15 are not medium sensitive, and so have the same quantum efficiency, ϕ. Fractions F_1 and F_1' of the cage species **1** and **2**, respectively, undergo recombination to regenerate $Co(CN)_5X^{3-}$, and fractions F_2 and F_2', to give the product $Co(CN)_5(H_2O)^{2-}$. Fractions F_3 and F_3' escape as the structurally equilibrated intermediate $Co(CN)_5{}^{2-}$ ion; in the absence of added free X^- ion, these fractions would also terminate as aquo product.

If $Co(CN)_5X^{3-}$ is photolyzed in the presence of a concentration (M^+) of a neutral electrolyte, then according to the above scheme

$$\phi_A = \phi(1 - F_1)/[1 + K_{ip}(M^+)] + \phi(1 - F_1')K_{ip}(M^+)/[1 + K_{ip}(M^+)] \quad (19)$$

or

$$\phi_A = \phi_A{}^0/[1 + K_{ip}(M^+)] + \phi_A{}'K_{ip}(M^+)/[1 + K_{ip}(M^+)] \quad (20)$$

where $\phi_A{}^0$ is the aquation quantum yield for $(M^+) = 0$, and $\phi_A{}'$ is the yield for the ion-paired species.

Equation 20 can be fitted to the data of Figure 5, as shown by the solid lines. In each case $\phi_A{}'$ is zero, implying a recombination efficiency for I^- of unity if the complex is ion paired; the K_{ip} values are 0.26, 0.75, and 1.28 M^{-1}, for Na^+, Ca^{2+}, and La^{3+} as the cation, respectively. Since activity coefficients are neglected, these results are merely indicative of the applicability of the model. An equally successful analysis could be made in terms of a Stern–Volmer treatment in which an excited state undergoes collisional deactivation by cations; *i.e.*, plots of $\phi_A{}^0/\phi_A$ *vs.* (M^+) are reasonably linear.

If the added electrolyte is sodium iodide, the reduction in ϕ_A is greater than with sodium perchlorate or nitrate, attributable, in terms of mechanism II, to scavenging of iodide by $Co(CN)_5{}^{2-}$ which escapes the cage reaction. Thus when $Co(CN)_5I^{3-}$ is irradiated at 25° with 500-mμ light, $\phi_A{}^0$ is 0.175. In the presence of 2 *M* neutral electrolyte, ϕ_A has the average value 0.115, the reduction being attributed to 35% ion pairing, for which $\phi_A{}'$ is zero. If F_2 is small, then 0.115 is also the quantum yield for formation of structurally equilibrated $Co(CN)_5{}^{2-}$, and the further reduction of ϕ_A to 0.105 in 2 *M* sodium iodide would imply that the fraction 0.010/0.115 is scavenged by free iodide ion. This corresponds to a k_2/k_3 ratio of 10, as compared to our directly determined value of 8.5. Also implied is a quantum yield of 0.010 for radioiodide exchange; this is to be compared with the value of 0.015 from Table IV (which included some exchange due to back-thermal reaction).

A remaining question is why the photoaquation quantum yield for $Co(CN)_6{}^{3-}$ is not appreciably affected by added neutral electrolytes, unlike the situation with $Co(CN)_5I^{3-}$. In the former case, however, the nascent free ligand, cyanide ion, would be protonated by the solvent very rapidly and might then be kinetically inert.

Summary

We conclude that photolysis of $Co(CN)_6{}^{3-}$, $Co(CN)_5(H_2O)^{2-}$, and $Co(CN)_5I^{3-}$ produces the active intermediate $Co(CN)_5{}^{2-}$, or the same as has been postulated to be present in the thermal anation reactions of $Co(CN)_5(H_2O)^{2-}$. Various anions show about the same relative scavenging preferences for the intermediate in the photochemical as in the thermal systems. It is necessary to assume, however, that the photochemically produced $Co(CN)_5{}^{2-}$ must escape cage recoordination reactions before participating in normal scavenging competition, and that the cage escape probability is strongly affected by the concentration and charge of cations present.

Acknowledgments. This investigation has been supported in part by Contract DA-31-124-ARO(D)-343 between the U. S. Army Research Office (Durham) and the University of Southern California. In addition, E. Z. wishes to thank the U. S. National Science Foundation for assistance through Grant GP 5725, and also the National Research Council of Italy.

Cobalt Complexes Containing the $B_7C_2H_9{}^{2-}$ Ligand. A Metallocene Analog

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Contribution from the Department of Chemistry, The University of California, Riverside, California 92502. *Received March 10, 1969*

Abstract: 1,3-Dicarba-*nido*-nonaborane(13), 1,3-$B_7C_2H_{13}$, reacts with 2 moles of sodium hydride to give 1,3-dicarba-*nido*-undecahydrononaborate(2−), 1,3-$B_7C_2H_{11}{}^{2-}$. The 1,3-$B_7C_2H_{11}{}^{2-}$ dianion and anhydrous cobalt(II) chloride react to give "dicarbazapide" ion, $B_7C_2H_9{}^{2-}$, complexes of formal cobalt(III). Depending upon reaction conditions, the complexed dicarbazapide ion ligand appears in either a 1,6- or 6,7-isomeric form. A thermal polyhedral rearrangement of these isomers, involving carbon atom migration, to give a 1,10 isomer is described. The preparation, characterization, and structures of these complexes are discussed.

Transition metal derivatives of the dicarbollide dianions (3)-1,2-$B_9C_2H_{11}{}^{2-}$ and (3)-1,7-$B_9C_2H_{11}{}^{2-}$ have been reported in the literature.[1] Further work in this area of carborane–transition metal chemistry has revealed the dianion, $B_7C_2H_9{}^{2-}$,[2] as a similar π ligand.

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(1) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

(2) M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967).

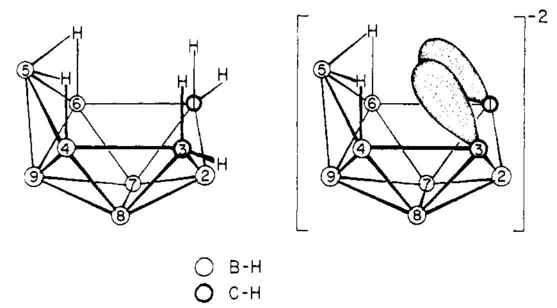

Figure 1. Structure of 1,3-dicarba-*nido*-nonaborane(13) and proposed structure of the 1,3-dicarba-*nido*-undecahydroborate(−2) ion in schematic form.

Furthermore, thermal rearrangement of this polyhedral system has been observed[3] to give a second isomer in which one of the carbon atoms has migrated to a new position, out of the metal-bonding face. More recently, a third isomer has been observed in the low-temperature preparation of $B_7C_2H_9{}^{2-}$ cobalt(III) complexes. The work concerning the dicarbazapide–cobalt(III) complexes are described in this paper.

