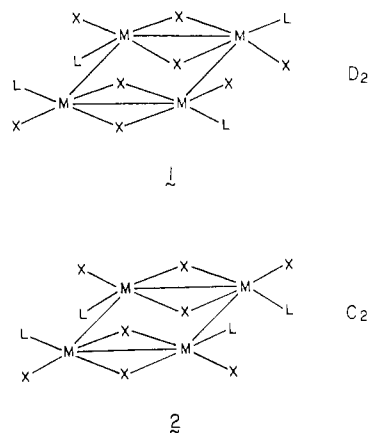


which there are trialkylphosphines seems to require more deliberate or forcing measures such as the use of a specially reactive intermediate or the use of a reagent intended to remove some PR_3 ligands. Much remains to be learned about the factors influencing reaction 1 but it appears, tentatively, that the more π acidic the phosphorus ligand the more the reaction tends to go to the right.



The other point worthy of discussion has to do with the fact that the $\text{M}_4\text{X}_8(\text{PY}_3)_4$ molecules are known to exist in either of two geometrically isomeric forms, **1** and **2**, with D_2 and C_{2h} symmetry, respectively. Previously² the molybdenum compound $\text{Mo}_4\text{Cl}_8[\text{P}(\text{C}_2\text{H}_5)_3]_4$ was known to have structure **2** while only the tungsten compound, $\text{W}_4\text{Cl}_8[\text{P}(\text{C}_4\text{H}_9)_3]_4$, had been found to have structure **1**. The new molybdenum compound also has the C_{2h} structure (**2**). The fact that $\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{P}(\text{OCH}_3)_3$ are very similar sterically but rather different electronically would seem to suggest, tentatively, that the relative stabilities of structures **1** and **2** may be more sensitive to steric than to electronic influences.

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grateful to Drs. Larry Falvello, Brian Kolthammer, and Graham Mott for interest and assistance.

Registry No. $\text{Mo}_4\text{Cl}_8[\text{P}(\text{OCH}_3)_3]_4$, 84454-20-6; $\text{Mo}_2\text{Cl}_4[\text{P}(\text{OCH}_3)_3]_4$, 38832-74-5; $\text{K}_4\text{Mo}_2\text{Cl}_8$, 25448-39-9; Mo, 7439-98-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Carbon-Rich Metallocarboranes. 12.¹ Synthesis and Structures of Chromium(III) Complexes with "Nonconforming" Cage Geometries

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The reaction of the $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ dianion with CrCl_2 and NaC_2H_5 in cold tetrahydrofuran (THF) gave primarily red, paramagnetic $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ (I). Column chromatography of the product mixture under N_2 gave also purple II, an unstable species isomeric with I. Air oxidation of solutions of I over prolonged periods gave yellow, unstable $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$ (III); products II and III were characterized only from mass spectra. On workup of the product mixture in air, a small quantity of green IV, isomeric with III, was obtained together with I (the major product) and III. Compounds I and IV were structurally characterized by X-ray diffraction studies and were shown to have respectively 13-vertex nido and 12-vertex nido cage geometries; each of these structures is a formal $(2n + 1)$ -electron system and appears to violate the Wade electron-count scheme, which requires $2n + 4$ electrons for nido geometry. However, if the deficiency of three electrons is localized in the metal nonbonding orbitals (rendering chromium a 15-electron atom), then both I and IV can be viewed as $(2n + 4)$ -electron cage systems in conformity with their observed structures. Crystal data for I: $\text{CrC}_{17}\text{B}_8\text{H}_{33}$; mol wt 376.94; space group $P\bar{1}$; $Z = 2$; $a = 8.637$ (8), $b = 8.664$ (5), $c = 16.484$ (8) Å; $\alpha = 99.19$ (5), $\beta = 92.06$ (4), $\gamma = 118.66$ (7)°; $V = 1059$ Å³; $R = 0.102$ for 2101 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for IV: $\text{CrC}_{17}\text{B}_7\text{H}_{32}$; mol wt 364.12; space group $Pna2_1$; $Z = 4$; $a = 14.763$ (8), $b = 10.828$ (4), $c = 12.348$ (2) Å; $V = 1974$ Å³; $R = 0.026$ for 1820 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

A principal focus of interest in the four-carbon $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ carboranes and their metallocarborane derivatives^{3,4} (indeed, our main objective in studying these molecules) is the intricate relationship between their cage structures and skeletal electron populations. Collectively, this family of compounds provides an excellent means of examining electronic influence on bonding in large covalent clusters. The $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ species (R

= alkyl) have 28 framework electrons and are "electron rich" relative to the 26 required for 12-vertex closo cages such as the icosahedral $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ carboranes.⁴ The $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ cages in which R is CH_3 , C_2H_5 , or $n\text{-C}_3\text{H}_7$ are fluxional in solution,^{3,5} alternating between pseudoicosahedral geometry and more open arrangements that reflect the "nido" character expected⁶ for $(2n + 4)$ -electron polyhedra, where n is the number of vertices. So sensitive is the cage geometry to electronic influence that the choice of alkyl substituent on carbon has major consequences in the observed stereochemistry.^{5c}

- (1) This article continues the "Tetracarbon Metallocarborane" series under a new, more general title. For paper 11 in this series, see: Maynard, R. B.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 3858.
- (2) (a) Present address: RCA Picture Tube Division, Lancaster, PA 17604. (b) Visiting scholar from the Institute of Chemistry, Academia Sinica, Beijing, China, 1981-1983.
- (3) For a recent review see: Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*.
- (4) Maynard, R. B.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 1201 and references therein.

- (5) (a) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1974**, *96*, 7116. (b) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1976**, *15*, 1343. (c) Venable, T. L.; Maynard, R. B.; Grimes, R. N., manuscript in preparation.
- (6) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (c) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99.

