

Insofar as we are aware the structure of  $Zr(BH_4)_4$  is unique in having three hydrogen bridge bonds linking each boron atom to the metal atom; otherwise the structure does not appear to be unusual. A tetrahedral arrangement of ligands around zirconium atoms has been observed in  $ZrCl_4$ ,<sup>18</sup> for example, and the structure of the  $BH_4$  groups is similar to that found in  $Al(BH_4)_3$ <sup>2</sup> ( $B-H_t = 1.196 \pm 0.012 \text{ \AA}$ ,  $B-H_b = 1.283 \pm 0.012 \text{ \AA}$ ,  $\angle H_bBH_b = 114.2 \pm 0.2^\circ$ ).

The bonds involving the zirconium atom are all considerably longer than the sum of the covalent radii corrected for electronegativity difference.<sup>19</sup> Thus, if one uses the value  $1.36 \text{ \AA}$  for the zirconium radius, deduced from  $r(Zr-Cl) = 2.32 \text{ \AA}$  in  $ZrCl_4$  with the aid of the formula<sup>20</sup>  $r(A-B) = r_A + r_B - 0.02|\chi_A - \chi_B|$ , then the lengths of the Zr-B and Zr-H bonds predicted from the same formula (but with the constant 0.02 replaced with 0.08<sup>21</sup>) are, respectively, 2.12 and 1.61  $\text{\AA}$ . Somewhat better agreement is obtained using Pauling's metallic radii,<sup>21</sup> which without the electronegativity correction yield the values 2.25 and 1.76  $\text{\AA}$ . At first glance these long distances appear to have no explanation in terms of simple valence-bond concepts except a qualitative one: each of the four zirconium bonding electrons is involved in bonding to three hydrogen atoms and a

boron atom with the result that on the average a one-quarter bond is formed with each. However, a somewhat more satisfying picture of the bonding may be developed using a method applied by one of us<sup>22</sup> to the hydroborons and their derivatives. In the case of  $Zr(BH_4)_4$ , as with these molecules, the ligancy of the heavier atoms exceeds the number of bonding orbitals suggesting bonding situations (from the valence-bond point of view) similar to those encountered in metals and intermetallic compounds. One might expect that Pauling's empirical equation<sup>20</sup>  $D(n) = D(1) - 0.600 \log n$ , where  $D(n)$  and  $D(1)$  are interatomic distances for a bond of fractional bond number and a single bond, could be applied. If one takes  $D(1)$  equal to 2.20, 1.76, and 1.16  $\text{\AA}$  for Zr-B, Zr-H, and B-H, respectively, calculated from Zr, B, and H radii of 1.45, 0.80, and 0.37  $\text{\AA}$  using the electronegativity correction, these bonds in  $Zr(BH_4)_4$  are calculated to have bond numbers of 0.66, 0.18, 0.66 ( $B-H_b$ ) and 0.93 ( $B-H_t$ ). The weighted sum of these is 16.44 corresponding to 32.88 bonding electrons, which is to be compared with the number 32 available from the outer shells of the atoms. The agreement is especially good in view of the sensitivity of the calculation: a decrease of only 0.01  $\text{\AA}$  in the radius of the hydrogen atom, for example, leads to 31.6 calculated bonding electrons.

**Acknowledgment.**—We wish to thank the National Science Foundation for financial support. We are indebted to Dr. R. Walsh for preparation of the sample.

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## Synthesis and Reactions of Novel Bridged Dicarbollide Complexes Having Electron-Deficient Carbon Atoms

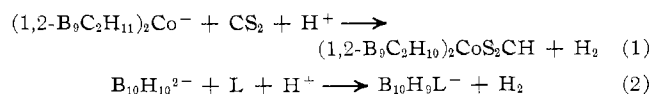
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Received August 4, 1970

Reaction of the bis- $\pi$ -dicarbollide ligand complexes of  $Co^{3+}$  and  $Fe^{3+}$  with  $CS_2$  in the presence of  $AlCl_3$  and  $HCl$  produced the first examples of zwitterionic species having an  $-S-C^+H-S-$  bridge between boron atoms of the two dicarbollide ion ligands of the complex. Similarly, a suspected  $-OC^+(CH_3)O-$  bridged species results from the reaction of acetic acid-acetic anhydride with an  $HClO_4$  catalyst. Further transformations of these species are described.

