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Synthesis of Icosahedral Metallocarboranes

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Using ethanolic potassium hydroxide as the reaction medium $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ has been prepared in 73% yield from $K\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{12}$, C_5H_6, and $CoCl_2$. A red by-product from the reaction was isolated and identified as $[\{\pi\text{-}C_5H_5)Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]$. The reaction between $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ and hydroxide ion in the presence of cobalt(II) afforded the brown trimetallic species $[\{(\pi\text{-}C_5H_5)Co(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]^-$. The electrochemical data for these complexes are discussed.

Studies on the chemistry[1-7] of icosahedral metallocarboranes and, more recently, the preparation of nonicosahedral metallocarboranes[8,9] frequently employ $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$ or $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ as starting materials. The cyclopentadienyl complex is especially useful since it often affords neutral products which are readily separated by column chromatography. In addition these products are amenable to mass spectroscopic study and the presence of only one type of carborane ligand greatly simplifies the interpretation of ^{11}B nmr spectral data. Unfortunately, the utility of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ as a starting point in reaction sequences has been limited by the low yields (16%) encountered in its preparation.[7] We now wish to report a convenient synthesis of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ in 73% yield along with the isolation of two new polymetallic species containing the previously characterized[5,10,11] $B_8C_2H_{10}^{4-}$ ligand.

Experimental Section

Physical Measurements. The 100-MHz ^1H nmr spectra were obtained using a Varian HA 100 spectrometer. The 80.5-MHz ^{11}B nmr spectra were recorded using an instrument designed and constructed by Professor F. A. L. Anet and Dr. C. H. Bradley of this department. Infrared spectral data were obtained using a Perkin-Elmer Model 137 spectrophotometer and electronic spectra using a Beckman Model DB spectrophotometer. Electrochemical measurements were made in acetonitrile solution, 0.1 *M* in $[(C_2H_5)_4N][ClO_4]$, using previously described[12] methods. Mass spectroscopic measurements were made using an Associated Electrical Industries Model MS-9 spectrometer. Analytical data were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. Reactions were carried out in a nitrogen atmosphere using solvents which had been saturated with nitrogen. Electronic spectral measurements were made using Spectrograde solvents; other solvents used were reagent grade. Cyclopentadiene was freshly distilled before use and $K\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{12}$ was prepared by previously described[13] methods. Column chromatography was carried out using 60–200 mesh silica gel supplied by the J. T. Baker Chemical Co.; quantities were estimated by the volume of the dry powder.

Preparation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ and $[\{\pi\text{-}C_5H_5)Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]$, I. A solution of potassium hydroxide (50 g of 85% KOH pellets; 0.76 mol) in absolute ethanol (400 ml) was prepared in a 1-l. three-necked flask fitted with an efficient stirrer, a reflux condenser, and an addition funnel. After cooling the solution to *ca.* 15° cyclopentadiene (24 ml; 0.29 mol) was added and the mixture was stirred for 5 min. A solution of anhydrous cobaltous chloride (20 g; 0.154 mol) in absolute ethanol (100 ml) was then added and the mixture was stirred for a further 1 hr. After this time a solution of $K\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{12}$ (10 g; 58 mmol) in absolute ethanol (100 ml) was added and the resulting slurry was stirred for 14 hr at room temperature. Solid potassium hydroxide (30 g of 85% KOH pellets; 0.455 mol) was then added and the reaction mixture was stirred for a further 3 hr at room temperature followed by 1 hr at reflux. The resulting brown suspension was poured into water (3 l.) and the mixture was thoroughly stirred to give a yellow-brown precipitate which was isolated by filtration, washed with water, and then thoroughly dispersed in acetone (800 ml). After the addition of dichloromethane (400 ml) the mixture was filtered and the residue was washed with dichloromethane. The combined washings and filtrate were dried over magnesium sulfate and filtered once again to give a clear orange solution. Addition of heptane followed by evaporation of the more volatile solvent precipitated the crude product (12.6 g) which was obtained by filtration and washed with hexane.

The crude product was redissolved in dichloromethane and the solution was stripped onto silica gel (*ca.* 300 ml) which was mounted on a silica gel column (*ca.* 2500 ml in a 3-in. column). Elution with dichloromethane–hexane developed two main bands; the first yellow band contained $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ (10.9 g; 73%) which was identified by ^1H nmr, ^{11}B nmr, and mass spectroscopy and recrystallized from dichloromethane–hexane; mp 246°. *Anal.* Calcd for $C_7H_{16}B_9Co$: C, 32.79; H, 6.25; B, 37.94; Co, 23.03. Found: C, 32.96; H, 6.43; B, 37.97; Co, 22.76.