Insertion of transition metals into the $R_4C_4B_8H_8$ species or the $R_4C_4B_8H_8^{2-}$ dianions gives four-carbon metallocarboranes of widely varying and often novel cage structure. In most previously characterized compounds of this class,^{1,3,4} the metal is iron, cobalt, or nickel, carrying an exopolyhedral ligand such as $\eta^5-C_5H_5$, $\eta^5-C_5(CH_3)_5$, or $[(C_6H_5)_2PCH_2]_2$, and the formal skeletal electron count usually exceeds $2n + 2$. As a result, the observed cage frameworks are almost invariably open (nido or arachno). Indeed, even in the case of the $(2n + 2)$ -electron $(\eta^5-C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ system where closo geometry is predicted by Wade's rules,⁶ the isomers obtained are nevertheless nido; only at high temperature is rearrangement to the thermodynamically favored closo species observed.⁷

As a part of our continuing investigation in this area, we are examining the structural consequences of inserting electron-poor metals into C_4 carborane cages. This paper reports the synthesis and structural characterization of two chromium complexes containing the $Cr(\eta^5-C_5H_5)$ group, a formal (-1)-electron donor that can also be described as a 1-electron "acceptor" in the Wade formalism.^{6a}

Results

Synthesis of Chromacarboranes. The addition of $CrCl_2$ and NaC_5H_5 to solutions of the $(C_2H_5)_4C_4B_8H_8^{2-}$ dianion in cold THF leads to rather complex reactions, which are marked by color changes and the formation of several detectable chromacarborane products. The course of these reactions is sensitive to experimental conditions, including the ratio of $NaC_{10}H_8$ to $(C_2H_5)_4C_4B_8H_8$ employed in forming the dianion, as well as the method of workup of products. Treatment of $(C_2H_5)_4C_4B_8H_8$ with 2–3 equiv of $NaC_{10}H_8$ in cold THF gave initially a dark green solution, which changed to yellow on warming to $-15^\circ C$. Addition of anhydrous $CrCl_2$ followed by NaC_5H_5 gave a red solution; column chromatography under an N_2 atmosphere gave one major product, red, crystalline $(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_8H_8$ (I) in 30% yield, and a purple, air-sensitive product (II) whose mass spectrum identified it as an isomer of I.

Compound I is an odd-electron species whose ^{11}B and 1H FT NMR spectra have not been observed, solutions of I exhibiting only the spectra of the carborane precursor $(C_2H_5)_4C_4B_8H_8$. This suggests partial dissociation or decomposition of I to release free carborane. Undissociated I may well escape detection by NMR owing to extreme peak broadening caused by its paramagnetism; this point has not been resolved. However, structural characterization of I was achieved via IR and mass spectroscopy and X-ray diffraction, as described below.

Complex I is moderately air stable, decomposing very slowly as a solid but more rapidly on exposure to air in THF solution. Air oxidation of I produces a yellow complex (III), which was identified mass spectroscopically as $(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_7H_7$, whose formation from I involves net loss of one BH unit. Direct structural characterization of III was not possible; however, from the established geometries of I and IV (an isomer of III to be described) one can project a likely cage structure for III, as discussed in the concluding section.

When the products of the $CrCl_2/C_2H_5^-/(C_2H_5)_4C_4B_8H_8^{2-}$ reaction were exposed to air for several hours prior to chromatographic separation, the products consisted of red I, yellow III, and a green species, IV, characterized via mass spectrometry and X-ray diffraction as $(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_7H_7$.

Molecular Structure of I. Table I lists the important crystallographic parameters for both compounds. Tables II–IV present atomic coordinates, bond distances, and selected bond angles for compound I [$(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_8H_8$], and

Table I. X-ray Diffraction Parameters and Crystal Data

	$(\eta^5-C_5H_5)Cr-$ $(C_2H_5)_4C_4B_8H_8$ (I)	$(\eta^5-C_5H_5)Cr-$ $(C_2H_5)_4C_4B_7H_7$ (IV) ^a
mol wt	376.94	364.12
space group	$P\bar{1}$	$Pna2_1$
<i>a</i> , Å	8.637 (8)	14.763 (8)
<i>b</i> , Å	8.664 (5)	10.828 (4)
<i>c</i> , Å	16.484 (8)	12.348 (2)
α , deg	99.19 (5)	
β , deg	92.06 (4)	
γ , deg	118.66 (7)	
<i>V</i> , Å ³	1059	1974
μ , cm ⁻¹	11.2	6.0
<i>d</i> (calcd), g cm ⁻³	1.182	1.225
<i>A</i>	0.60	0.60
<i>B</i>	0.30	0.35
trans fac (max)		0.95
trans fac (min)		0.91
2θ range, deg	1.4–48	1.5–52
reflcs obsd	2708	2018
reflcs refined	2101	1820
<i>R</i>	0.102	0.026
<i>R</i> _w	0.115	0.033
esd unit wt	2.38	1.67
<i>Z</i>	2	4

^a Crystal dimensions (mm from centroid) for IV: (100), 0.20; (100), 0.20; (011), 0.22; (011), 0.22; (011), 0.26; (011), 0.26. (The crystal of I was irregular and faces were not indexed.)

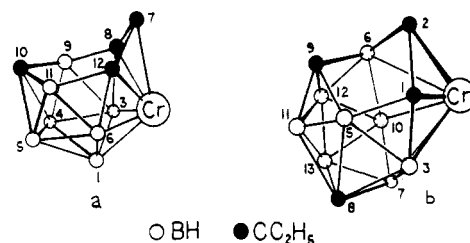


Figure 1. Cage geometry and numbering for $(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_7H_7$ (a) and $(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_8H_8$ (b).

Tables V–VII contain the corresponding data for $(\eta^5-C_5H_5)Cr(C_2H_5)_4C_4B_7H_7$ (IV). The molecular structures of the two compounds are depicted in Figures 1–3.

The CrC_4B_8 cluster framework in I is a 13-vertex open polyhedron (the first example of this geometry) and represents an *apparent* violation of the polyhedral skeletal electron pair theory (PSEPT), also known as Wade's rules.⁶ If the $Cr(C_5H_5)$, $C(C_2H_5)$, and BH units are regarded as donors of -1, 3, and 2 electrons, respectively, the cage is a 27-electron ($2n + 1$) system, corresponding to 3 fewer electrons than the $2n + 4$ normally required for nido (open-cage) geometry in an *n*-vertex cluster. Indeed, the electron count falls short even of the 28 ($2n + 2$) electrons usually associated with closo (i.e., entirely triangulated) clusters. Yet the cage clearly is not closo, as shown by the presence of an open face [C(1)–C(2)–B(6)–C(9)–B(5)] whose transannular distances are distinctly nonbonding (Table III).

