Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850

Thermal Rearrangement of 1-(η-C_5H_5)-1-Co-2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$

G. D. MERCER, M. TRIBO, and F. R. SCHOLER*

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The thermal rearrangement of the nonicosahedral metallocarborane 1-(η-C_5H_5)-1-Co-2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$ (I) at 110° yields an orange metallocarborane, 10-(η-C_5H_5)-10-Co-2,3-$(CH_3)_2$-2,3-$C_2B_8H_8$ (II), which rearranges upon heating at 125° to the thermodynamically stable isomer 1-(η-C_5H_5)-1-Co-2,3-$(CH_3)_2$-2,3-$C_2B_8H_8$ (III). The orange complex is identified as an intermediate formed in the rearrangement of I → III and is the second known example of a monometallocarborane with five boron atoms in the π-bonding face. Whereas the rearrangement of I → II involves the combined migration of the cobalt and carbon atoms, the rearrangement II → III involves only the C_5H_5Co group and indicates the mobility of the C_5H_5Co vertex in the octadecahedral metallocarborane. The rearrangements are examined in light of the empirical rules developed for thermal rearrangements in the polyhedral metallocarboranes. The three isomers were identified on the basis of their electrochemical and spectral properties.

Introduction

The thermally induced migration of carbon atoms over the surface of the icosahedral complex (η-C_5H_5)$CoC_2B_9H_{11}$ and its carbon-substituted derivatives has been thoroughly studied and all possible isomers have been isolated.[1] The structures of the complete isomeric series have been established on the basis of their chromatographic, electrochemical, and spectral properties. A more limited study of the thermal rearrangements of the nonicosahedral cobaltacarboranes has also been reported, but not all isomers of these polyhedra have been reported.[2] These investigations have led to the development of some basic empirical rules, which govern the thermal rearrangements of the compounds (η-C_5H_5)$CoC_2B_nH_{n+2}$, n = 6–10. Recently, these rearrangements have been extended to the bimetallic carboranes (η-C_5H_5)$_2Co_2C_2B_nH_{n+2}$, n = 6–8. Rearrangements involving migration of cobalt as well as carbon atoms in the polyhedral surface were observed.[3]

In the nonicosahedral metallocarborane series, 1-(η-C_5H_5)-1-Co-2,4-$C_2B_8H_{10}$ rearranges to 1-(η-C_5H_5)-1-Co-2,3-$C_2B_8H_{10}$ at 150° (see Figure 1) in cyclooctane. This rearrangement conforms to the rules in that migration of the two carbon atoms occurs to increase their mutual separation and to occupy the vertex position with the lowest coordination number. The cobalt atom also remains at the highest coordination position in accord with the empirical rules. We wish to report the thermally induced rearrangement of the 1-(η-C_5H_5)-1-Co,2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$, which further defines the applicability of these empirical rules to the rearrangements of metallocarborane polyhedra.

Experimental Section

Physical Measurements. Proton nmr spectra were measured using a Varian A-60A. The 70-MHz ^{11}B nmr were measured on a Varian Associates Model HA-220 spectrometer interfaced with a Nicolet pulsed Fourier transform computer. Polarograms were obtained on a Heathbuilt Model EVA-19 dropping-mercury electrode apparatus. Constant-potential electrolyses were performed using a Wenking Electronic Potentiostat, Model 68 FR 0.5 and a cell design previously described in the literature.[4] The cyclic voltammograms were obtained from an instrument designed by Professor R. Reed and previously described in the literature.[5] The cyclic voltammetric data were measured in acetonitrile (0.1 M tetrabutylammonium bromide) at a hanging-drop mercury electrode and a platinum-button electrode. Redox potentials are reported as $E_{p/2}$ *vs.* sce. The ultraviolet–visible spectra were measured in acetonitrile using a Cary 14 spectrophotometer. Mass spectra were obtained using an Associated Electrical Industries MS-902 spectrometer.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. All reactions were routinely carried out in an inert atmosphere using standard Schlenk techniques.

Materials. Silica gel powder, 60–200 mesh, was obtained from J. T. Baker Chemical Co. for use in column chromatography. Spectroquality acetonitrile was obtained from Matheson Coleman and Bell and distilled from CaH_2 under nitrogen prior to use. Octane was distilled from potassium–benzophenone under nitrogen. Hexane and methylene chloride were reagent grade. [(η-C_5H_5)Co-η-(3)-1,2-$(CH_3)_2$-1,2-$B_9C_2H_9$][6] and [1-(η-C_5H_5)-1-Co-2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$][7] were prepared by literature methods.