The 1,3-Dicarba-*nido*-undecahydroborate(2−) Dianion. Preparation. The acidity of the hydrogen atoms in the apical positions of the methylene groups of 1,3-dicarba-*nido*-nonaborane(13) and its C-substituted derivatives was previously demonstrated[4] by acid-catalyzed deuterium exchange and by the preparation and characterizarion of a monoanion, $1,3\text{-}(CH_3)_2B_7C_2H_{10}{}^-$, from the reaction of the neutral carborane $1,3\text{-}(CH_3)_2B_7C_2H_{11}$ with base. It was therefore reasonable to anticipate the existence of a dianion, $1,3\text{-}B_7C_2H_{11}{}^{2-}$, formed by the removal of one apical proton from each of the methylene groups or by the removal of one apical methylene proton and one bridge B–H–B proton. Treatment of $1,3\text{-}B_7C_2H_{13}$ in diethyl ether with 2 moles of sodium hydride produced 2 moles of hydrogen and a white sodium salt suspension. The great reactivity of the resulting ion precluded characterization, but quantitative hydrogen evolution measurements supported the formation of a dianion $1,3\text{-}B_7C_2H_{11}{}^{2-}$.

$$1,3\text{-}B_7C_2H_{13} + 2NaH \longrightarrow 2Na^+ + 1,3\text{-}B_7C_2H_{11}{}^{2-} + 2H_2$$

Hydrogen evolution measurements were also carried out with $1,3\text{-}(C_6H_5)B_7C_2H_{12}$ and $1,3\text{-}(CH_3)_2B_7C_2H_{11}$ carboranes, and the results are presented in Table I.

Table I. Hydrogen Evolution Results on the Formation of the 1,3-Dicarba-*nido*-undecahydrononaborate(2−) Ions and Sodium Bis-π-(2)-6,9-dicarbazapylcobalt(III)

Compound with excess NaH	Moles of hydrogen × 10^3 Calcd	 Found
$B_7C_2H_{13}$	6.27	6.15
$B_7C_2H_{11}(CH_3)_2$	4.86	4.47[a]
$B_7C_2H_{12}(C_6H_5)$	3.44	3.35[b]
$B_7C_2H_{11}{}^{2-} + {}^3/_4CoCl_2$[c]	3.08	2.98

[a] 120 hr at room temperature. [b] 31 hr at 48°. [c] Characterized as the tetramethylammonium salt (yield, 75%, based on starting $1,3\text{-}B_7C_2H_{13}$).

The $1,3\text{-}(CH_3)_2B_7C_2H_9{}^{2-}$ dianion prepared in the hydrogen evolution measurement experiment was acidified with DCl and the carborane, $1,3\text{-}(CH_3)_2B_7C_2H_9D_2$, sublimed and characterized spectroscopically. The infrared spectrum contained absorption bands characteristic of B–H–B bridge hydrogen atoms at 2020 cm^{-1} and a C–D stretching band appeared at 2230 cm^{-1}. The ^1H nmr spectrum showed a sharp singlet at τ 8.66 due to methyl protons, but no carborane C–H resonances were observed.

$$1,3\text{-}(CH_3)_2B_7C_2H_9{}^{2-} + 2DCl \longrightarrow 1,3\text{-}(CH_3)_2B_7C_2H_9D_2 + 2Cl^-$$

Voet and Lipscomb[5] have determined the structure of $1,3\text{-}(CH_3)_2B_7C_2H_{11}$ by a single-crystal, X-ray diffraction ion study and it seems unlikely that the gross structure of the dianion $1,3\text{-}B_7C_2H_{11}{}^{2-}$ would differ greatly from the neutral carborane. The structure of $1,3\text{-}B_7C_2H_{13}$ and the proposed structure of $1,3\text{-}B_7C_2H_{11}{}^{2-}$ are shown in Figure 1.

The reaction of anhydrous cobalt(II) chloride with $1,3\text{-}B_7C_2H_{11}{}^{2-}$ liberates an additional mole of hydrogen (see Table I) giving a complex with the empirical formula $Co[B_7C_2H_9]_2{}^-$. The loss of additional hydrogen must be due to the loss of the bridge hydrogen atoms. Cobalt metal is also observed among the reaction products.

$$2(1,3\text{-}B_7C_2H_{11}{}^{2-}) + 1.5Co^{2+} \longrightarrow 0.5Co^0 + 2H_2 + Co[B_7C_2H_9]_2{}^-$$

The removal of two protons, one from each methylene group of $1,3\text{-}B_7C_2H_{13}$ to give $1,3\text{-}B_7C_2H_{11}{}^{2-}$, leaves two electrons in essentially an sp^3 hybrid orbital on each carbon atom. However, cleavage of the bridge hydrogen atoms with the liberation of hydrogen leaves two electrons delocalized among three boron atoms. Therefore, the $B_7C_2H_9{}^{2-}$ ion can be considered to have six electrons in five atomic orbitals. While $1,3\text{-}B_7C_2H_{13}$ and $1,3\text{-}B_7C_2H_{11}{}^{2-}$ can be considered to be icosahedral fragments,[6] it is probably more appropriate to consider $B_7C_2H_9{}^{2-}$ as a fragment of a bicapped Archimedean antiprism (or $B_8C_2H_{10}$). In this case the five atomic orbitals in the open face would be directed toward a vacant equatorial vertex, and the $B_7C_2H_9{}^{2-}$ ion would have a pentagonal open face similar to the 1,2-(3)- and $1,7\text{-}(3)\text{-}B_9C_2H_{11}{}^{2-}$ ions. Although a rationalization of the bonding involved in these complexes is probably premature at this time, it most likely bears a close resemblance to that for the $1,2\text{-}(3)\text{-}B_9C_2H_{11}{}^{2-}$, $1,7\text{-}(3)\text{-}B_9C_2H_{11}{}^{2-}$, and $C_5H_5{}^-$ ions. A schematic drawing of the hypothetical $B_7C_2H_9{}^{2-}$ ion is shown in Figure 2.

Preparation and Characterization of Bis-π-(2)-1,6- and Bis-π-(2)-6,7-Dicarbazapylcobalt(III) Ions. Unsubstituted 1,3-dicarba-*nido*-undecahydrononaborate(2−) ion was allowed to react with anhydrous cobalt(II) chloride in diethyl ether solution and gave a brown

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(3) T. A. George and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 1661 (1968).

(4) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **90**, 869 (1968).

(5) D. Voet and W. N. Lipscomb, *Inorg. Chem.*, **6**, 113 (1967).