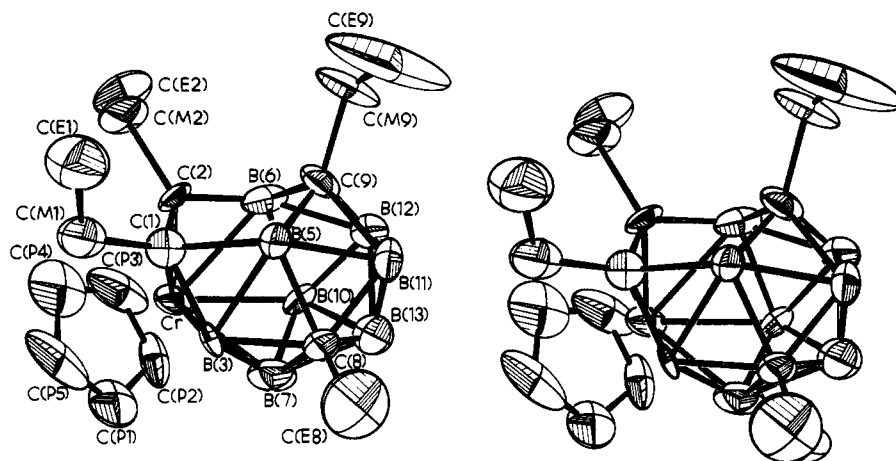
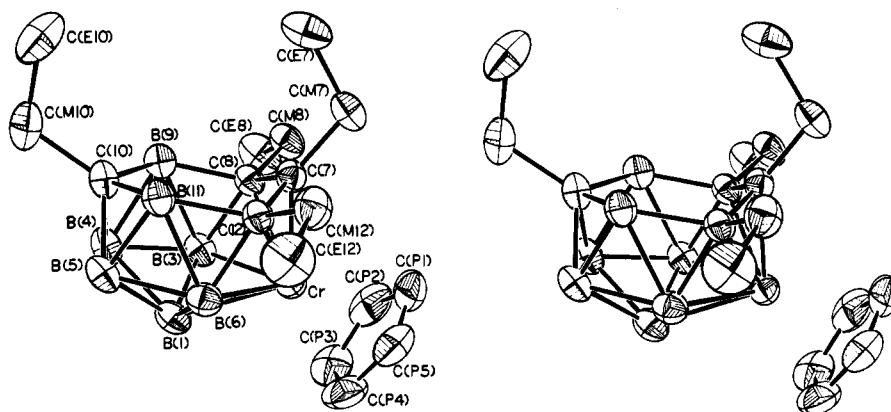
The cluster geometry in I is irregular with no elements of symmetry, but bond lengths are within normal ranges. The C(1)–C(2) distance is notably short [1.475 (8) Å], a feature characteristic of carbon–carbon edges on open faces in carboranes. This effect, discussed elsewhere,⁸ is associated with low-coordinate skeletal carbon atoms adjacent to each other, in which the C–C interaction evidently acquires some degree of multiple-bond character. In compound I, the phenomenon is accentuated by the low (three-) coordination of C(2) with respect to its cage neighbors.

(7) Maxwell, W. M.; Weiss, R.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4016.

(8) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 10. (b) Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Ibid.* **1978**, *17*, 1447.

Table II. Positional Parameters and Their Estimated Standard Deviations for $(\text{C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$

atom	x	y	z	atom	x	y	z
Cr	0.0784 (2)	-0.2080 (2)	-0.1595 (1)	B(12)	-0.229 (2)	-0.078 (2)	-0.2174 (12)
C(P1)	0.082 (2)	-0.429 (1)	-0.1088 (9)	B(13)	-0.334 (2)	-0.315 (2)	-0.2491 (12)
C(P2)	0.040 (2)	-0.311 (2)	-0.0421 (8)	H(3)	-0.01 (1)	-0.42 (1)	-0.319 (6)
C(P3)	0.192 (2)	-0.141 (2)	-0.0261 (9)	H(5)	0.02 (1)	-0.16 (1)	-0.398 (8)
C(P4)	0.322 (2)	-0.152 (2)	-0.0821 (9)	H(6)	0.01 (1)	0.12 (1)	-0.130 (6)
C(P5)	0.240 (2)	-0.330 (2)	-0.1290 (9)	H(7)	-0.25 (1)	-0.52 (1)	-0.186 (7)
C(1)	0.154 (1)	-0.138 (1)	-0.2727 (7)	H(10)	-0.17 (2)	-0.17 (1)	-0.083 (8)
C(M1)	0.308 (1)	-0.138 (1)	-0.3138 (9)	H(11)	-0.38 (2)	-0.21 (1)	-0.367 (8)
C(E1)	0.372 (2)	-0.033 (2)	-0.3864 (11)	H(12)	-0.26 (1)	0.04 (1)	-0.168 (7)
C(2)	0.185 (1)	0.002 (1)	-0.2002 (8)	H(13)	-0.49 (2)	-0.42 (2)	-0.269 (9)
C(M2)	0.368 (2)	0.186 (2)	-0.1848 (9)	H(P1)	-0.00 (2)	-0.57 (1)	-0.138 (8)
C(E2)	0.405 (2)	0.298 (2)	-0.0940 (11)	H(P2)	-0.06 (1)	-0.36 (1)	-0.025 (7)
C(8)	-0.219 (1)	-0.358 (1)	-0.3226 (9)	H(P3)	0.22 (1)	-0.04 (1)	0.002 (7)
C(M8)	-0.328 (2)	-0.522 (2)	-0.3932 (10)	H(P4)	0.44 (1)	-0.05 (1)	-0.085 (7)
C(E8)	-0.278 (2)	-0.503 (2)	-0.4733 (10)	H(P5)	0.29 (1)	-0.37 (1)	-0.174 (7)
C(9)	-0.065 (1)	-0.003 (1)	-0.2801 (7)	H(M11)	0.29 (2)	-0.25 (1)	-0.340 (8)
C(M9)	-0.020 (2)	0.177 (1)	-0.3063 (9)	H(M12)	0.40 (2)	-0.09 (1)	-0.271 (7)
C(E9)	-0.049 (4)	0.172 (2)	-0.3924 (12)	H(M21)	0.38 (2)	0.26 (1)	-0.233 (8)
B(3)	-0.018 (1)	-0.334 (1)	-0.2913 (9)	H(M22)	0.47 (2)	0.17 (1)	-0.203 (8)
B(5)	-0.031 (2)	-0.152 (1)	-0.3353 (8)	H(M81)	-0.47 (1)	-0.55 (1)	-0.389 (7)
B(6)	0.005 (2)	0.010 (2)	-0.1757 (9)	H(M82)	-0.32 (2)	-0.61 (1)	-0.382 (8)
B(7)	-0.187 (2)	-0.395 (2)	-0.2232 (11)	H(M91)	-0.03 (2)	0.26 (1)	-0.278 (8)
B(10)	-0.176 (2)	-0.205 (2)	-0.1503 (10)	H(M92)	0.11 (2)	0.23 (1)	-0.287 (7)
B(11)	-0.258 (1)	-0.185 (2)	-0.3221 (11)				