In a previous communication<sup>2</sup> we have briefly reported the structure and synthesis of the compound shown in Figure 1 in conjunction with Churchill and Gold. It was obtained by an acid-catalyzed addition of carbon disulfide to  $(1,2-B_9C_2H_{11})_2Co^-$  with concomitant evolution of hydrogen gas (eq 1). Similar reactions (eq 2, 3) with a variety of ligands have been pre-

viously observed<sup>3</sup> with the  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$  ions but not with any metallocarborane complexes. We



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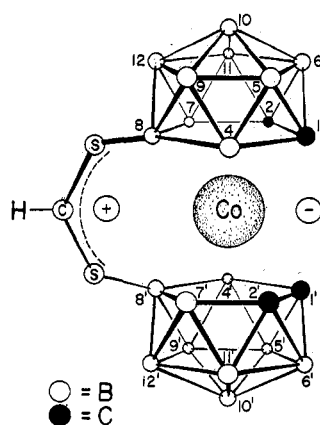
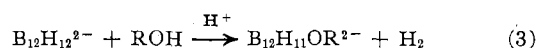


Figure 1.—Schematic drawing of bridged product containing sulfur-bridged system and previously reported.<sup>2</sup>



report here the details of our examination of the applicability of this reaction to the  $(\text{B}_9\text{C}_2\text{H}_{11})_2\text{M}^-$  complexes.

### Experimental Section

The dicarbollylmetal complexes were prepared by literature methods;<sup>4</sup> other chemicals were of reagent grade and were used as received. Infrared spectra were recorded with a Perkin-Elmer Model 137 spectrophotometer and are recorded in Table I. The 32-MHz <sup>11</sup>B and 60-MHz <sup>1</sup>H nmr spectra were obtained with Varian HA-100 and A-60 spectrometers, respectively. Peak positions of <sup>11</sup>B resonances are given with respect to boron trifluoride etherate. Microanalyses were conducted by Schwarzkopf Analytical Laboratories.

**K<sup>+</sup>(B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>M<sup>-</sup>.**—Preparations of these compounds<sup>4</sup> yield aqueous solutions of the sodium salt, which cannot be adequately dried. The potassium salts may be obtained by use of an ion-exchange resin or by precipitating them with a saturated solution of KCl (rubidium and cesium salts are easily obtained by precipitation and dried but react much more slowly). An aqueous solution of K<sup>+</sup>(B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>M<sup>-</sup> containing 1–2% KCl was extracted with a 1:1 mixture of ether and toluene. The organic phase was thoroughly dried (Na<sub>2</sub>SO<sub>4</sub> followed by CaSO<sub>4</sub>) and reduced in volume under vacuum until precipitation was complete.