(6) The difficulty associated with naming the ligands present in carborane–transition metal complexes has already been dealt with,[1] and hence a trivial name has been adopted for these new ligands. The Spanish noun "zapato" describes a shoe which resembles the shape of the $B_7C_2H_9{}^{2-}$ dianion, and the hypothetical $B_9H_9{}^{4-}$ and $B_8CH_9{}^{3-}$ ions could be named "zapide" and "carbazapide" ions, respectively, while the $B_7C_2H_9{}^{2-}$ dianion would become the "dicarbazapide" ion. The position of the vacant vertex is denoted by a prefix numeral in parentheses and the numbering of all positions is in accordance with the rules set forth by R. M. Adams, *Inorg. Chem.*, 7, 1945 (1968). The three isomeric forms of the $B_7C_2H_9{}^{2-}$ appearing in the $Co[B_7C_2H_9]_2{}^-$ system are (2)-1,6-, (2)-6,7-, and (2)-1,10-dicarbazapide ions (*vide infra*). Their transition metal complexes will be named as appropriately numbered "dicarbazapyl" complexes by analogy with the dicarbollyl complexes.[1]

Table II. Elemental Analyses, Equivalent Weight Data, Formula Weights, and Yields of π-(2)-1,6-, π-(2)-6,7-, and π-(2)-1,10-Dicarbazapylcobalt(III) Derivatives

Compound		% B	% C	% H	% Co	% other	Equiv wt[a]	Formula wt[b]	Yield, %
$(CH_3)_4N[(6,7\text{-}B_7C_2H_9)_2Co]$	Calcd	43.15	27.41	8.61	16.81	N, 4.00	351	351	65
	Found	43.12	27.17	8.60	17.09	N, 4.27	362	345	
$(CH_3)_4N[(1,6\text{-}B_7C_2H_9)_2Co]$	Calcd	43.15	27.41	8.61	16.81	N, 4.00	351	407	53
	Found	43.22	27.12	8.60	16.93	N, 4.30	340	405[c]	
$Cs[(1,10\text{-}B_7C_2H_9)_2Co]$	Calcd	36.97	11.74	4.43	14.37	Cs, 32.26	407	351	95
	Found	37.08	12.13	4.48	14.38	Cs, 32.26	427	350[d]	
$(C_5H_5)Co(1,6\text{-}B_7C_2H_9)$	Calcd	32.50	36.12	6.06	25.31			233	36
	Found	32.90	36.10	6.09	25.07			230[e]	
$(C_5H_5)Co(1,10\text{-}B_7C_2H_9)$	Calcd	32.50	36.12	6.06	25.31			233	98
	Found	30.57	36.14	6.02	24.51			231[e]	

[a] Determined by titrating the hydronium salts with standard base. [b] Determined by osmometry with acetonitrile as solvent. [c] Determined for the tetraethylammonium salt. [d] Determined for the tetramethylammonium salt. [e] Determined by osmometry with benzene as solvent.

reaction mixture. The reaction was found to proceed as described in the following equations.

$$2(1,3\text{-}B_7C_2H_{11}{}^{2-}) + 1.5Co^{2+} \xrightarrow{70°} 0.5Co^0 + 2H_2 + \underset{\text{brown}}{[\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9]_2Co^-}$$

$$2(1,3\text{-}B_7C_2H_{11}{}^{2-}) + 1.5Co^{2+} \xrightarrow{25°} 0.5Co^0 + 2H_2 + \underset{\text{red}}{[\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9]_2Co^-}$$

The ionic products containing formal Co(III) were isolated from water as their tetramethylammonium salts. When the reaction was carried out at room temperature in diethyl ether under nitrogen, the tetramethylammonium salt isolated was red. However, if the reaction mixture was immediately refluxed in 1,2-dimethoxyethane the tetramethylammonium salt isolated was brown. The yield and characterization data of these two salts are given in Table II. Elemental analyses, equivalent weight, and formula weight support the view that these compounds are indeed isomeric forms of the same $Co[B_7C_2H_9]_2^-$ system. Structural assignments were made as described below.

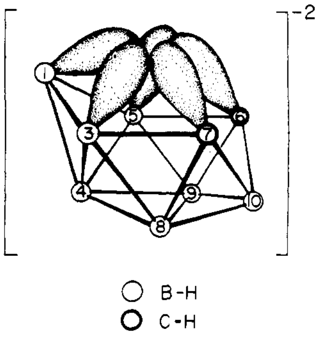

Figure 2. Proposed structure of the dicarbazapide ion shown in schematic form.

The 60-Mc/sec ^1H nmr spectra for the tetramethylammonium salts of the two isomers are given in Table III. The red isomer shows only one type of carborane C–H resonance of relative intensity 4 indicating that the two carbon atoms in each $B_7C_2H_9{}^{2-}$ ligand are in identical environments. However, the brown isomer has two carborane C–H resonances, each of relative intensity 2. Assuming that the two ligands are identical in this isomer, then the two carbon atoms in each of the $B_7C_2H_9{}^{2-}$ ligands are in different environments. Figure 3 presents the 32-Mc/sec ^{11}B nmr spectra of the two isomers. The brown isomer spectrum consists of a low-field doublet of relative intensity 2 and an overlapping array of six distinct doublets which correspond to seven distinct types of B atoms in the complex. In the case of the red isomer, the spectrum is simpler and comprises a broad low-field doublet of relative intensity 2, a doublet of relative intensity 4, and an apparent triplet of relative intensity 8. These nmr results prove that the $B_7C_2H_9{}^{2-}$ ligand in the brown isomer has very low symmetry with all carbon and boron atoms in unique environments, whereas for the red isomer the $B_7C_2H_9{}^{2-}$ ligand apparently has a higher symmetry with each of the carbon atoms and some of the boron atoms in equivalent environments.

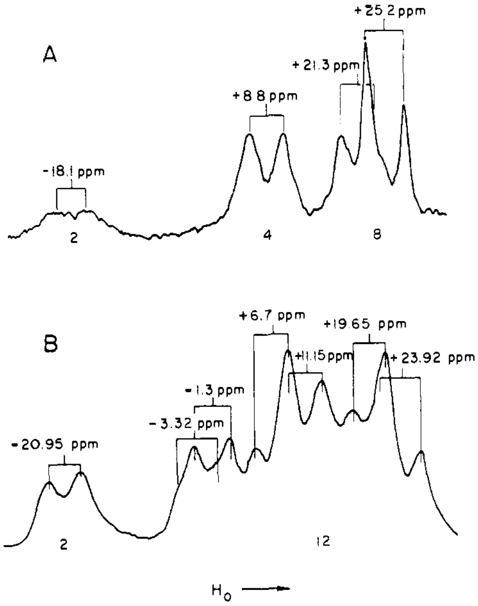

Figure 3. Boron-11 nmr spectra (32 Mc/sec) in acetone solvent of (A) $(CH_3)_4N[(\pi\text{-}6,7\text{-}B_7C_2H_9)_2Co]$ (red isomer) and (B) $(C_2H_5)_4N\text{-}[(\pi\text{-}1,6\text{-}B_7C_2H_9)_2Co]$ (brown isomer). The chemical shifts were measured relative to $BF_3 \cdot O(C_2H_5)_2 = 0$.