Figure 2. Stereoview of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ (I).Figure 3. Stereoview of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$ (IV).

It is important to note that there are no "extra" hydrogen atoms (as in BHB bridges or RCH groups) in this molecule. Mass spectroscopic evidence combined with a thorough search for additional hydrogens in the X-ray study, as well as the observed paramagnetism,⁹ strongly supports the formula as given. This conclusion is relevant to the discussion below.

The cyclopentadienyl ligand is planar and lies 1.854 Å (perpendicular vector) from the metal; the mean Cr-C(C₅H₅) distance is 2.223 (3) Å, slightly longer than the corresponding value in chromocene [2.169 (4) Å, determined by electron diffraction¹⁰] despite the larger formal charge on Cr in I as

(9) Brewer, G., unpublished ESR observations.

(10) Gard, E.; Haaland, A.; Novak, D. P.; Seip, R. *J. Organomet. Chem.* 1975, 88, 181.

Table III. Distances (Å) in ($\eta^5\text{-C}_5\text{H}_5$)Cr(C₂H₅)₄C₄B₈H₈ (I)

Bond Distances in CrC ₄ B ₈ Cage Framework			
Cr-C(1)	2.085 (6)	B(6)-C(9)	1.770 (8)
Cr-C(2)	1.856 (5)	B(6)-B(10)	1.896 (8)
Cr-B(3)	2.201 (6)	B(6)-B(12)	1.842 (9)
Cr-B(6)	2.314 (6)	B(7)-C(8)	1.759 (9)
Cr-B(7)	2.169 (6)	B(7)-B(10)	1.840 (10)
Cr-B(10)	2.223 (7)	B(7)-B(13)	1.787 (10)
C(1)-C(2)	1.475 (8)	C(8)-B(11)	1.683 (7)
C(1)-B(3)	1.599 (7)	C(8)-B(13)	1.699 (12)
C(1)-B(5)	1.812 (6)	C(9)-B(11)	1.674 (7)
C(2)-B(6)	1.658 (10)	C(9)-B(12)	1.717 (11)
B(3)-B(5)	1.884 (7)	B(10)-B(12)	1.866 (9)
B(3)-B(7)	1.802 (11)	B(10)-B(13)	1.875 (9)
B(3)-C(8)	1.702 (7)	B(11)-B(12)	1.772 (12)
B(5)-C(8)	1.799 (7)	B(11)-B(13)	1.711 (12)
B(5)-C(9)	1.612 (9)	B(12)-B(13)	1.776 (9)
B(5)-B(11)	1.871 (9)	B-H)	1.15 (1)
Nonbonded Distances on Open Face			
C(1)-B(6)	2.637 (9)	C(2)-C(9)	2.469 (6)
C(1)-C(9)	2.667 (6)	B(5)-B(6)	2.710 (6)
C(2)-B(5)	2.567 (7)		
Bond Distances in Ethyl Groups and Cyclopentadienyl Ring			
C(1)-C(M1)	1.517 (9)	Cr-C(P3)	2.240 (6)
C(M1)-C(E1)	1.575 (9)	Cr-C(P4)	2.217 (6)
C(2)-C(M2)	1.585 (6)	Cr-C(P5)	2.208 (6)
C(M2)-C(E2)	1.580 (10)	C(P1)-C(P2)	1.556 (11)
C(8)-C(M8)	1.539 (8)	C(P2)-C(P3)	1.402 (11)
C(M8)-C(E8)	1.416 (12)	C(P3)-C(P4)	1.508 (13)
C(9)-C(M9)	1.556 (6)	C(P4)-C(P5)	1.423 (10)
C(M9)-C(E9)	1.422 (11)	C(P5)-C(P1)	1.309 (12)
Cr-C(P1)	2.224 (6)	(C _{alkyl} -H)	0.97 (1)
Cr-C(P2)	2.228 (5)	(C _{CP} -H)	0.93 (1)

Table IV. Selected Bond Angles (deg) in I

Cr-C(1)-C(M1)	127.4 (3)	B(11)-C(8)-C(M8)	115.3 (4)
C(2)-C(1)-C(M1)	120.8 (4)	B(13)-C(8)-C(M8)	116.5 (5)
B(3)-C(1)-C(M1)	111.5 (4)	B(5)-C(9)-C(M9)	122.2 (6)
B(5)-C(1)-C(M1)	119.4 (5)	B(6)-C(9)-C(M9)	116.9 (4)
B(5)-C(1)-C(2)	102.2 (4)	B(11)-C(9)-C(M9)	118.0 (4)
Cr-C(2)-C(M2)	139.2 (4)	B(12)-C(9)-C(M9)	115.9 (5)
C(1)-C(2)-C(M2)	118.4 (6)	B(5)-C(9)-B(6)	106.4 (4)
B(6)-C(2)-C(M2)	117.8 (5)	B(5)-C(9)-B(11)	69.4 (4)
Cr-C(2)-C(1)	76.6 (3)	B(5)-C(9)-B(12)	116.8 (4)
Cr-C(2)-B(6)	82.2 (3)	B(11)-C(9)-B(12)	63.0 (4)
C(1)-C(2)-B(6)	114.5 (4)	C(P2)-C(P1)-C(P5)	109.0 (7)
C(1)-B(5)-C(9)	102.2 (4)	C(P1)-C(P2)-C(P3)	105.6 (7)
C(2)-B(6)-C(9)	92.1 (5)	C(P2)-C(P3)-C(P4)	106.8 (6)
B(3)-C(8)-C(M8)	112.7 (5)	C(P3)-C(P4)-C(P5)	107.3 (8)
B(5)-C(8)-C(M8)	124.4 (6)	C(P4)-C(P5)-C(P1)	111.3 (9)
B(7)-C(8)-C(M8)	118.3 (4)		

compared to that in chromocene (3+ vs. 2+).