**(1,2-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>CoS<sub>2</sub>CH.**—To a dry flask containing a stirring bar, 100 ml of CS<sub>2</sub>, and 1.5 g of AlCl<sub>3</sub> was added 2 g (5.5 mmol) of (1,2-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>Co<sup>-</sup>K<sup>+</sup>. A slow stream of HCl (equivalent to 1 or 2 bubbles/sec) was passed over the stirred solution for 5 hr. By this time gas evolution had nearly ceased, and the solution was a deep brownish orange. The mixture was filtered, the solid was washed with 100 ml of CS<sub>2</sub>, and the combined filtrates were reduced to dryness. The orange and red product was dissolved in 100 ml of dichloromethane, and the solution was run through a 2-cm diameter column of about 5 g of silica gel. About 50 ml of heptane was added to the orange solution which was reduced to a volume of 50 ml. This produced a thick slurry of the voluminous yellow product; it amounted to 1.6 g (4 mmol, 70%). It was contaminated with some sulfur-containing compounds, and in this form was easily electrified, making transfers difficult. Recrystallization from boiling 1:1 heptane–benzene afforded large brownish yellow crystals containing 30% by weight of benzene. These were more easily handled, and the benzene could be removed easily by washing with hexane or drying *in vacuo*. The pure material melted at 302–304°. Pmr (acetone-d<sub>6</sub>): δ 11.6 (broad, s, 1, S–CH<sup>+</sup>–S), 4.65 (s, 9 Hz wide, 4, carborene CH). <sup>11</sup>B nmr (tetrahydrofuran, relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>): –20 ppm (s, 2), –1 to +28 ppm (multiplet, 16). The mass spectrum was consistent with the formula known from the single-crystal X-ray diffraction study.

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TABLE I

INFRARED SPECTRA (NUJOL MULLS) (cm <sup>-1</sup> )	
(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> ) <sub>2</sub> CoS <sub>2</sub> CH and (1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> ) <sub>2</sub> FeS <sub>2</sub> CH	3.30 w, 3.87 vs, 7.80 m, 8.36 m, 8.80 m, 8.97 w, 9.12 s, 9.75 vs, 9.90 sh, 10.22 s, 10.58 w, 10.85 m, 11.01 m, 11.40 w, 11.50 w, 11.74 w, 11.93 s, 12.60 w, 13.29 s, 13.52 m
(1,7-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> ) <sub>2</sub> CoS <sub>2</sub> CH	3.28 w, 3.87 vs, 7.78 s, 8.78 m, 8.90 w, 8.98 s, 9.03 s, 9.13 s, 9.24 m, 9.70 vs, 10.02 s, 10.20 m, 10.45 w, 10.63 s, 10.83 m, 10.92 m, 11.12 m, 11.38 w, 11.85 sh, 11.93 vs, 12.05 sh, 12.95 m, 13.52 s, 13.82 s, 14.23 m
[(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> ) <sub>2</sub> CoS <sub>2</sub> CH <sub>2</sub> ] <sup>-</sup> Cs <sup>+</sup>	3.28 w, 3.90 vs, 7.17 m, 8.29 m, 8.34 m, 8.80 m, 8.97 w, 9.10 s, 9.25 w, 9.87 m, 10.05 sh, 10.20 s, 10.46 sh, 10.58 m, 10.80 sh, 10.92 m, 11.21 w, 11.36 m, 11.55 m, 11.70 s, 11.85 s, 12.02 s, 12.65 m, 13.32 s, 13.76 s, 14.46 w
[(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> SH) <sub>2</sub> Co] <sup>-</sup> Cs <sup>+</sup>	3.30 m, 3.90 vs, 8.31 m, 8.70 m, 8.77 sh, 8.96 w, 9.08 s, 9.23 w, 9.82 br, w, 10.12 s, 10.50 br, w, 10.85 m, 11.03 m, 11.32 sh, 11.41 m, 11.70 m, 11.89 s, 12.70 br, m, 13.32 s, 13.60 br, m
[(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> S) <sub>2</sub> Co] <sup>-</sup> Cs <sup>+</sup>	3.30 m, 3.90 vs, 8.34 m, 8.81 m, 8.96 m, 9.13 s, 9.23 sh, 9.41 w, 9.82 m, 9.90 m, 10.20 s, 10.54 m, 10.90 s, 11.12 m, 11.32 m, 11.69 s, 11.80 s, 12.00 m, 12.45 w, 12.68 w, 13.28 s, 13.70 m, 14.50 w
(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> ) <sub>2</sub> CoO <sub>2</sub> CCH <sub>3</sub>	3.29 w, 3.85 vs, 3.92 vs, 6.55 s, 6.80 vs, 7.15 w, 8.36 m, 8.90 s, 9.14 s, 9.28 s, 9.60 w, 9.85 m, 10.12 m, 10.39 m, 10.51 w, 10.80 m, 10.98 m, 11.28 m, 11.41 m, 11.62 s, 12.50 m, 12.62 m, 13.12 m, 13.52 s, 14.13 m, 14.32 w
[(1,2-B <sub>9</sub> C <sub>2</sub> H <sub>10</sub> OH) <sub>2</sub> Co] <sup>-</sup> (CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	2.80 w, 3.29 m, 3.90 vs, 6.76 s, 6.95 w, 7.10 w, 7.49 m, 7.83 w, 8.38 m, 8.80 s, 9.15 m, 9.30 w, 9.46 m, 9.88 m, 10.31 s, 10.54 m, 10.86 w, 10.97 w, 11.05 w, 11.18 w, 11.38 w, 12.72 w, 13.40 s, 13.80 br, m