The most reasonable structure for the brown isomer, assuming no gross rearrangement of the carborane ligand, is shown in Figure 4. Both *syn* and *anti* forms are

Table III. ^{1}H Nmr Data of the π-(2)-6,7-, π-(2)-1,6-, and π-(2)-1,10-Dicarbazapylcobalt(III) Derivatives[a]

Compound	Resonance,[b] τ (rel area)	Assignment
	Broad singlet, 5.33 (4)	Carborane C–H
$(CH_3)_4N[(6,7\text{-}B_7C_2H_9)_2Co]$	Sharp singlet, 6.55 (12)	Methyl protons of cation
	Broad singlet, 4.15 (2)	Carborane C–H
$(CH_3)_4N[(1,6\text{-}B_7C_2H_9)_2Co]$	Broad singlet, 5.40 (2)	Carborane C–H
	Sharp singlet, 6.60 (12)	Methyl protons of cation
	Broad singlet, 1.97 (2)	Carborane C–H
$(CH_3)_4N[(1,10\text{-}B_7C_2H_9)_2Co]$	Broad singlet, 3.77 (2)	Carborane C–H
	Sharp singlet, 6.53 (12)	Methyl protons of cation
	Broad singlet, 3.03 (1)	Carborane C–H
$(C_5H_5)Co(1,6\text{-}B_7C_2H_9)$	Sharp singlet, 4.55 (5)	Cyclopentadienyl protons
	Broad singlet, 6.77 (1)	Carborane C–H
	Broad singlet, 0.94 (1)	Carborane C–H
$(C_5H_5)Co(1,10\text{-}B_7C_2H_9)$	Broad singlet, 3.50 (1)	Carborane C–H
	Sharp singlet, 4.65 (5)	Cyclopentadienyl protons

[a] Determined in deuterioacetone. [b] Relative to tetramethylsilane.

Table IV. Infrared Spectral Data (cm^{-1}) for the π-(2)-6,7-, π-(2)-1,6-, and π-(2)-1,10-Dicarbazapylcobalt(III) Derivatives (Nujol Mull)

$(CH_3)_4N[(6,7\text{-}B_7C_2H_9)_2Co]$	2525 (s), 1104 (s), 1070 (s), 1058 (s), 1028 (w), 974 (m), 949 (s), 938 (ssh), 896 (s), 867 (m), 861 (m), 842 (m), 815 (w), 782 (m), 751 (w), 748 (w), 721 (m)
$(C_2H_5)_4N[(1,6\text{-}B_7C_2H_9)_2Co]$	2525 (s), 1183 (w), 1170 (s), 1109 (m), 1065 (m), 1050 (s), 996 (s), 974 (m), 928 (m), 889 (m), 868 (m), 836 (m), 810 (m), 786 (s), 742 (m), 723 (w), 681 (w)
$Cs[(1,10\text{-}B_7C_2H_9)_2Co]$	2500 (s), 1110 (s), 1072 (msh), 1025 (s), 939 (m), 894 (s), 870 (msh), 831 (s), 775 (m), 720 (m)
$(C_5H_5)Co(6,7\text{-}B_7C_2H_9)$	3048 (w), 2538 (s), 1101 (m), 1089 (m), 1055 (s), 1034 (m), 1004 (s), 971 (s), 888 (m), 877 (w), 864 (w), 844 (s), 835 (s), 777 (m), 737 (m), 725 (m), 676 (m)
$(C_5H_5)Co(1,10\text{-}B_7C_2H_9)$	3086 (w), 2525 (s), 1252 (m), 1120 (s), 1104 (s), 1058 (m), 1049 (m), 1007 (m), 943 (w), 930 (w), 905 (m), 889 (w), 863 (m), 825 (s), 804 (m), 776 (m), 739 (w), 716 (w)

Table V. Electronic Spectral Data for the π-(2)-1,6-, π-(2)-6,7-, and π-(2)-1,10-Dicarbazapylcobalt(III) Derivatives in Acetonitrile Solution

λ_{max}, mμ (ϵ)				
$(CH_3)_4N[(6,7\text{-}B_7C_2H_9)_2Co]$	$(CH_3)_4N[(1,6\text{-}B_7C_2H_9)_2Co]$	$Cs[(1,10\text{-}B_7C_2H_9)_2Co]$	$(C_5H_5)Co(1,6\text{-}B_7C_2H_9)$	$(C_5H_5)Co(1,10\text{-}B_7C_2H_9)$
228 (19,200)	224 (16,000)	229 (19,100)	270 (15,400)	236 sh (11,250)
298 (11,000)	261 sh (8950)	281 (8260)	315 (4800)	254 (14,400)
368 (5600)	290 sh (7900)	348 (5360)	365 sh (1800)	327 (5220)
450 sh (680)	373 (5050)	483 (300)	502 (345)	455 (252)
530 (340)				

possible, but at present no chemical evidence for more than one isomer of this type has been found.

Preliminary X-ray diffraction results[7] obtained by using the tetraethylammonium salt of the brown isomer confirm the ligand structure with the cobalt atom positioned between the two ligands in the complex. However, the observation was made that positions 6 *and* 7 were equally occupied by C and B atoms in the complex crystal. This could arise in a racemate crystal containing equal amounts of the two enantiomeric forms of the *anti* isomer packed into the same crystal lattice.

Figure 5 shows the proposed structure for the red isomer with carbon atoms as nearest neighbors. The gross structure is the same, and only the relative position of the carbon atoms differs, being placed in the 6 and 7 positions. This accommodates both the ^{1}H nmr spectrum and the increased symmetry apparent in the ^{11}B nmr spectrum.

The infrared data for the bis-π-(2)-1,6- and bis-π-(2)-6,7-dicarbazapylcobalt(III) ions are presented in Table IV. The electronic spectra presented in Table V are complex and, as in the case of the bis-(3)-1,2- and bis-(3)-1,7-dicarbollylmetal derivatives, no satisfactory interpretation has been obtained.

The fact that two isomers of $Co[B_7C_2H_9]_2^-$ complexes may be obtained from the preparative reaction, depending upon the reaction temperature, suggests that the less stable 6,7 isomer is always initially produced and readily rearranges to the more stable 1,6 isomer at higher temperatures. This would constitute the most facile polyhedral isomerization reaction yet known. Results presented below militate against this simple suggestion.

