar and roughly parallel to the C_5H_5 ring. The two molecules are thus well-defined 11-vertex baskets having single five-membered open faces, with no structural anomalies of the kind we have previously found in other four-carbon metallacarboranes, especially those of 12–14 vertices.[1,2,4–7] Moreover, to our knowledge, other crystallographically characterized 11-vertex nido cages are similarly well-behaved; in no case is there any unusual distortion, even in the presence of electron-rich metals such as platinum, which often produce unconventional cage geometries[11a] in systems where $n \neq 11$.

The strong preference for icosahedral-fragment geometry among 11-vertex, 26-electron systems is very much to be expected, given the predominance of closed icosahedral geometry among 12-vertex, 26-electron systems. Similarly, one expects 10-vertex, 26-electron species to adopt an arachno icosahedral-fragment cage structure corresponding to an icosahedron

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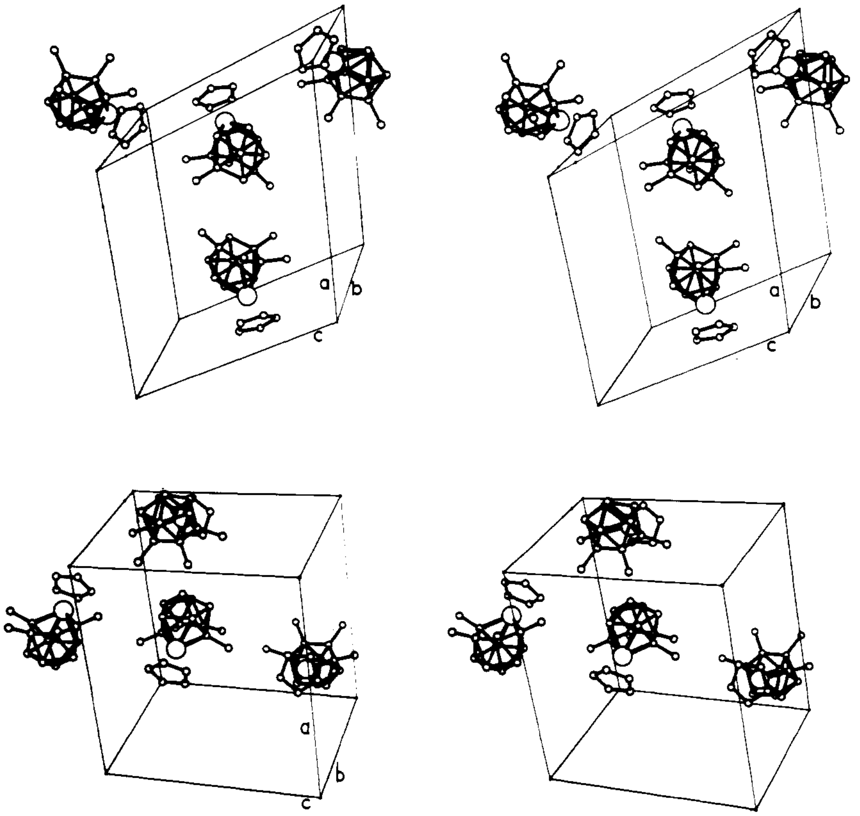

Figure 3. Stereoviews of unit cell packing of isomers I (top) and II (bottom).

Table VII

Selected Mean Planes in Isomer I

atom	dev, Å	atom	dev, Å
Plane 1 (Cyclopentadienyl Ring)			
$0.6630x + 0.6417y + 0.3855z = 1.1318$			
C(P1)	0.0051	C(P4)	−0.0066
C(P2)	−0.0095	C(P5)	0.0010
C(P3)	0.0099	Co	1.6829
Plane 2 (Cage Atoms Bonded to Co): B(1), B(3), B(6), C(7), C(11)			
$-0.5766x - 0.6852y - 0.4450z = 1.6745$			
B(1)	0.035	C(11)	0.010
B(3)	−0.029	Co	−1.451
B(6)	−0.028	C(M7)	−0.510
C(7)	0.012	C(M11)	−0.524
Plane 3 (Lower Belt): Co, B(3), B(4), B(5), B(6)			
$0.8645x + 0.0714y - 0.4976z = -2.4603$			
Co	0.037	B(5)	0.020
B(3)	−0.033	B(6)	−0.037
B(4)	0.013	B(1)	0.921
Plane 4 (Open Face): C(7), C(8), B(9), C(10), C(11)			
$0.8848x + 0.1185y - 0.4507z = -4.0982$			
C(7)	−0.018	Co	1.718
C(8)	0.049	C(M7)	−0.902
B(9)	−0.061	C(M8)	−0.679
C(10)	0.051	C(M10)	−0.666
C(11)	−0.021	C(M11)	−0.904

Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1,2	6.51	2,3	109.03
1,3	115.29	2,4	113.00
1,4	119.27	3,4	3.98

Table VIII

Selected Mean Planes in Isomer II

atom	dev, Å	atom	dev, Å
Plane 1 (Cyclopentadiene Ring)			
$0.4368x - 0.8996z = 1.8129$			
C(P1)	0.0057	C(P2′)	−0.0155
C(P1′)	0.0057	C(P3)	0.0196
C(P2)	−0.0155	Co	1.4009
Plane 2 (Lower Belt): B(2), B(3), B(3′), B(4), B(4′)			
$0.9967x - 0.0808z = -0.3378$			
B(2)	0.032	B(4)	0.009
B(3)	−0.025	B(4′)	0.009
B(3′)	−0.025	Co	1.690
Plane 3 (Cage Carbon Atoms)			
$0.9900x - 0.1412z = 0.9961$			
C(7)	0.000	C(M7)	0.743
C(7′)	0.000	C(M7′)	0.743
C(8)	0.000	C(M8)	0.630
C(8′)	0.000	C(M8′)	0.630
Co	0.343		
Plane 4 (Cage Atoms Bonded to Co)			
$0.3984x - 0.9172z = -1.3357$			
C(8)	0.000	Co	1.387
C(8′)	0.000	C(M8)	0.459
B(4)	0.000	C(M8′)	0.459
B(4′)	0.000		

Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1,2	59.47	2,3	3.48
1,3	55.99	2,4	61.89
1,4	2.42	3,4	58.41

minus two vertices (the $B_{10}H_{14}^{2-}$ ion provides one of the few examples). Electron-counting arguments[11,22] lead to the prediction that *any* 26-electron cluster will adopt the shape of an icosahedron (if $n = 12$) or an icosahedral fragment (if

$n < 12$). In striking contrast, when the number of skeletal valence electrons is 28, the situation is very different and there is no single dominant geometry; a number of earlier papers from our laboratory have dealt with this problem.[23]

The formation of the two $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$ isomers from $(CH_3)_3C_4B_8H_8$ and $(\eta\text{-}C_5H_5)Co(CO)_2$ has been discussed elsewhere.[3] Since $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ is also a product of the reaction, it has been proposed that loss of BH from this species followed by minor cage rearrangement (movement of one C–CH$_3$ unit) generates the CoC_4B_6 isomers. If the proposed scheme[3] is correct, then the facts that the two compounds are isolated in equal amounts and are known to be of similar oxidative and thermal stability suggest that the processes leading to their formation are roughly competitive. If this is the case, it would seem that the metal exhibits no strong preference between occupying a four-coordinate vertex on the open face, as in isomer II, as opposed to a five-coordinate vertex off the open face (isomer I). It is interesting to note that a third possible isomer, similar to I and II but with the cobalt in the apex (1) position, was not found among the products.[3] While the possibility of its presence in trace quantity cannot be excluded, this isomer is clearly not a major isolable product. Either it was formed in the reaction but subsequently rearranged (to I or II) before it could be detected, or it was not generated at all. Since there is no reason to expect such a species to rearrange under the mild conditions of workup, it is probable that its absence among the isolated products reflects the lack of a facile pathway for its formation from $(CH_3)_4C_4B_8H_8$. This idea is consistent with the scheme proposed earlier[3] and also conforms to the general principle that metal insertion into carboranes takes place at sites adjacent to framework carbon atoms; the hypothetical 1,7,8,9,10-isomer would have no cage metal-carbon bonds, an unprecedented situation in tetracarbon metallacarborane structures.