(1,7-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>CoS<sub>2</sub>CH was prepared as above. Several recrystallizations from dichloromethane–hexane afforded a 50% yield of orange crystals melting at 225–238°. The ion peaks of the mass spectrum matched those of the 1,2 isomer in both intensity and position.

(1,2-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>FeS<sub>2</sub>CH was prepared as above. It was a paramagnetic gray-green solid decomposing at 240° when heated rapidly. The infrared spectrum was identical with that of the analogous cobalt complex. *Anal.* Calcd for C<sub>5</sub>H<sub>21</sub>B<sub>13</sub>FeS<sub>2</sub>: C, 15.17; H, 5.35; B, 49.17; S, 16.20. Found: C, 14.65; H, 5.28; B, 47.82; S, 15.92.

(1,2-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>CoS<sub>2</sub>CH<sub>2</sub><sup>-</sup>Cs<sup>+</sup>.—A 1-g sample of (1,2-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>

$\text{CoS}_2\text{CH}$  was dissolved in 40 ml of ethanol, and small portions of  $\text{NaBH}_4$  were added until foaming no longer occurred upon each addition. The red solution was poured into 100 ml of water after several minutes, and  $\text{Cs}^+$  or  $(\text{CH}_3)_4\text{N}^+$  was added to precipitate the product. Either salt could be recrystallized from acetone-toluene mixtures. Pmr of  $(\text{CH}_3)_4\text{N}^+$  salt in acetone- $d_6$ :  $\delta$  3.40 [s, 12,  $(\text{CH}_3)_4\text{N}^+$ ], 4.03 (broad s, 6 Hz wide, 4, carborane  $\text{CH} + \text{S}-\text{CH}_2-\text{S}$ ). *Anal.* Calcd for  $\text{C}_5\text{H}_{22}\text{B}_{18}\text{CoCsS}_2$ : C, 11.27; H, 4.16; B, 36.52; S, 12.04. Found: C, 11.76; H, 3.72; B, 35.47; S, 12.16.

$\text{Cs}^+(1,2\text{-B}_9\text{C}_2\text{H}_{10}\text{SH})_2\text{Co}^-$ .— $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$  was dissolved in 4:1 ethanol-water 0.1 *N* in  $\text{HCl}$  and refluxed for 1 hr under nitrogen. Two volumes of water and one volume of saturated  $\text{NaCl}$  solution were added, and the product was precipitated with cesium chloride. It was recrystallized from acetone-toluene and dried at  $140^\circ$  under vacuum. The yield was nearly quantitative. Pmr (acetone- $d_6$ ):  $\delta$  4.47 (s, 9 Hz wide, 4, carborane  $\text{CH}$ ), 0.40 (s, 10 Hz wide, 2,  $\text{SH}$ ). *Anal.* Calcd for  $\text{C}_4\text{H}_{22}\text{B}_{18}\text{CoCsS}_2$ : C, 9.22; H, 4.26; B, 37.37; Co, 11.33; Cs, 25.52. Found: C, 10.62; H, 4.23; B, 35.81; Co, 11.28; Cs, 25.60.