The second band to elute was red and contained the complex I (450 mg; 2%) which was recrystallized from dichloromethane–hexane; mp >350°. *Anal.* Calcd for $C_{12}H_{20}B_8Co_2$: C, 39.09; H, 5.43; B, 23.45; Co, 32.03. Found: C, 39.20; H, 5.48; B, 23.56; Co, 31.70.

Preparation of $[(CH_3)_4N][\{\pi\text{-}C_5H_5)Co(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]$, II. $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ (1.0 g; 3.9 mmol) was added to a solution of potassium hydroxide (15 g of 85% KOH pellets; 0.223 mol) in ethylene glycol–ethanol (120 ml of 5:7 v/v mixture) and the mixture was heated until all of the metallocarborane was dissolved. At this point a solution of hydrated cobalt chloride (1.0 g; 4.2 mmol) in ethanol (30 ml) was added and the solution was stirred at reflux for a further 24 hr. After this time the bulk of the ethanol was evaporated under reduced pressure and the remaining brown liquid was poured into aqueous potassium chloride (400 ml of a 10% w/v solution). The resulting suspension was filtered through Celite and the residue was washed with a little water. The Celite was then extracted with acetone (500 ml) giving a brown solution to which ethanol (100 ml) and aqueous tetramethylammonium chloride (2.0 g of the salt in 100 ml of water) were added. Evaporation of most of the acetone under reduced pressure caused the brown crystalline product, II (0.91 g; 75%), to precipitate. The material was

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isolated by filtration, washed with ethanol and then diethyl ether, and recrystallized from acetone–ethanol. *Anal.* Calcd for $C_{18}H_{42}B_{16}NCo_3$: C, 34.74; H, 6.75; B, 27.79; N, 2.25; Co, 28.47. Found: C, 34.47; H, 6.90; B, 27.50; N, 2.40; Co, 28.07.

Discussion

The reaction of cyclopentadiene, anhydrous cobalt chloride, K-(3)-1,2-$B_9C_2H_{12}$, and potassium hydroxide in ethanol afforded two neutral products which were separated by column chromatography. The first material to elute was the yellow [(π-C_5H_5)Co(π-(3)-1,2-$B_9C_2H_{11}$)] formed in 73% yield and identified by ^{1}H nmr, ^{11}B nmr, and mass spectrometry. The second material to elute was the red complex I formed in 2% yield. The mass spectrum of I showed a cutoff at *m/e* 370 and an ion distribution in the parent ion array which was within 5% of that calculated for $C_{12}H_{20}B_8Co_2$ assuming normal isotopic abundances. The 100-MHz ^{1}H nmr spectrum[14] exhibited a signal of relative area 10 at −5.52 ppm assigned to cyclopentadienyl protons and a signal of relative area 2 at −5.22 ppm assigned to carborane CH protons. The 80.5-MHz ^{11}B nmr spectrum of I (Figure 1) contained three signals of relative areas 2:4:2 indicating a symmetric structure for the carborane ligand. In view of the similarity between the conditions used to prepare I and those used to prepare[5] [{(π-(3)-1,2-$B_9C_2H_{11}$)Co}$_2$(π-(3,6)-1,2-$B_8C_2H_{10}$)]$^{2-}$, whose structure has been determined[10] by X-ray diffraction methods, we propose a structure for I in which the carbon atoms occupy positions 1 and 2, and the cobalt atoms positions 3 and 6, in an icosahedral metallocarborane (Figure 2).