Molecular Structure of IV. The 12-vertex CrC₄B₇ cage, in contrast to I, has well-defined nido geometry (formally derived from a 13-vertex polyhedron by removal of one vertex) and has approximate mirror symmetry with respect to a plane containing Cr, C(7), B(1), and C(10). Compound IV, like I, is a formal (2n + 1)-electron cluster and thus apparently fails to conform to the electron-counting rules. Indeed, the skeletal geometry of IV closely resembles that of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CH₃)₄C₄B₇H₈,¹¹ a (2n + 4)-electron cage, although the skeletal carbon locations are not the same and the iron species has a B-H-B bridge on the open rim.

The bond distances in IV are normal, although the short C(7)-C(8) and C(7)-C(12) vectors of 1.499 (3) and 1.492 (3) Å again suggest C-C multiple-bond character on the open rim, as noted in I above; also as in I, there are no "extra" hydrogen atoms. The C₅H₅ ring is planar, and its vector distance to the metal is 1.848 Å, nearly the same as in I.

Discussion

The main chromacarborane product obtained under all conditions examined in this study was the 13-vertex CrC₄B₈ species, I. Its structure bears no simple or obvious relationship to the neutral carborane precursor, (C₂H₅)₄C₄B₈H₈,^{5c} but this can be attributed to rearrangement of the cage framework that undoubtedly occurs on reduction to the anion prior to reaction with CrCl₂. Similar observations have been noted in metal-lacarborane syntheses^{11,12} from the (CH₃)₄C₄B₈H₈²⁻ ion and FeCl₂ or CoCl₂, and mechanistic schemes have been proposed¹³ to account for the observed structures of the metal complexes. We will make no attempt to develop such a rationale for I but will focus instead on the structure itself.

The mechanistic origin of the green 12-vertex species, IV, is even more obscure; in a series of experiments, IV was obtained only once, and we think that it may have originated from insertion of chromium into a C₄B₇ fragment [perhaps (C₂H₅)₄C₄B₇H₇²⁻] formed in small amounts during reduction of (C₂H₅)₄C₄B₈H₈ with NaC₁₀H₈. This question could no doubt be resolved by further investigation but is beyond the scope of this particular study and was not pursued. It is, however, clear that III (the yellow isomer of IV) forms via oxidative degradation of I in air; a likely pathway would involve removal of B(5)-H from I, thereby allowing all four cage carbons to occupy low-coordinate vertices on the open rim of a nido CrC₄B₇ cage. Thus, we tentatively suggest that the structure of III resembles that of IV (Figure 1a) but with the carbon atoms in vertices 7, 8, 9, and 11.

Of primary interest here are the established cage geometries of I and IV, which, as noted above, seem to violate the skeletal electron-count rules for clusters. It is worthwhile to consider the implications of this. One hypothesis is that these complexes are kinetically stabilized, i.e., locked into thermodynamically unfavorable structures by the absence of accessible pathways for rearrangement; several examples have been encountered in C₄ metallacarborane chemistry, including the 14-vertex Fe₂C₄B₈ system⁷ mentioned in the Introduction. In the present chromium species, however, this seems unlikely. Cage closure in I would require only slight atomic movement of C(9) or C(2), and in the 12-vertex IV one would expect formation of an icosahedral cage to be strongly favored if, indeed, the framework holds only 2n + 1 electrons.

A second hypothesis might be that nonterminal (e.g., bridging or "methylenic") hydrogen atoms are present, thus forcing open structures in I and IV; however, the total absence of crystallographic or spectroscopic evidence for such extra hydrogens has already been noted.

We are left with the possibility that the observed open structures are, in fact, electronically dictated and that the formal (2n + 1)-electron count is misleading. In the standard construction of Wade's rules,⁶ there is the assumption that the metal has a complete 18-electron valence shell. For an ($\eta^5\text{-C}_5\text{H}_5$)Cr group, the total of 11 valence electrons on Cr (6 from Cr and 5 from C₅H₅) falls one short of the 12 needed to populate the three Cr-C₅H₅ bonding MOs and the three "nonbonding" orbitals on the metal; this is the basis for designating ($\eta^5\text{-C}_5\text{H}_5$)Cr as a "(-1)-electron donor", i.e. a 1-electron acceptor,^{6a} with respect to the carborane ligand. If, however, these nonbonding orbitals contain less than the full quota of 6 electrons, the electron-donating capacity of the ($\eta^5\text{-C}_5\text{H}_5$)Cr group will be different. If one postulates only 3 such electrons (giving chromium a 15-electron shell), then ($\eta^5\text{-C}_5\text{H}_5$)Cr becomes a 2-electron donor and both I and IV are actually (2n + 4)-electron cages, consistent with their observed nido geometries.

(11) Maxwell, W. M.; Bryan, R. F.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4008.

(12) Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2174.

(13) Grimes, R. N.; Pipal, J. R.; Sinn, E. *J. Am. Chem. Soc.* **1979**, *101*, 4172.