$\text{Cs}^+(1,2\text{-B}_9\text{C}_2\text{H}_{10}\text{S})_2\text{Co}^-$ .—Before precipitating the  $(1,2\text{-B}_9\text{C}_2\text{H}_{10}\text{SH})_2\text{Co}^-$  in the previous preparation, the solution was made basic (pH 10) with  $\text{NaOH}$ , and several equivalents of  $\text{H}_2\text{O}_2$  was added. The solution changed from a deep red to a deep purple color in a few minutes. The product was isolated and purified in the same manner as the dithiol and the yield was again nearly quantitative. The pmr showed only one broad (9 Hz) singlet at  $\delta$  3.82 in  $\text{CD}_3\text{CN}$ . Average particle weight (osmometer,  $\text{CH}_3\text{CN}$ ): calcd, 230.1 amu; found, 240. *Anal.* Calcd for  $\text{C}_4\text{H}_{20}\text{B}_{18}\text{CoCsS}_2$ : C, 9.26; H, 3.89; B, 37.51; Co, 11.36; Cs, 25.62; S, 12.36. Found: C, 9.75; H, 4.03; B, 35.43; Co, 11.48; Cs, 26.59; S, 12.57.

$(\text{CH}_3)_4\text{N}^+(1,2\text{-B}_9\text{C}_2\text{H}_{10})_2\text{CoSHSCHO}^-$ .— $(1,2\text{-B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$  was dissolved in 4:1 ethanol-water and cooled to  $0^\circ$ , and 0.98 equiv of  $\text{NaOH}$  solution was added with rapid stirring. The product was precipitated with excess 50% aqueous  $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$  and two volumes of water. The infrared spectrum of the product contained a strong band at  $1710\text{ cm}^{-1}$ . Pmr (acetone- $d_6$ ):  $\delta$  10.60 (s, 1,  $\text{CHO}$ ), 4.40 (s, 14 Hz wide, 4, carborane  $\text{CH}$ ), 3.99 [s, 12,  $(\text{CH}_3)_4\text{N}^+$ ], 0.60 (broad s, 1,  $\text{SH}$ ).

$(1,2\text{-B}_9\text{C}_2\text{H}_{10})_2\text{CoO}_2\text{CCH}_3$ .—A 1-g sample of  $\text{K}^+(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^-$  was dissolved in 10 ml of a 4:1 mixture of acetic acid-acetic anhydride 0.05 *N* in  $\text{HClO}_4$  and heated at  $100^\circ$  for 24 hr. The solution was cooled, and the orange solid (300 mg, 29%) was collected and washed with acetic acid. It could be recrystallized from benzene-heptane to give golden yellow crystals. Pmr (benzene):  $\delta$  2.61 (s, 10 Hz wide, 4, carborane  $\text{CH}$ ), 1.17 (s, 3,  $\text{CH}_3$ ). The  $^{11}\text{B}$  nmr in tetrahydrofuran and relative to  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  showed one singlet of area 2 at  $-20$  ppm and a broad multiplet of area 16 from  $-1$  to  $+28$  ppm. The mass spectrum was consistent with the formula proposed. *Anal.* Calcd for  $\text{C}_6\text{H}_{23}\text{B}_{18}\text{CoO}_2$ : C, 18.9; H, 6.04; B, 51.7; Co, 15.5. Found: C, 19.3; H, 6.02; B, 48.7; Co, 15.2.