Thermal Rearrangement of the Bis-π-(2)-1,6- and Bis-π-(2)-6,7-dicarbazapylcobalt(III) Ions to a Third Isomer. When cesium bis-π-(2)-1,6-dicarbazapylcobalt(III) was heated in a sealed tube at 315° for 24 hr, the orange product, isolated quantitatively, was characterized and shown to be a third isomer of the $Co[B_7C_2H_9]_2^-$

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[7] We are indebted to D. H. Templeton, A. Zalkin, and D. St. Clair for the communication of these preliminary results.

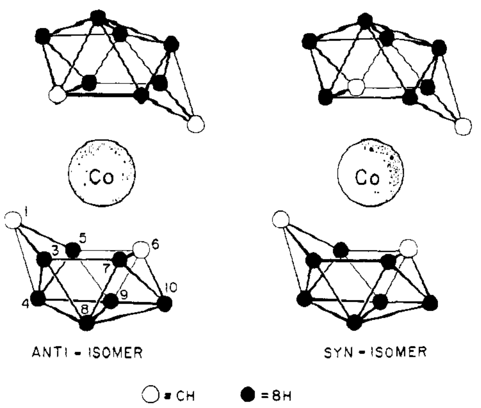

Figure 4. Schematic drawing of the bis-π-(2)-1,6-dicarbazapylcobalt(III) ion structure.

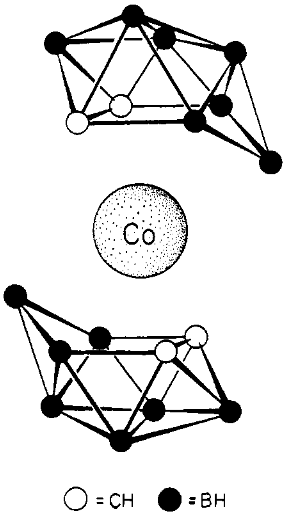

Figure 5. Proposed structure of the bis-π-(2)-6,7-dicarbazapylcobalt(III) ion in schematic form.

system. The elemental analyses, equivalent weight, and formula weight are presented in Table II.

The 60-Mc/sec ^1H nmr spectrum of the tetramethylammonium salt is given in Table III. It contains two broad carborane C–H resonances each of relative intensity 2. In comparing this spectrum with that of the precursor, $Co[\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9]_2^-$, one of the carborane C–H resonances has moved significantly downfield to τ 1.92 from τ 5.40 while the other carborane C–H resonance remained in approximately the same position. This suggests that one carbon atom in each ligand has moved into a very different environment, probably away from the direct bonding influence of the cobalt atom.

The 32-Mc/sec ^{11}B nmr spectrum of the tetramethylammonium salt is presented in Figure 6 and shows two doublets of relative intensities 3 and 4. This ^{11}B spectrum represents a much more symmetrical system with no low-field doublet, which had previously been assigned to an apex boron atom,[2,3] namely boron atom 10.

As a result of the apparent high symmetry of the third isomeric $B_7C_2H_9^{2-}$ ligand, as shown by the ^{11}B spectrum, it is suggested that the thermal rearrangement has moved the nonapical carbon atom out of the bonding face and into the other apex position to generate $Co[\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9]_2^-$. The proposed structure for this new isomer is shown in Figure 7. The known thermal rearrangement of 1,6- to 1,10-$B_8C_2H_{10}$,[8] which occurs at 350°, is an analogous rearrangement. The infrared and electronic spectra of $Co[\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9]_2^-$ are presented in Tables IV and V.

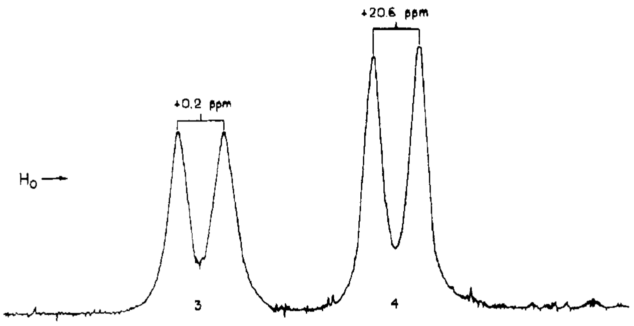

Figure 6. Boron-11 nmr spectrum (32 Mc/sec) in acetone solvent of the bis-π-(2)-1,10-dicarbazapylcobalt(III) ion. Chemical shifts were measured relative to $BF_3 \cdot O(C_2H_5)_2 = 0$.

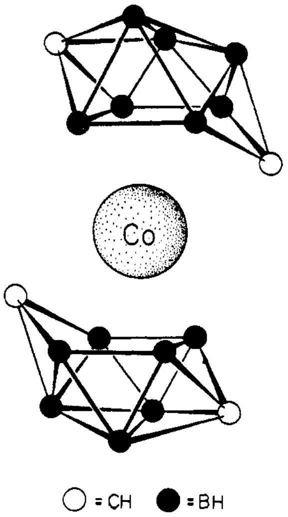

Figure 7. Proposed structure of the bis-π-(2)-1,10-dicarbazapylcobalt(III) ion in schematic form.

The tetramethylammonium salt of bis-π-(2)-6,7-dicarbazapylcobalt(III) was also thermally rearranged at 250° with no apparent decomposition to give $Co[\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9]_2^-$. However, at no temperature was $Co[\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9]^{2-}$ observed as a product from $Co[\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9]_2^-$. In a melting point capillary, rearrangement of $Co[(2)\text{-}6,7\text{-}B_7C_2H_9]_2^-$ was observed as low as 150° over a 12-hr period. Differential thermal analysis results are presented in Table VI which show that while both $Co[\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9]_2^-$ and $Co[\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9]_2^-$ rearrange under similar thermal conditions, the 6,7 and 1,6 isomers are not thermally interconvertible. This suggests that the 1,6 isomer arises *via* rearrangement of a *6,7 intermediate* produced in the preparative reaction.

Preparation and Characterization of π-Cyclopentadienyl-π-(2)-1,6-dicarbazapylcobalt(III). The reaction of a mixture of 1,3-dicarba-*nido*-undecahydrononaborate-

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[8] F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

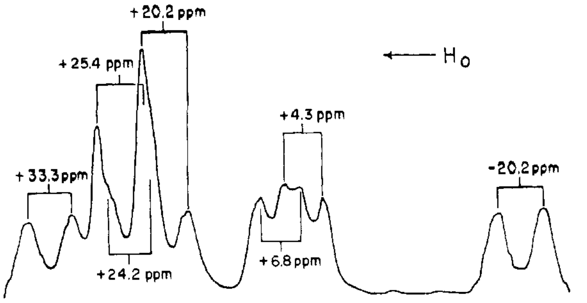

Figure 8. Boron-11 nmr spectrum (32 Mc/sec) in acetone solvent of π-cyclopentadientyl-π-(2)-(1,6-dicarbazapylcobalt(III). Chemical shifts were measured relative to $BF_3{\cdot}O(C_2H_5)_2 = 0$.