Table V. Positional Parameters and Their Estimated Standard Deviations for $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$

atom	x	y	z	atom	x	y	z
Cr	0.17371 (2)	0.07410 (3)	0.2500 (0)	H(P4)	0.173 (3)	0.139 (4)	0.033 (4)
C(P1)	0.0320 (2)	0.1150 (4)	0.2149 (3)	H(P5)	0.084 (2)	0.270 (3)	0.146 (3)
C(P2)	0.0498 (2)	-0.0096 (4)	0.1896 (3)	H(1)	0.331 (2)	-0.016 (3)	0.139 (3)
C(P3)	0.1129 (2)	-0.0113 (3)	0.1047 (3)	H(3)	0.232 (2)	-0.174 (2)	0.286 (2)
C(P4)	0.1339 (3)	0.1127 (4)	0.0798 (3)	H(4)	0.413 (2)	-0.149 (2)	0.334 (2)
C(P5)	0.0851 (2)	0.1884 (3)	0.1472 (3)	H(5)	0.466 (2)	0.101 (2)	0.276 (2)
C(7)	0.1671 (2)	0.1190 (2)	0.4042 (2)	H(6)	0.315 (2)	0.239 (2)	0.200 (2)
C(M7)	0.0991 (2)	0.1684 (2)	0.4840 (2)	H(9)	0.291 (2)	-0.116 (2)	0.521 (2)
C(E7)	0.1415 (2)	0.1836 (3)	0.5965 (3)	H(11)	0.371 (2)	0.254 (2)	0.436 (2)
C(8)	0.1862 (2)	-0.0169 (2)	0.4035 (2)	H(M71)	0.042 (2)	0.106 (3)	0.484 (3)
C(M8)	0.1108 (2)	-0.0974 (3)	0.4549 (3)	H(M72)	0.080 (2)	0.244 (2)	0.457 (3)
C(E8)	0.1157 (2)	-0.2359 (3)	0.4415 (3)	H(M81)	0.050 (2)	-0.064 (2)	0.430 (3)
C(10)	0.3726 (2)	0.0419 (2)	0.4295 (2)	H(M82)	0.108 (2)	-0.081 (2)	0.518 (3)
C(M10)	0.4476 (2)	0.0330 (3)	0.5135 (3)	H(M101)	0.497 (2)	0.067 (2)	0.484 (3)
C(E10)	0.4240 (3)	0.0905 (3)	0.6212 (3)	H(M102)	0.465 (2)	-0.055 (2)	0.524 (3)
C(12)	0.2342 (2)	0.2068 (2)	0.3569 (2)	H(M121)	0.146 (2)	0.348 (3)	0.344 (2)
C(M12)	0.2053 (2)	0.3447 (3)	0.3636 (2)	H(M122)	0.208 (2)	0.378 (3)	0.437 (3)
CE12	0.2652 (3)	0.4407 (2)	0.3102 (3)	H(E71)	0.207 (3)	0.221 (3)	0.596 (3)
B(1)	0.3116 (2)	0.0094 (3)	0.2209 (2)	H(E72)	0.149 (2)	0.121 (3)	0.627 (3)
B(3)	0.2471 (2)	-0.0868 (3)	0.3081 (3)	H(E73)	0.093 (3)	0.229 (3)	0.647 (4)
B(4)	0.3657 (2)	-0.0666 (3)	0.3332 (3)	H(E81)	0.066 (3)	-0.268 (4)	0.486 (4)
B(5)	0.3970 (2)	0.0930 (3)	0.3027 (3)	H(E82)	0.178 (2)	-0.271 (3)	0.458 (3)
B(6)	0.3018 (2)	0.1704 (2)	0.2539 (3)	H(E83)	0.103 (2)	-0.259 (3)	0.369 (3)
B(9)	0.2877 (2)	-0.0496 (3)	0.4463 (3)	H(E101)	0.473 (3)	0.091 (3)	0.684 (4)
B(11)	0.3379 (2)	0.1799 (3)	0.3979 (3)	H(E102)	0.373 (3)	0.070 (3)	0.645 (4)
H(P1)	-0.004 (2)	0.151 (3)	0.259 (3)	H(E103)	0.416 (3)	0.181 (4)	0.615 (4)
H(P2)	0.024 (2)	0.086 (3)	0.225 (3)	H(E121)	0.243 (2)	0.512 (3)	0.309 (3)
H(P3)	0.137 (2)	-0.073 (2)	0.075 (3)	H(E122)	0.335 (3)	0.436 (3)	0.322 (5)
				H(E123)	0.258 (2)	0.433 (2)	0.241 (4)

Table VI. Bond Distances (Å) in $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$ (IV)

CrC ₄ B ₇ Cage Framework			
Cr-B(1)	2.183 (3)	B(4)-B(9)	1.820 (4)
Cr-B(3)	2.174 (3)	B(4)-C(10)	1.675 (4)
Cr-B(6)	2.160 (2)	B(5)-B(6)	1.799 (4)
Cr-C(7)	1.967 (2)	B(5)-C(10)	1.668 (4)
Cr-C(8)	2.144 (2)	B(5)-B(11)	1.801 (4)
Cr-C(12)	2.146 (2)	B(6)-B(11)	1.858 (4)
B(1)-B(3)	1.776 (4)	B(6)-C(12)	1.664 (4)
B(1)-B(4)	1.800 (4)	C(7)-C(8)	1.499 (3)
B(1)-B(5)	1.802 (4)	C(7)-C(12)	1.492 (3)
B(1)-B(6)	1.796 (3)	C(8)-B(9)	1.627 (3)
B(3)-B(4)	1.791 (4)	B(9)-C(10)	1.612 (3)
B(3)-C(8)	1.663 (3)	C(10)-B(11)	1.628 (3)
B(3)-B(9)	1.853 (4)	B(11)-C(12)	1.638 (3)
B(4)-B(5)	1.726 (4)	<B-H>	1.08 (1)
Ethyl Groups and Cyclopentadienyl Ring			
C(7)-C(M7)	1.505 (3)	Cr-C(P3)	2.209 (3)
C(M7)-C(E7)	1.531 (4)	Cr-C(P4)	2.222 (3)
C(8)-C(M8)	1.550 (3)	Cr-C(P5)	2.203 (3)
C(M8)-C(E8)	1.511 (4)	C(P1)-C(P2)	1.410 (5)
C(10)-C(M10)	1.519 (3)	C(P2)-C(P3)	1.403 (5)
C(M10)-C(E10)	1.509 (5)	C(P3)-C(P4)	1.411 (5)
C(12)-C(M12)	1.555 (3)	C(P4)-C(P5)	1.373 (5)
C(M12)-C(E12)	1.514 (4)	C(P5)-C(P1)	1.394 (5)
Cr-C(P1)	2.182 (3)	<C _{alkyl} -H>	0.95 (1)
Cr-C(P2)	2.173 (3)	<C _{cp} -H>	0.89 (1)