Thermal Rearrangement of [1-(η-C_5H_5)-1-Co-2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$], I. A 250-ml three-neck flask equipped with a reflux condenser, gas inlet tube, and a magnetic stirring bar was degassed, charged with 500 mg (1.8 mmol) of I and 125 ml of degassed octane distilled directly into the reaction vessel. The reaction mixture was heated at reflux for 5 hr, cooled to room temperature, and then cooled at −15° for 2 days. Filtration yielded a bright blue precipitate, [1-(η-C_5H_5)-1-Co-2,3-$(CH_3)_2$-2,3-$B_8C_2H_8$], III (100 mg, 0.36 mmol). Evaporation of the filtrate yielded an orange residue, which was recrystallized from a minimum amount of n-hexane cooled to −60° giving 155 mg (0.57 mmol) of pure [10-(η-C_5H_5)-10-Co-2,3-$(CH_3)_2$-2,3-$B_8C_2H_8$], II.

I. *Anal.* Calcd for $CoB_8C_9H_{19}$: C, 39.64; B, 31.72; H, 6.97; Co, 21.66. Found: C, 39.92; B, 31.01; H, 7.02; Co, 21.77. Nmr ($CDCl_3$): τ 3.15 (s, 5, C_5H_5), 5.6 (s, 3, C-CH_3), 6.55 (s, 3, C-CH_3). Uv–visible [λ_{max}, nm (ϵ)]: 576 (620), 470 sh (260), 332 (3100), 291 (8500), 251 (16,800).

II. *Anal.* Found: C, 40.17; B, 31.92; H, 7.08; Co, 21.45. Nmr ($CDCl_3$): τ 4.7 (s, 5, C_5H_5), 7.66 (s, 6, C-CH_3). Uv–visible [λ_{max}, nm (ϵ)]: 600 (30), 419 (360), 265 (24,700), 234 sh (7750).

III. *Anal.* Found: C, 40.05; B, 31.61; H, 7.05; Co, 21.89. Nmr ($CDCl_3$): τ 4.36 (s, 5, C_5H_5), 7.17 (s, 6, C-CH_3). Uv–visible [λ_{max}, nm (ϵ)]: 595 (610), 452 (330), 355 (5900), 292 (9600), 242 (27,000).

Results and Discussion

The purple C,C'-dimethyl derivative 1-(η-C_5H_5)-1-Co-2,-4-$(CH_3)_2$-2,4-$C_2B_8H_8$, I, thermally rearranges in refluxing octane over a 5-hr period to give a mixture of two isomers (II, III). By cooling the reaction mixture at −15° a blue crystalline material (III) precipitates, which is isolated by filtration. Evaporation of the filtrate and recrystallization of the residue from n-hexane gives an orange crystalline material, II. The blue product, III, initially separated by cooling the reaction mixture, exhibits a mass spectral cutoff at m/e 274 corresponding to the $^{11}B_8{}^{12}C_9{}^{1}H_{19}{}^{59}Co^+$ ion. Characterization of III by ^1H and ^{11}B nmr identified III as the C,C'-dimethylmetallocarborane 1-(η-C_5H_5)-1-Co-2,3-$(CH_3)_2$-2,3-$B_8C_2H_8$, analogous to the previously reported parent compound $C_5H_5CoB_8C_2H_{10}$.[8]

The second metallocarborane isolated from this reaction, II, also exhibited a cutoff in the mass spectrum at m/e 274 corresponding to $^{11}B_8{}^{12}C_9{}^{1}H_{19}{}^{59}Co^+$ ion. The 70-MHz ^{11}B nmr spectrum (Table I) and the ^1H nmr spectrum (see Experimental Section) of this orange species are consistent with the structure shown in Figure 1 assuming octadecahedral geometry for the 11-atom polyhedron. The ^1H nmr spectrum of 10-(η-C_5H_5)-10-Co-2,3-$(CH_3)_2$-2,3-$B_8C_2H_8$, II, contains a sharp singlet of intensity 6 at τ 7.66 ($W_{1/2} \approx 7$ Hz) assigned to the two equivalent carborane methyl groups. The ^1H nmr spectrum of II is also invariant to changes in temperature from −60 to +25°. No signals attributable to a BHB bridge hydrogen to the high-field side of TMS were observed. The