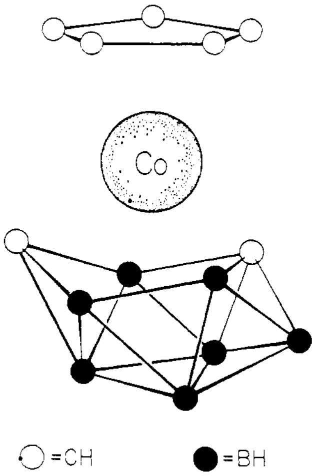

Figure 9. Proposed structure of π-cyclopentadienyl-π-(2)-1,6-dicarbazapylcobalt(III) in schematic form.

(2−) ion and cyclopentadienide ion with anhydrous cobalt(II) chloride gave a mixture of π-cyclopentadienyl-π-(2)-1,6-dicarbazypylcobalt(III),[2] bis-π-(2)-6,7-dicarbazapylcobalt(III) ion, cobaltocinium ion, cobalt metal, and hydrogen. The yield and characterization

$$C_5H_5^- + 1.5Co^{2+} + B_7C_2H_{11}^{2-} \longrightarrow H_2 + 0.5Co^0 + (C_5H_5)Co(B_7C_2H_9)$$

data are presented in Table II. The above formulation for the product was verified by high-resolution mass spectroscopy which gave a parent peak at *m/e* 234.109 (calcd for $(^{12}C_5{}^1H_5)^{59}Co(^{11}B_7{}^{12}C_2{}^1H_9)$: 234.108).

Table VI. Differential Thermal Analysis of π-(2)-6,7- and π-1,6-Dicarbazapylcobalt(III) Derivatives Observed for the Temperature Range 27–280°

Compound	Rearrangement temp, °C	Heating rate, °C/min
$(CH_3)_4N[(6,7\text{-}B_7C_2H_9)_2Co]$	239	40
$(CH_3)_4N[(1,6\text{-}B_7C_2H_9)_2Co]$	231	40
$(C_5H_5)Co(1,6\text{-}B_7C_2H_9)$	226	40

The 60-Mc/sec ¹H nmr spectrum is presented in Table III. There is one sharp singlet of relative intensity 5 at τ 4.55 due to the presence of a π-C_5H_5 ring and two broad carborane C–H resonances, each of relative intensities 1 at τ 3.03 and 6.77. Figure 8 shows the 32-Mc/sec ^{11}B nmr spectrum of the neutral red complex. It consists of a low-field doublet of relative intensity 1, a triplet of relative intensity 2, and a multiplet of relative intensity 4, and resembles that obtained for bis-π-(2)-1,6-dicarbazapylcobalt(II) in that it contains seven discrete doublets. The low symmetry apparent in the ^{11}B nmr spectrum led to the proposed structure shown in Figure 9 with the carbon atoms of the $B_7C_2H_9{}^{2-}$ ligand in the 1,6 configuration and cobalt in the formal oxidation state +3 placed between $C_5H_5^-$ and $B_7C_2H_9{}^{2-}$. No evidence for the presence of a π-cyclopentadienyl-π-(2)-6,7-dicarbazapylcobalt(III) isomer was observed. The infrared and electronic spectra are presented in Tables IV and V.

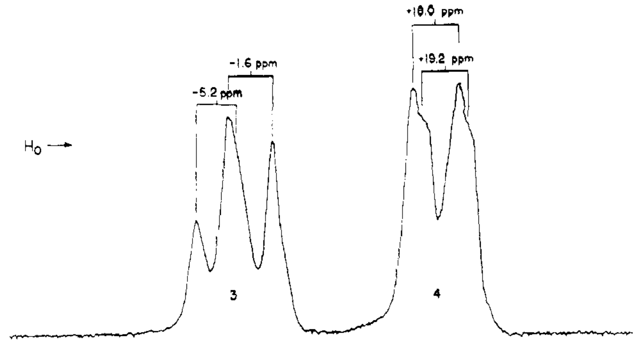

Figure 10. Boron-11 nmr spectrum of π-cyclopentadienyl-π-1,10-dicarbazapylcobalt(III) in acetone. Chemical shifts measured relative to $BF_3{\cdot}O(C_2H_5)_2 = 0$.

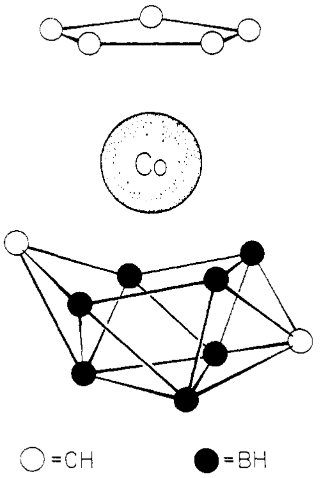

Figure 11. Proposed structure of π-cyclopentadienyl-π-(2)-1,10-dicarbazapylcobalt(III) in schematic form.

The Thermal Rearrangement of π-Cyclopentadienyl-π-(2)-1,6-dicarbazapylcobalt(III). It was found that π-cyclopentadienyl-π-(2)-1,6-dicarbazapylcobalt(III) quantitatively rearranged to give an orange complex at 315° over a period of 24 hr. Elemental analyses and molecular weight data, presented in Table II, support the evidence for a new isomer produced from (π-C_5H_5)-Co(π-(2)-1,6-$B_7C_2H_9$). The mass spectrum of the product exhibited a parent peak at *m/e* 234.108 (calcd for

$(^{12}C_5{}^1H_5)^{59}Co(^{11}B_7{}^{12}C_2{}^1H_9)$: 234.108) and confirmed the assigned molecular composition.

Figure 10 presents the 32-Mc/sec ^{11}B nmr spectrum which consists of four doublets of relative areas 1:2:2:2. No low-field doublet was observed. The 60-Mc/sec ^1H nmr data presented in Table III contains a sharp cyclopentadienyl resonance at τ 4.65 of relative intensity 5, and the carbon proton resonances associated with the $B_7C_2H_9{}^{2-}$ ligand appear as broad singlets at τ 0.94 and 3.50 of relative intensity 1 each. A significant shift downfield has occurred for one of the carbon C–H resonances, from τ 6.77 to 0.97, as was observed in the thermal rearrangement of bis-π-(2)-1,6- and bis-π-(2)-6,7-dicarbazapylcobalt(III) ions to bis-π-(2)-1,10-dicarbazapylcobalt(III) ion. The other carbon C–H resonance has shifted relatively little.