The concept of electron deficiency in nonbonding metal orbitals of metallacarboranes has been discussed elsewhere¹⁴ and receives further experimental support in the species^{15,16} $\text{Cr}[(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_9]_2^-$ and $\text{Ti}[(\text{CH}_3)_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2^{2-}$. These complexes have regular closo structures despite the apparent shortage of 1.5 and 2.0 electrons per cage, respectively, for the Cr and Ti species relative to the requirement of $2n + 2$ electrons for each closo cage. If the deficiency is in the metal

Table VII. Selected Bond Angles (deg) in IV

Cr-C(7)-C(M7)	139.0 (2)	B(9)-C(10)-B(11)	110.5 (2)
C(8)-C(7)-C(M7)	118.6 (2)	B(4)-C(10)-B(5)	62.2 (2)
C(12)-C(7)-C(M7)	118.2 (2)	B(4)-C(10)-B(9)	67.2 (2)
C(12)-C(7)-C(8)	119.9 (2)	B(5)-C(10)-B(11)	66.3 (2)
Cr-C(7)-C(12)	75.3 (1)	C(10)-B(11)-C(12)	122.1 (2)
Cr-C(7)-C(8)	75.1 (1)	Cr-C(12)-C(M12)	124.1 (2)
Cr-C(8)-C(M8)	124.0 (2)	B(6)-C(12)-C(M12)	115.6 (2)
B(3)-C(8)-C(M8)	115.0 (2)	C(7)-C(12)-C(M12)	114.1 (2)
C(7)-C(8)-C(M8)	114.5 (2)	B(11)-C(12)-C(M12)	114.2 (2)
B(9)-C(8)-C(M8)	113.9 (2)	B(1)-C(12)-C(7)	112.8 (2)
C(7)-C(8)-B(9)	112.7 (2)	C(P2)-C(P1)-C(P5)	107.9 (3)
C(8)-B(9)-C(10)	122.7 (2)	C(P1)-C(P2)-C(P3)	107.6 (3)
B(4)-C(10)-C(M10)	119.0 (2)	C(P2)-C(P3)-C(P4)	107.3 (3)
B(5)-C(10)-C(M10)	120.0 (2)	C(P3)-C(P4)-C(P5)	108.7 (3)
B(9)-C(10)-C(M10)	116.1 (2)	C(P4)-C(P5)-C(P1)	108.6 (3)
B(11)-C(10)-C(M10)	116.8 (2)		

orbitals, as suggested, then the skeletal bonding molecular orbitals are filled and the $2n + 2$ quota is, in fact, satisfied.

In compounds I and IV, the effect appears more dramatic because the open structures depart drastically from the closo or hypercloso geometries one expects from an overly simplistic application of Wade's rules. In summary, this work provides further strong evidence that in metal-boron clusters of electron-poor transition metals, *the nonbonding orbitals on the metal may be incompletely filled and structural predictions based on Wade's rules must be modified accordingly*. A better perspective on this aspect of boron cluster chemistry can be expected as additional examples of early transition-metal complexes of C₄ carboranes are structurally characterized.

Experimental Section

Materials. Tetra-C-ethyl-2,3,7,8-tetracarbadodecaborane(12) $[(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8]$ was prepared from $[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ as described elsewhere.^{5b,17} Cyclopentadiene was distilled from dicyclopentadiene (Aldrich); anhydrous chromium(II) chloride (Research Organic/Inorganic Chemical Corp.) and naphthalene (Baker) were used as received. All solvents were reagent grade, and tetrahydrofuran (THF) was dried over sodium metal and then over lithium aluminum hydride before use. Column chromatography was conducted

(14) (a) O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum: New York, 1982. (b) Nishimura, E. K. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 269.

(15) St. Clair, D.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1971**, *10*, 2587.

(16) Lo, F. Y.; Strouse, C. E.; Callahan, K. P.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 428.

(17) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.*, in press.

with silica gel 60 (Merck), and thin-layer chromatography (TLC) was performed on precoated plates of silica gel F-254 (Brinkmann Instruments, Inc.).

Instrumentation. ^{11}B and ^1H FT NMR spectra at 115.8 and 360 MHz, respectively, were obtained on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer. Unit resolution EI mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer, and infrared spectra were obtained on a Beckman IR-8 instrument.

Reaction of $\text{Na}_2[(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8]$ with CrCl_2 and NaC_5H_5 in THF. (a) Under N_2 Atmosphere. A 100-mL three-neck flask was charged with 815 mg (3.19 mmol) of $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$, and to it was added, at liquid-nitrogen temperature, 7.5 mmol of sodium naphthalenide ($\text{NaC}_{10}\text{H}_8$) in 20 mL of THF. On warming to $\sim -15^\circ\text{C}$, the dark green solution acquired the light yellow color of $\text{Na}_2[(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8]$, following which it was cooled to -30°C and 615 mg (5.0 mmol) of anhydrous CrCl_2 was added via a tip-in attachment to the reaction flask. The mixture was warmed to room temperature and stirred magnetically for 3 h, during which the solution became dark brown and bubbled slightly. The solution was refrozen in liquid nitrogen and 20 mL of THF containing 3.1 mmol sodium cyclopentadienide (NaC_5H_5) was added; the mixture was warmed to room temperature and stirred overnight. The solvent was removed via distillation in vacuo, and the residue was pumped on for 1 h to remove traces of naphthalene. The solid remaining was chromatographed in a drybox under high-purity N_2 (<5 ppm of O_2 and H_2O), by extraction with benzene and elution from a column of silica gel. Two bands were obtained, the first of which was red ($(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ (I), purified by TLC in 1:1 hexane–methylene chloride (R_f 0.54) to give 360 mg of I (30% yield based on carborane employed), mp $103 \pm 1^\circ\text{C}$. Compound I survives prolonged exposure to air as a dry solid but decomposes in days in solution on silica columns or plates (see below). IR absorptions (CCl_4 solution vs. CCl_4 ; cm^{-1}): 2960 vs, 2930 vs, 2880 vs, 1720 m, 1140 s, 1420 w, 1370 s, 1325 m, 1180 sh, 1160 s, 1120 sh, 1045 m, 1005 s, 900 s, br, 700 w. The EI mass spectrum exhibits a cutoff at m/e 379, corresponding to the $^{53}\text{Cr}^{13}\text{C}^{12}\text{C}_{16}^{11}\text{B}_8^{11}\text{H}_{33}^+$ parent peak, with relative intensities in the parent region corresponding to the calculated intensities for the indicated composition based on natural isotope distribution. All attempts to obtain ^{11}B and ^1H NMR spectra of I gave only the spectra of $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$, identical with those of authentic samples of the carborane¹⁷ except for very slight peak broadening.