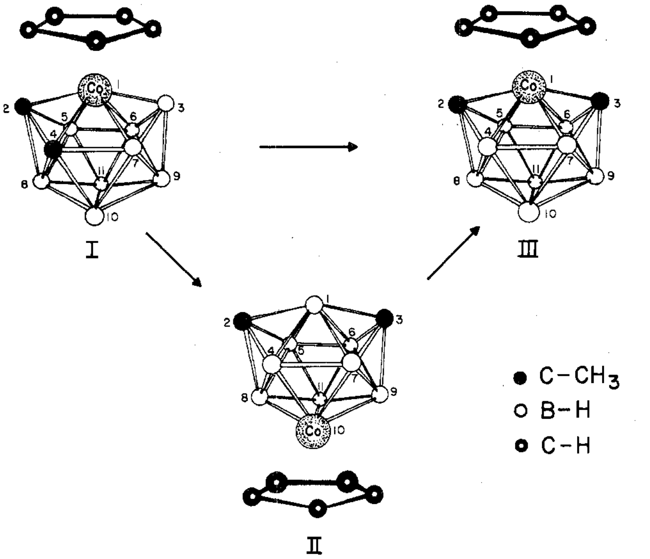

Figure 1. Rearrangement of 1,2,4-$(C_5H_5)Co(CCH_3)_2B_8H_8$, I, to 1,2,3-$(C_5H_5)Co(CCH_3)_2B_8H_8$, III, *via* an intermediate 10,2,3-$(C_5H_5)Co(CCH_3)_2B_8H_8$, II.

Table I. ^{11}B Nmr Spectra

Compd	Chem shift,[a]
1-(η-C_5H_5)-1-Co-2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$ (I)[b]	−76.2 (1), −12.2 (1), −6.0 (1), −1.4 (1), +5.4 (1), +11.0 (1), +19.4 (1), +35.3 (1)
1-(η-C_5H_5)-1-Co-2,4-$C_2B_8H_{10}$[c]	−71.7 (1), −13.3 (1), −3.0 (2), +8.8 (1), +19.9 (1), +21.6 (1), +40.8 (1)
10-(η-C_5H_5)-10-Co-2,3-$(CH_3)_2$-2,3-$C_2B_8H_8$ (II)[b]	−8.1 (2), −6.0 (1), −5.1 (2), +2.7 (2), +9.8 (1)
1-(η-C_5H_5)-1-Co-2,3-$(CH_3)_2$-2,3-$C_2B_8H_8$ (III)[b]	−13.4 (2), +6.8 (4), +21.3 (2)
1-(η-C_5H_5)-1-Co-2,3-$C_2B_8H_{10}$[d]	−8.5 (2), +9.5 (4), +21.7 (2)

[a] In ppm from $BF_3{\cdot}OEt_2$. [b] 70-MHz ^{11}B. [c] 80-MHz ^{11}B. [d] 32.1-MHz ^{11}B.

70-MHz ^{11}B nmr spectrum of the orange isomer, II, consists of five doublets of relative intensity 2:1:2:2:1. The absence of a low-field doublet of intensity 2 in the ^{11}B nmr spectrum indicates there are no boron atoms in the low-coordinate positions. For metallocarboranes the chemical shift of a boron in a low-coordinate position adjacent to a cobalt atom usually occurs at approximately −70 ppm below $BF_3{\cdot}OEt_2$.[9] For the ten- and nine-membered carborane polyhedra the chemical shift of a boron atom located in the low-coordinate position occurs at approximately −20 ppm. Although the ^{11}B nmr evidence is not definitive, we favor placing the two equivalent carborane methyl groups at the 2,3 positions. Also, a resonance of area 1 at highest field indicates the unique seven-coordinate position is occupied by a boron atom and not the C_5H_5Co group. Assuming the octadecahedral geometry for the isomer II, the cobalt atom can be located at only two possible positions and be consistent with the molecular symmetry indicated by the ^1H and ^{11}B nmr spectra. The cobalt atom must be located at either of the equivalent B(10) or B(11) positions yielding, potentially, a *dl* pair.