The reaction between [(π-C_5H_5)Co(π-(3)-1,2-$B_9C_2H_{11}$)] and hydroxide ion in the presence of cobalt(II) afforded a brown anionic complex, II, which was isolated in 75% yield as the tetramethylammonium salt. The 100-MHz ^{1}H nmr spectrum of II contained signals of relative area 10 at −5.40 ppm, relative area 4 at −4.34 ppm, and relative area 12 at −3.09 ppm. These signals are assigned to cyclopentadienyl protons, equivalent carborane CH protons, and the tetramethylammonium cation, respectively. The 80.5-MHz ^{11}B nmr spectrum of II (Figure 1) contained four signals of relative areas 1:1:4:2 whose shifts were similar to those observed in the spectrum of I. However, the low-field signal of area 2 in the spectrum of I appeared as two signals of area 1 in the spectrum of II. The nmr spectral data for II can be understood in terms of a structure analogous to that established[11] for [{(π-(3)-1,2-$B_9C_2H_{11}$)Co(π-(3,6)-1,2-$B_8C_2H_{10}$)}$_2$Co]$^{3-}$ by X-ray diffraction methods (Figure 3). This structure contains the $B_8C_2H_{10}{}^{4-}$ ligand as is believed to be the case in I. However, in II the symmetry of the metallocarborane moiety is lowered since the ligand is bonded on one side to a {(π-C_5H_5)Co} unit and on the other side to a {(π-C_5H_5)Co(π-(3,6)-1,2-$B_8C_2H_{10}$)Co} unit. Thus the metallocarborane now contains two unique boron atoms ([B(8) and B(10)]) and three pairs of equivalent boron atoms ([B(4), B(7)], [B(5), B(11)] and [B(9), B(12)]). The boron atoms [B(8)] and [B(10)] are most sensitive to this lowering of symmetry and give rise to two distinct resonances of area 1 in the ^{11}B nmr spectrum of II, while the two pairs of boron atoms [B(4), B(7)] and [B(5), B(11)] still appear as a resonance of area 4 at 80.5 MHz, as was the case in I (Figure 1). These observations allow the 80.5-MHz ^{11}B nmr spectrum of I to be assigned; the resonance of area 4 at +1.6 ppm can be assigned to the four equivalent boron atoms [B(4), B(5), B(7), B(11)]. The low-field doublet of area 2 at −18.9 ppm can be assigned to the pair of boron atoms [B(8), B(10)] since this signal is split into two resonances of area 1 in the spectrum of II. The remaining doublet of area 2 at +8.7 ppm is thus due to the remaining pair of boron atoms [B(9), B(12)]. This information has been helpful in the characterization[15] of another isomer of [{(π-C_5H_5)Co}$_2$(π-$B_8C_2H_{10}$)].

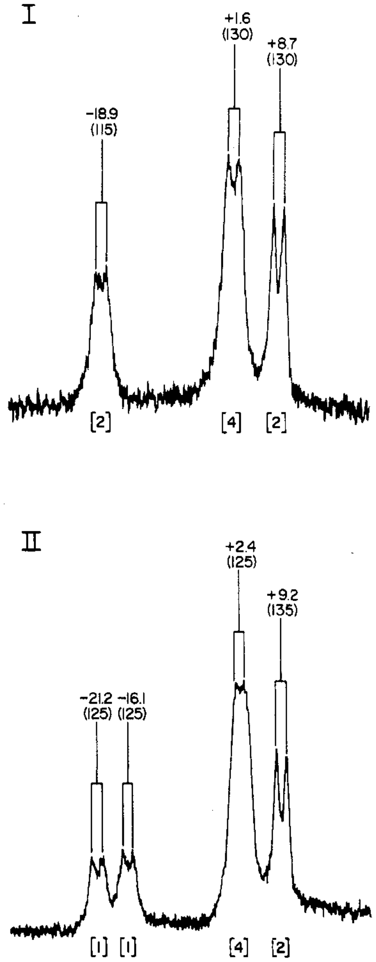

Figure 1. The 80.5-MHz ^{11}B nmr spectra of I ((CH$_3$)$_2$SO solution) and II (CD$_3$CN solution).

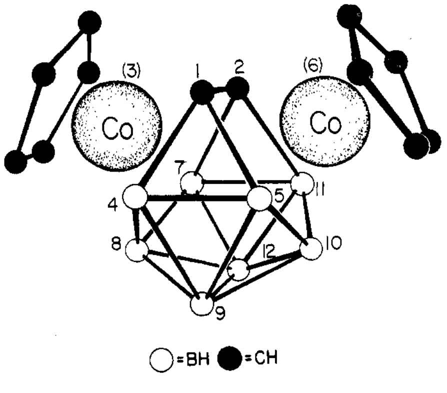

Figure 2. Proposed structure for I.

The infrared spectra of I and II (Table I) both contained bands at *ca.* 2500 cm^{-1} attributable to terminal B–H stretching vibrations and at 830 cm^{-1} attributable to the cyclopentadienyl ligand. In addition, the spectrum of II contains a band at 950 cm^{-1} attributable to the tetramethylammonium cation.

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(14) Shifts are quoted in ppm relative to tetramethylsilane; the spectrum of I was obtained in dimethyl sulfoxide-d_6 solution and that of II in acetonitrile-d_3 solution.

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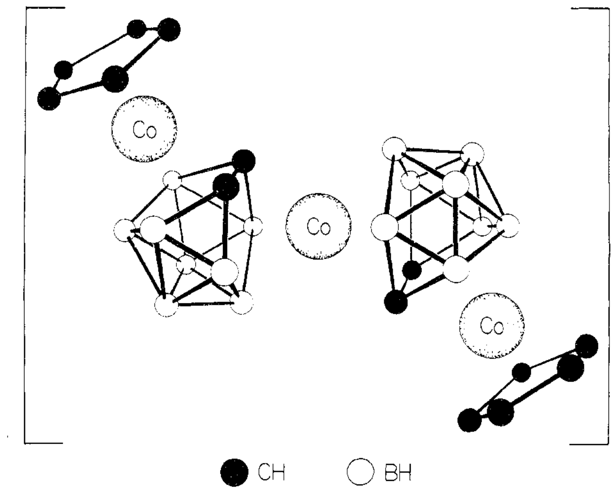

Figure 3. Proposed structure for II.