Figure 11 shows the proposed structure of the rearrangement product. A carbon atom has migrated to the 10 position from the 6 position and out of the bonding face.

The kinetics of the thermal rearrangement of π-cyclopentadienyl-π-(2)-1,6-dicarbazapylcobalt(III) to π-cyclopentadienyl-π-(2)-1.10-dicarbazapylcobalt(III) has been studied[9] by following the disappearance of an absorbance at 5800 Å in the visible spectrum. The rearrangement was conducted in diphenyl ether solvent at varying temperatures and initial reactant concentrations. The thermodynamic data for rearrangement are $\Delta H^{\ddagger} = 34$ kcal/mole and $\Delta S^{\ddagger} = 3 \pm 2$ cal mole^{-1} deg^{-1}. The low positive entropy of activation suggests that there is very little change in the degrees of freedom in going into the transition state and that the over-all rearrangement does not involve any drastic change in the basic structure, but rather a smooth change of atomic positions without discrete bond-breaking and bond-making.

The electronic and infrared spectra are presented in Tables IV and V.

The differential thermal analysis results presented in Table VI show that under identical heating rates the observed rearrangement temperature for bis-π-(2)-1,6- and bis-π-(2)-6,7-dicarbazapylcobalt(III) are very similar and undoubtedly involve similar rearrangement processes.

Experimental Section

Physical Measurements. Proton nmr spectra were obtained by means of a Varian A-60 spectrometer and ^{11}B nmr spectra with a Varian HA-100 at 32.1 Mc/sec. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Ultraviolet-visible spectra were measured with a Cary Model 14 spectrophotometer. Molecular weights were determined with a Mecrolab Model 301A osmometer. Titrations were carried out using a Leeds Northrup Model 7664 pH meter with a Thomas combination glass–calomel electrode. Differential thermal analysis was investigated using a Perkin-Elmer differential scanning calorimeter, DSC-1. Mass spectra were determined with a CEC Type 21-103B mass spectrometer.

Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. 1,3-Dicarbanonaborane(13), $B_7C_2H_{13}$, was prepared by the oxidation of the potassium salt of (3)-1,7-dicarbadodecahydoundecaborate(1−) ion, (3)-1,7-$B_9C_2H_{12}{}^-$, with chromic acid.[10] Cobalt(II) chloride was dried according to the procedure of King.[11] Sodium hydride, as a 57–60% dispersion in mineral oil, was obtained from Metal Hydrides, Inc.

Diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane were freshly distilled from lithium aluminum hydride and collected under nitrogen. Ultraviolet and visible spectral measurements were made in Spectrograde acetonitrile.

Preparation of the 1,3-Dicarba-*nido*-undecahydrononaborate(2−) Ion, Na_2-1,3-$B_7C_2H_{11}$. A solution of 1.0 g (8.86 moles) of $B_7C_2H_{13}$ in 50 ml of diethyl ether was added slowly to a stirred suspension of 0.5 g (20.8 mmoles) of sodium hydride (0.88 g of a 57.2% dispersion in mineral oil), in 50 ml of the same solvent. The reaction was stirred at reflux temperature under nitrogen for 3 hr. Stirring was then stopped and the reaction mixture was allowed to cool to room temperature. The resulting suspension was then ready for use in further reactions.

Preparation of the Bis-π-(2)-6,7-dicarbazapylcobalt(III) Anion, $(CH_3)_4N[\pi$-(2)-6,7-$B_7C_2H_9]_2Co$. To the above suspension of Na_2-1,3-$B_7C_2H_{11}$, at room temperature, was added a slurry of 1.2 g (9.25 mmoles) of anhydrous cobalt(II) chloride in 100 ml of diethyl ether. The resulting green mixture was stirred for 36 hr at room temperature under nitrogen. The reaction mixture was then filtered and the solvent removed on a rotary evaporator using a water aspirator. The residue was shaken with 150 ml of water and filtered. The pink precipitate which resulted from the addition of excess 50% aqueous tetramethylammonium chloride to the solution was separated by filtration and dried *in vacuo* over P_2O_5. Purification was carried out by chromatography on a silica gel column by eluting with dichloromethane. Red crystals of $(CH_3)_4N[\pi$-(2)-6,7-$B_7C_2H_9]_2Co$ (mp 235°) were obtained from an acetone–toluene mixture by allowing the acetone to slowly evaporate at ambient temperature; total yield of product was 1.0 g (2.8 mmoles, 64.5%).

Preparation of the Bis-π-(2)-1,6-dicarbazapylcobalt(III) Anion, $(CH_3)N_4[\pi$-(2)-1,6-$B_7C_2H_9]_2Co$. To 8.86 mmoles of Na_2-1,3-$B_7C_2H_{11}$ in 150 ml of diethyl ether was added a slurry of 1.4 g (10.8 mmoles) of anhydrous cobalt(II) chloride in 150 ml of a 1,2-dimethoxyethane. After refluxing (70°) for 10 hr, the reaction mixture was cooled to room temperature, filtered, and stripped to dryness *in vacuo*. The residue was dissolved in 150 ml of water and filtered and the brown tetramethylammonium salt, $(CH_3)_4N[\pi$-(2)-1,6-$B_7C_2H_9]_2Co$ (mp 240°), precipitated by adding of an excess 50% aqueous tetramethylammonium chloride. The salt was purified by chromatography on a silica gel column, eluting with dichloromethane. Crystallization was achieved by adding hexane to the dichloromethane solution and slowly removing the dichloromethane at room temperature and reduced pressure. Brown crystals of product (0.80 g, 2.28 mmoles, 53%) were obtained. Further recrystallization was effected from a dichloromethane–hexane mixture by allowing the solvent to slowly evaporate at ambient temperature.

Preparation of Bis-π-(2)-1,10-dicarbazapylcobalt(III) Anion, $Cs[\pi$-(2)-1,10-$B_7C_2H_9]_2Co$. (a) From $Cs[\pi$-(2)-1,6-$B_7C_2H_9]_2Co$. A 0.27-g (0.77 mmole) sample of $(CH_3)_4N[\pi$-(2)-1,6-$B_7C_2H_9]_2Co$ was dissolved in the minimum amount of acetone and washed onto an ion-exchange column (1 in. × 16 in.) of Dowex resin (Dowex 50W-X6, 50–100 mesh). The material was eluted with 15 ml of a 60:40 water–acetone mixture and then with distilled water. The acetone was removed from the solution under reduced pressure and a saturated solution of cesium chloride added. The cesium salt was recrystallized from hot water. A 0.13-g (0.32 mmole) sample of $Cs[\pi$-(2)-1,6-$B_7C_2H_9]_2Co$ was sealed off in a thick-walled tube and heated at 315–325° for 22 hr. The orange product was dissolved in acetone and chromatographed on a silica gel column eluting with a 75:25 dichloromethane–acetone solvent mixture. Microcrystals, 0.125 g (0.305 mmole, 95%), of $Cs[\pi$-(2)-1,10-$B_7C_2H_9]_2Co$ (mp 210°) were obtained from hot water by chilling to 0°.