Alternate structures have been considered. Assuming the cobalt atom can be located at either the B(10) or B(1) position in the intermediate isomer II, the molecular symmetry of II indicated by the ^{11}B and ^1H nmr can be satisfied by assigning the carborane methyl groups to the adjacent 4,7 positions. These possibilities have been rejected in favor of the proposed structure shown in Figure 1. The alternate structures would require the carbon atoms to remain adjacent during the rearrangement while moving no further from the cobalt atom as well as moving the carbon at the low-coordinate 2 position to the high-coordinate 4 or 7 position. We also note the absence of the low-field boron resonance in the 70-MHz spectrum of II due to the presence of low-coordinate boron atoms, which are required in the alternate structures.

The third alternate structure for II would place the cobalt at the high-coordinate 1 position and the carborane methyl groups at either of the equivalent 2,7 and 2,6 positions. In order to satisfy the molecular symmetry requirements indicated by the ^1H and ^{11}B nmr spectra, the proposed molecule would have to exhibit fluxional behavior such as noted for the (η-C_5H_5)$CoC_2B_{10}H_{12}$.[2] Since no change in either the line width or the shape is noted in the ^1H nmr spectrum on cooling to −65°, the fluxional model is also rejected. In the absence of an X-ray diffraction study,[10] it is not possible to make a definitive structural assignment, but the structure proposed for the orange isomer, II, is consistent with the available data.

Additional evidence for the structure of II was obtained by analysis of its ultraviolet–visible spectrum and electrochemical data and comparison to those of isomers I and III. For the isomeric series (I, II, III) there is a hypsochromic shift of the λ_{max} values for the d–d transitions as the corresponding π-bonding face changes from the B_4C_2 in I and III to B_5 in II. Also, the λ_{max} (d–d region) values of I and III, as well as their colors are quite similar, suggesting the C_5H_5Co units are in like environments; *i.e.*, both are in the high-coordinate position π bonded to a B_4C_2 face. In contrast, II is a bright orange crystalline material and has a λ_{max} at 419 nm indicating a shift toward a stronger ligand field. Hawthorne, *et al.*, have already suggested for the $C_5H_5CoB_9C_2H_{11}$ series that a B_5 face will stabilize a high positive charge on a cobalt atom better than a B_4C or B_3C_2 face, which indicates a stronger ligand field.[1] For the $C_5H_5CoB_8H_8(CCH_3)_2$ series the same trend is observed due to the change in symmetry about the cobalt atom as well as variations in the number of carbon atoms in the open face.

The electrochemical data are also in accord with this observation. The $E_{p/2}$ values (Table II) indicate II is reduced with greater difficulty than the isomers I and III. Using a hanging-drop mercury electrode each isomer has a second reduction wave at approximately −1.6 V. For I and II the second wave represents the addition of one electron and is a reversible process. Sharp color changes are noted during the controlled-potential analysis. For I and II, respectively, the color change is purple → orange and orange → green → red → orange. For the blue isomer (III) the second reduction wave contains two electrons and is irreversible, and the color change observed is blue → purple → orange. The total reduction represents the formal change of Co^{III} to Co^{II} followed by addition of two electrons to the octadecahedral metallocarborane forming the anodic species $[C_5H_5Co^{II}(CH_3C)_2B_8H_8]^{2-}$. Hawthorne and Evans have observed that the blue isomer 1,2,3-$C_5H_5CoC_2B_8H_{10}$ is reduced cleanly and rapidly compared to the 1,2,4-$C_5H_5CoC_2B_8H_{10}$ isomer and upon addition of $CoCl_2$ and NaC_5H_5 produces bimetallic icosahedral carboranes.[11]

The cyclic voltammograms are shown in Figure 2 for the series I → III. In accordance with the proposed structure for II its cyclic voltammogram has a reduction wave at −1.23 V, whereas those for I and III occur at −0.83 and −0.75 V, respectively. The cyclic voltammogram of I indicates a chemical reaction, possibly an intramolecular rearrangement, has occurred after addition of the first electron to the octadecahedral metallocarborane. Similar behavior has been noted for the {bis[η-μ-1,2-trimethylene-(3)-1,2-dicarbollyl]nickel(III)}(1−) system.[12]