The second band eluted from the silica column under N_2 was purple II, an extremely air-sensitive material whose mass spectrum was nearly identical with that of I and is presumed to be an isomer of I. Compound II proved to be thermally unstable at room temperature, decomposing even in the drybox.

(b) With Exposure of Products to Air. To a 1.63-g (6.27 mmol) sample of $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ in a 100-mL three-neck flask was added 15.0 mmol of $\text{NaC}_{10}\text{H}_8$ in 40 mL of THF while the flask was cooled in liquid nitrogen. After warming to room temperature, the dark green solution was cooled to -30°C and 0.87 g (7.1 mmol) of anhydrous CrCl_2 was added. The solution was warmed to room temperature, during which it turned yellow-brown with slight gas evolution, and was subsequently refrozen in liquid nitrogen, and 7.0 mmol of NaC_5H_5 in 20 mL of THF was added. The mixture was again warmed to room temperature, exposed to the atmosphere, and stirred for several hours. Solvent was removed by evaporation, the residue was extracted with benzene and filtered through filter paper, and the solvent was removed by evaporation. The residue was loaded onto a silica-gel column and eluted with 10:90 benzene–hexane to give three bands, which were further purified on a silica preparative TLC plate in 50:50 CH_2Cl_2 –hexane. Band 1 was yellow III, identified (vide infra) as $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$; this material decomposes rapidly on silica columns. Band 2 (R_f 0.54) was red I (80 mg, 0.21 mmol), and band 3 (R_f 0.26) was green IV (6 mg), identified from its mass spectrum as $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$, isomeric with III. The EI mass spectrum of IV exhibits a cutoff at m/e 367, which corresponds to the $^{53}\text{Cr}^{13}\text{C}^{12}\text{C}_{16}^{11}\text{B}_7^{11}\text{H}_{32}^+$ parent peak, with relative intensities in the parent region in agreement with calculated intensities based on natural isotope abundances. As with the other chromacarborane products, NMR spectra on paramagnetic IV could not be obtained, but an X-ray diffraction analysis was completed, as described below.

Conversion of I to III in Air. While I is moderately air stable as a solid, exposure of the solid to air over a period of weeks, or of solutions over several days, produces yellow III (R_f 0.32 in 50:50 hexane–

CH_2Cl_2) plus other unidentified degradation products. The mass spectrum of III is very similar to that of its isomer IV, described above.

X-ray Structure Determinations on $(\text{C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_5)_4\text{B}_8\text{H}_8$ (I) and $(\text{C}_5\text{H}_5)\text{Cr}(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_7\text{H}_7$ (IV). Crystals of both compounds were grown from CH_2Cl_2 solutions and mounted on glass fibers for data collection following preliminary precession photography. For each crystal, the Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections, which were then employed in the program INDEX to obtain an orientation matrix for data collection and also to 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 each crystal was examined by the ω -scan technique and found to be satisfactory, and space groups were chosen on the basis of systematic absences and mass spectroscopic information.

Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using $\text{Mo K}\alpha$ radiation from a highly oriented graphite-crystal monochromator (see Table I for data collection parameters). Reduction of the data was carried out by standard procedures described elsewhere.¹⁸ Raw intensity data were corrected for Lorentz–polarization effects and (in the case of IV only) for absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where F_o^2 was estimated from counting statistics ($P = 0.03$),¹⁹ were used in the final refinement of the structural parameters.

Full-matrix least-squares refinement was based on F , and the function minimized was $\sum w(|F_o| - |F_c|)^2$. 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, respectively. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber,²⁰ and those for hydrogen from Stewart et al.²¹ The effects of anomalous dispersion were included in F_c by using values of Cromer and Ibers²² for $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.²³ Tables of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

For each compound, the chromium atom position was located from a three-dimensional Patterson function calculated from all of the intensity data. Subsequent Fourier syntheses then served to establish all other non-hydrogen atom positions. Following introduction of anisotropic temperature factors for all non-hydrogen atoms, Fourier difference maps located most of the hydrogen atoms for I and all of them for IV. In both structures, hydrogen positions were refined for several cycles and thereafter held fixed. For compound I, two different crystals were employed; only data collected on the first crystal were used in refinement, but reflections obtained from the second were employed in locating some of the hydrogen atoms by using high-angle data. In the case of IV, the systematic absences were consistent with space groups $Pnma$ and $Pna2_1$, but $Pnma$ requires a molecular mirror plane. Such a condition could be met only if the C_5H_5 ring, the C_2H_5 groups, and several cage atoms were disordered; even for allowance of disordered atomic positions, the data did not refine satisfactorily in $Pnma$. The choice of $Pna2_1$ was ultimately confirmed by the excellent agreement with experimental data.

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Registry No. I, 84520-39-8; III, 84472-79-7; IV, 84520-40-1; $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$, 83096-06-4; CrCl_2 , 10049-05-5; NaC_5H_5 , 4984-82-1.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, and least-squares planes (23 pages). Ordering information is given on any current masthead page.

- (18) Finster, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 2675.
- (19) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.
- (20) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
- (21) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
- (22) Cromer, D. T.; Ibers, J. A. Reference 20.
- (23) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.