(b) From $(CH_3)_4N[\pi$-(2)-6,7-$B_7C_2H_9]_2Co$. An 0.31-g (0.88 mmole) sample of $(CH_3)_4N[\pi$-(2)-6,7-$B_7C_2H_9]_2$ was sealed in a thick-walled tube and heated at 250° for 22 hr. The product was chromatographed on a silica gel column, eluting with dichloromethane to produce 0.29 g (0.85 mmole, 90%) of $(CH_3)_4N[\pi$-(2)-1,10-$B_7C_2H_9]_2Co$ (mp 192°) which was crystallized from a dichloromethane–hexane solvent mixture.

Preparation of π-Cyclopentadienyl-π-(2)-1,6-dicarbazapylcobalt(III), $(\pi$-$C_5H_5)Co(\pi$-(2)-1,6-$B_7C_2H_9)$. A diethyl ether solution of 7.05 g (107.0 mmoles) of freshly distilled cyclopentadiene and 2.0 g

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(9) Y. Ta-Ching, M.S. Dissertation University of California, Riverside, Calif.

(10) P. M. Garrett, T. A. George, J. C. Burr, D. A. Owen, J. C. Smart, and M. F. Hawthorne, *Inorg. Chem.*, in press.

(11) R. B. King in "Organometallic Syntheses," Vol. I, R. B. King and J. J. Eisch, Ed., Academic Press, New York, N. Y., 1965.

(17.75 mmoles) of $B_7C_2H_{13}$ were treated with an excess of sodium hydride as described above for the preparation of Na_2-1,3-$B_7C_2H_{11}$. The resulting solution was cooled to 0°, and a slurry of 15.0 g (115.5 mmoles) of anhydrous cobalt(II) chloride in 100 ml of diethyl ether was added. The red reaction mixture was stirred at 0° under nitrogen for 8 hr. After filtering the solution, the solvent was removed *in vacuo*. The residue was extracted with 100 ml each of water and benzene. The benzene extract was dried over anhydrous $MgSO_4$ and chromatographed on a silica gel column. Elution with a 1:1 benzene–hexane mixture gave a red solution. Crystallization from hot hexane gave 1.485 g (6.38 mmoles, 36%) of pure (π-C_5H_5)Co(π-(2)-1,6-$B_7C_2H_9$) (mp 158–159°). To the aqueous extract was added excess 50% aqueous tetramethylammonium chloride. The pink precipitate was dried *in vacuo* over P_2O_5. After chromatographing on silica gel as described previously, 0.225 g (0.64 mole, 7%) of red $(CH_3)_4N[\pi$-(2)-6,7-$B_7C_2H_9]_2Co$ was recovered and identified by its ^{11}B nmr spectrum.

Preparation of π-Cyclopentadienyl-π-(2)-1,10-dicarbazapylcobalt(III), (π-C_5H_5)Co(π-(2)-1,10-$B_7C_2H_9$). A 1.35-g (5.80 mmoles) sample of (π-C_5H_5)Co(π-(2)-1,6-$B_7C_2H_9$) was sealed off in a thick-walled tube and heated at 310° for 24 hr. The tube was cracked open and the orange product dissolved in acetone. Purification was accomplished by chromatography of a silica gel column, eluting with benzene. Solvent was removed *in vacuo* and 1.32 g (5.67 mmoles, 98%) of (π-C_5H_5)Co(π-(2)-1,10-$B_7C_2H_9$) (mp 113°) was obtained. Crystallization was achieved from a dichloromethane–hexane mixture and allowing the dichloromethane to evaporate slowly at ambient temperature.

Hydrogen Evolution Experiments. (a) **Preparation of 1,3-Dicarba-*nido*-undecahydrononaborate(2−) Ion.** A 0.354-g (3.14 mmoles) sample of $B_7C_2H_{13}$ and 0.151 g (6.28 mmoles; 0.264 g of a 57.2% dispersion in mineral oil) of sodium hydride were placed in a 200-ml round-bottomed flask which had two break-seals, one open neck, and a side arm attached to its neck. Into the side arm was placed 0.306 g (2.37 mmoles) of anhydrous cobalt(II) chloride. Dry ether (50 ml) was condensed into the flask at −196° and the open neck sealed off. The reaction mixture was stirred at room temperature for 14 days. Gas evolution measurements using a Toepler pump and calibrated volume indicated 6.15 mmoles (98%) of hydrogen had been liberated.

(b) **Preparation of Bis-π-(2)-6,7-dicarbazapylcobalt(III).** The system described above was sealed off and tipped sideways to allow the anhydrous cobalt(II) chloride to mix with the 1,3-$B_7C_2H_{11}^{2-}$ dianion. This reaction mixture was stirred at room temperature for 5 days. Gas evolution measurements using a Toepler pump and a calibrated volume indicated that 2.98 mmoles (96% based on $B_7C_2H_{11}^{2-}$ formed) of hydrogen had been evolved. The product was a mixture of bis-π-(2)-1,6- and bis-π-6,7-dicarbazapylcobalt(III) ions, and the combined yield of the tetramethylammonium salts of the isomer was 75% (based on starting 1,3-$B_7C_2H_{13}$).

(c) **Preparation of 1,2-Dimethyl-1,2-dicarba-*nido*-undecahydrononaborate(2−) and 1-Phenyl-1,2-dicarba-*nido*-undecahydrononaborate(2−) Ions.** In a manner similar to that described above for 1,3-$B_7C_2H_{11}^{2-}$, Na_2-1,3-$B_7C_2H_{10}(C_6H_5)$ and Na_2-1,3-$B_7C_2H_9(CH_3)_2$ were prepared in a sealed system and the hydrogen evolution was measured using a Toepler pump and calibrated volume. These results are presented in Table I.

Reaction of DCl with Disodium 1,3-Dimethyl-1,3-dicarba-*nido*-undecahydrononaborate(2−), Na_2-1,3-$(CH_3)_2B_7C_2H_9$. Into Na_2-1,3-$(CH_3)_2B_7C_2H_9$, prepared in the hydrogen evolution above, was condensed an excess of DCl. After evaporating diethyl ether and excess DCl, the 1,3-$(CH_3)_2B_7C_2H_9D_2$ product was purified by sublimation to give 0.27 g (80% based on starting 1,3-$(CH_3)_2B_7C_2H_{11}$) of product which was characterized by its infrared and ^1H nmr spectra.

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