Experimental Section

Yellow plates of 2,7,8,10,11-$(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$ (isomer I) were grown by slow evaporation of a CH_2Cl_2 solution. A crystal was selected for data collection and mounted on a glass fiber for data collection. Crystal data: $CoC_{13}B_6H_{23}$; mol wt 303; space group $P2_1/c$; $Z = 4$; $a = 14.638$ (3) Å, $b = 8.701$ (3) Å, $c = 13.483$ (7) Å; $\beta = 115.74$ (4)°; $V = 1547$ Å^3; μ(Mo Kα) = 11.3 cm^{-1}; $\rho_{\text{calcd}} = 1.30$ g cm^{-3}; crystal dimensions (distances in mm from centroid) (100) 0.02, ($\bar{1}$00) 0.02, (011) 0.14, (0$\bar{1}\bar{1}$) 0.14, (01$\bar{1}$) 0.09, (0$\bar{1}$1) 0.09.

For this crystal the Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω scan technique and judged to be satisfactory. Systematic absences for $l = 2n + 1$ on $h0l$ and $k = 2n + 1$ on $0k0$ uniquely establish the space group as $P2_1/c$. for $Z = 4$ this is consistent with the molecular formula with the assumption of 19.3 Å^3 per nonhydrogen atom.

Deep golden plates of 9,7,8,10,11-$(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$ (isomer II) were grown by slow evaporation of an hexane solution. Data were collected on a crystal mounted on a glass fiber in an arbitrary orientation. Crystal data: $CoC_{13}B_6H_{23}$; mol wt 303; space group *Pnma*; $Z = 4$; $a = 13.252$ (3) Å, $b = 12.310$ (3) Å, $c = 9.521$ (2) Å; $V = 1553$ Å^3; μ(Mo Kα) = 11.3 cm^{-1}; $\rho_{\text{calcd}} = 1.32$ g cm^{-3}; crystal dimensions, given as above: (100) 0.225, ($\bar{1}$00) 0.225, (010) 0.09, (0$\bar{1}$0) 0.09 (001) 0.055, (00$\bar{1}$) 0.055. The same procedure as described for isomer I was followed to produce an orientation matrix and approximate cell constants. The initial choice of the centric space group *Pnma* instead of the acentric $Pna2_1$ was based on the mirror symmetry of the molecule as deduced from solution ^{1}H and ^{11}B NMR spectra.[3] In *Pnma* with $Z = 4$, the molecule is required to be on a special position, i.e., the mirror at $y = {}^1/_4$. This choice was later confirmed by the successful solution and refinement of the structure.

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 Kα radiation from a highly oriented graphite-crystal monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $1.4° \leq 2\theta \leq 47°$. Scan widths were calculated from the formula SW = $A + B \tan \theta$, where A is estimated from the mosaicity of the crystal and B compensates for the increase in the width of the peak due to Kα_1–Kα_2 splitting. The values of A and B respectively were 0.60 and 0.35 for both compounds. 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 integrated peak intensity. For each compound, the intensities of three standard reflections were monitored at intervals of 100 reflections and showed no systematic trends. Raw intensity data were corrected for Lorentz–polarization effects and their standard deviations were calculated in the usual manner from counting statistics ($p = 0.03$).[24] This resulted in 1749 reflections for isomer I, of which 1309 had $F_o^2 > 3\sigma(F_o^2)$, and in 1360 reflections for isomer II, of which 1009 had $F_o^2 > 3\sigma(F_o^2)$, after averaging of equivalent reflections. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of structural parameters.

Solution and Refinement of the Structures. For both compounds, three-dimensional Patterson syntheses were used to locate the metal atom, whose positions phased the data sufficiently to allow the location of other nonhydrogen atoms from difference Fourier maps. In each case, anisotropic refinement of these atomic positions with subsequent difference Fourier maps disclosed the location of all remaining atoms, including all hydrogens. Following absorption corrections (maximum and minimum transmission coefficients were, respectively, 0.98 and 0.88 for isomer I and 0.91 and 0.89 for isomer II), refinement was continued to convergence to final values of $R = 0.041$ and $R_w = 0.043$ for isomer I and $R = 0.044$ and $R_w = 0.047$ for isomer II where $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. All atomic positions were included in the first three cycles, and thereafter the hydrogen coordinates were held fixed.

Full-matrix 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[25] and those for hydrogen from Stewart et al.[26] The effects of anomalous dispersion for all nonhydrogen atoms were included in F using the values of Cromer and Ibers[27] for $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[28]

The error in an observation of unit weight was 1.40 for isomer I and 1.49 for isomer II, while the largest parameter shifts in the last cycle of refinement were 0.02 and 0.17 times the estimated standard deviation, for isomers I and II, respectively. Tables of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE 79-09948.

Registry No. Isomer I, 70281-11-7; isomer II, 70281-12-8.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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