Table I. Infrared Spectral Data (Nujol Mull) (cm^{-1})

$[\{(\pi\text{-}C_5H_5)Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]$ (I)

2550 s, 2500 s, 1860 w, 1790 w, 1410 m, 1250 w, 1180 w, 1120 w, 1055 w, 1060 m, 1030 m, 1000 m, 995 w, 970 m, 935 w, 920 w, 898 w, 880 w, 870 w, 850 m, 830 s, 760 w, 740 w

$[(CH_3)_4N][\{(\pi\text{-}C_5H_5)Co(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]$ (II)

2500 s, 1600 w, 1480 s, 1420 m, 1195 w, 1160 w, 1140 w, 1130 w, 1060 w, 1020 m, 970 m, 950 m, 900 w, 870 m, 840 m, 830 s, 760 w

Table II. Electronic Spectral Data (CH_3CN Solution)

$[\{(\pi\text{-}C_5H_5)Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]$ (I)		$[(CH_3)_4N][\{(\pi\text{-}C_5H_5)Co(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]$ (II)	
λ_{max}, mμ	ε	λ_{max}, mμ	ε
465 sh	935	410 sh	7,800
390 sh	1,355	320 sh	32,800
295	30,300	275	42,500
265 sh	21,200		

Table III. Electrochemical Data[a]

Complex	Half-peak potentials L = (3)-1,2-$B_9C_2H_{11}^{2-}$		Half-peak potentials L = $C_5H_5^-$		
$[LCo(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]^z$	+1.57 −1.46	z = 1−	Irreversible −1.25	z = 0	
$[\{LCo\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]^z$	+1.07 −1.36	z = 2−	+0.96 −1.19	z = 0	(I)
$[\{LCo(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]^z$	+0.70 −1.53	z = 3−	+0.75 −1.42	z = 1−	(II)

[a] Half-peak potentials *vs.* the sce determined by cyclic voltammetry using a Pt button electrode. Measurements were made in acetonitrile solution 0.1 *M* in $[(C_2H_5)_4N][ClO_4]$; anionic complexes were run with $(CH_3)_4N^+$ as the cation. All the reported waves were reversible.

The electronic spectra of I and II (Table II) showed strong absorption bands in the region 250–350 mμ whose positions and intensities were similar to those reported[5] for $[\{(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]^{2-}$ and $[\{(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]^{3-}$ thus providing further support for the supposition that the two sets of complexes are analogus except for the terminal π-bonding ligand.

A comparison of the electrochemical data[1,5,16] for complexes containing the (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand with that for complexes containing the $C_5H_5^-$ ligand (Table III) shows that the cyclopentadienyl complexes are more readily reduced than those containing the (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand. Also, of the two bimetallic species, I is more readily oxidized despite the negative charge on $[\{(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]^{2-}$. The oxidation potentials become less positive as the number of metal atoms is increased from one to three in both sets of complexes. This change cannot be solely attributed to charge effects since the cyclopentadiene complexes do not carry the high negative charges found in the dicarbollide complexes. Thus more facile oxidation would appear to be a property of the extended metal atom arrays in complexes of this type. The reduction potentials show a less systematic variation with the number of metal atoms in the complex. Although the bimetallic complexes are more readily reduced than the corresponding monometallic species, the trimetallic complexes have the most negative reduction potentials of all.

The new complexes I and II may provide a convenient means of studying "mixed valence" complexes containing the $B_8C_2H_{10}^{4-}$ ligand since they do not have the disadvantage (*viz.*, a high negative charge and the presence of two different carborane ligands) associated with complexes containing the dicarbollide ligand.

Registry No. Cyclopentadiene, 542-92-7; cobalt chloride, 10241-04-0; cobaltous chloride, 7646-79-9; $[\{(\pi\text{-}C_5H_5)Co\}_2(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})]$ (I), 37224-60-5; K-(3)-1,2-$B_9C_2H_{12}$, 12304-72-2; $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$, 11056-78-3; $[(CH_3)_4N][\{(\pi\text{-}C_5H_5)Co(\pi\text{-}(3,6)\text{-}1,2\text{-}B_8C_2H_{10})\}_2Co]$, 37224-62-7.

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(16) Table II in ref 5 has an incorrect caption. The values quoted for I should be attributed to III; those for II attributed to I, and those for III attributed to II.