The thermal rearrangement of I yields both isomers II and III. However, pyrolysis of the orange isomer in the solid state

Table II. Electrochemical Data

Compd	$-E_{p/2}$, V	No. of electrons transferred
1-(η-C_5H_5)-1-Co-2,4-$(CH_3)_2$-2,4-$C_2B_8H_8$ (I)	0.83	2.21
	1.64	
10-(η-C_5H_5)-10-Co-2,3-$(CH_3)_2$-2,3-$C_2B_8H_8$ (II)	1.23	2.02
	1.57	
1-(η-C_5H_5)-1-Co-2,3-$(CH_3)_2$-2,3-$C_2B_8H_8$ (III)	0.75	2.86
	1.66	

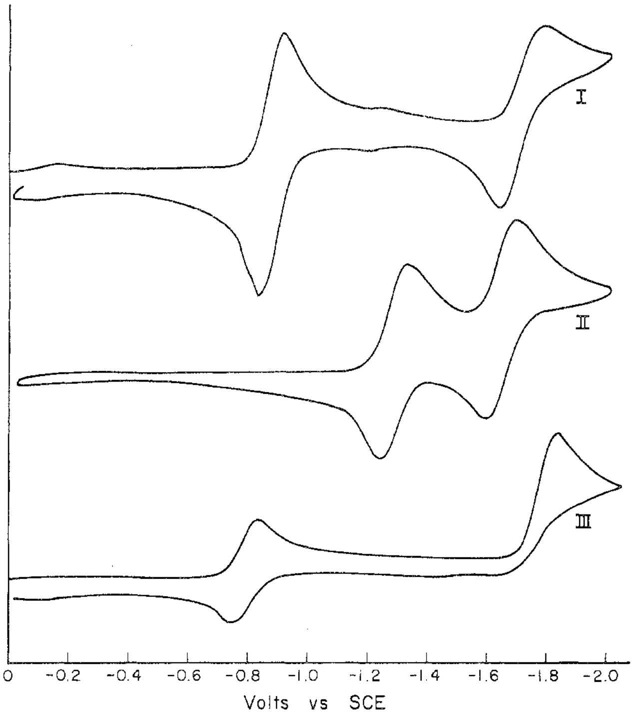

Figure 2. Cyclic voltammetry of 1,2,4-$(C_5H_5)Co(CCH_3)_2B_8H_8$, I, 10,2,3-$(C_5H_5)Co(CCH_3)_2B_8H_8$, II, and 1,2,3-$(C_5H_5)Co(CCH_3)_2B_8H_8$, III, in acetonitrile; scan rate 0.2 V/sec.

at 125° or at continuous reflux in octane yields the blue isomer, III. This indicates the orange isomer is an intermediate in the rearrangement of I → III. The proposed structure for II is unusual since it requires movement of a cobalt vertex out of the high-coordinate position for the I → II process. Conversion of II → III then produces the most thermodynamically favored isomer by returning the cobalt to the high coordination position, while maintaining the carbon atoms at the low-coordinate 2,3 positions. The thermal migration involved in the rearrangement I → II is not in accord with the empirical rules for monometallocarborane isomerizations.[2] However, II is not the most stable isomer and thus rearranges to III, where the structure is more in accord with prior observations of the 11-vertex series.[2] In support of this proposed rearrangement, Hawthorne, *et al.*, have observed in the bimetallic 11-vertex series that on prolonged heating 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ produces 8,9,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$.[13,14] Here, as in our case, the 8,9,2,3 isomer, where the cobalt atom is not in the high-coordinate position, is the least stable isomer to be isolated and also rearranges to 1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$. The rearrangement of the monometallic carborane (II → III) and the rearrangement of the 8,9,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ to the 1,10,2,3 isomer observed by Hawthorne[13] are two examples known, where the C_5H_5Co species migrates over the polyhedral surface and emphasizes the mobility of the C_5H_5Co vertex and its similarity to the isoelectronic BH vertex.

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Registry No. I, 54019-85-1; II, 54142-89-1; III, 54019-86-2; 1-(η-C_5H_5)-1-Co-2,4-$C_2B_8H_{10}$, 39015-00-4; 1-(η-C_5H_5)-1-Co-2,3-$C_2B_8H_{10}$, 42790-88-5.

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