$[(1,2\text{-B}_9\text{C}_2\text{H}_{10}\text{OH})_2\text{Co}]^-(\text{CH}_3)_4\text{N}^+$  was prepared by the hydrolysis of  $(1,2\text{-B}_9\text{C}_2\text{H}_{10})_2\text{CoO}_2\text{CCH}_3$  using the procedure for the hydrolysis of  $(1,2\text{-B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$ . Pmr (acetone- $d_6$ ):  $\delta$  2.97 [s, 12,  $(\text{CH}_3)_4\text{N}^+$ ], 3.64 (s, 9 Hz wide, carborane  $\text{CH}$ ). *Anal.* Calcd for  $\text{C}_5\text{H}_{34}\text{B}_{18}\text{CoNO}_2$ : C, 22.32; H, 7.95; N, 3.25. Found: C, 21.63; H, 7.83; N, 3.06.

## Results and Discussion

**Reaction with Carbon Disulfide.**—We had selected  $(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^-$  to begin our work because of its great thermal, hydrolytic, and electrochemical stability but subsequently found several closely related complexes also suitable for study. The substitution reaction with carbon disulfide proceeded as readily with  $(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Fe}^-$  as with  $(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^-$ , yielding products with identical structures. Both of these complexes contained the metal in the preferred +3 oxida-

tion state. The corresponding nickel complex, however, has a low  $\text{Ni(III)-Ni(IV)}$  oxidation potential<sup>4</sup> ( $-0.3\text{ V}$ ) and under the reaction conditions yields only the neutral  $(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Ni}^0$ .

The  $(1,7\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^-$  ion, in which the two carbon atoms of each ligand are no longer adjacent, also reacted readily. Mass spectrometry indicated that the products from the 1,2 and 1,7 cobalt complexes had the same composition, and we have assigned the structure of Figure 2 to the 1,7 isomer on the basis of the pmr spec-

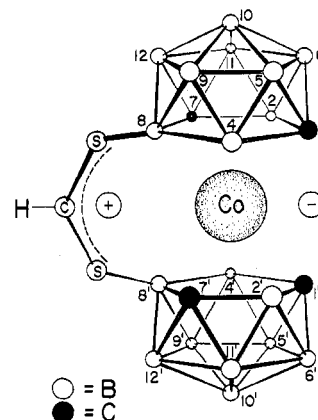


Figure 2.—Proposed structure of one enantiomer of *dl*-(1,7- $\text{B}_9\text{C}_2\text{H}_{10}$ ) $_2\text{CoS}_2\text{CH}$  in schematic form with H atoms omitted.

trum, which exhibits two carborane  $\text{CH}$  resonances of equal weight. The spectrum of the 1,2 isomer, by contrast, has only one  $\text{CH}$  resonance. The  $^{11}\text{B}$  nmr spectra of the two products were similar in that both exhibited one low-field singlet of weight 2, indicating that the two sulfur atoms of the bridge were bonded to equivalent boron atoms. A meso form of  $(1,7\text{-B}_9\text{C}_2\text{H}_{10})_2\text{CoS}_2\text{CH}$  can also exist; the broad melting point of the material obtained ( $225\text{--}238^\circ$  after several recrystallizations) is probably due to the product containing a mixture of *dl* and meso forms.

Although the substitution reaction takes place on boron atoms well separated from the carbon atoms of the carborane cage, the 1,1',2,2'-tetramethyl derivative of  $(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^-$  yielded only a small amount of a purple tar when we attempted to carry out this reaction with this material. The difficulty may be due to either side reactions occurring on the methyl groups or more probably to the inability of the methylated complex to assume the necessary cisoid configuration.

**Reaction with Acetic Acid.**—When  $\text{K}^+(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}^-$  was heated in 4:1 acetic acid-acetic anhydride with  $\text{HClO}_4$  as a catalyst, a moderately low yield of a neutral orange compound was obtained. Microanalysis and mass spectrometry established the formula as  $(\text{B}_9\text{C}_2\text{H}_{10})_2\text{CoO}_2\text{CCH}_3$ . As written, the resemblance to the  $\text{CS}_2$  product is obvious, and we have assigned the structure of Figure 3 to this material on the basis of the following significant spectral features: (i) the infrared spectrum lacks any absorption in the regions in which carbonyl or hydroxyl group stretching frequencies would be expected to occur; (ii) the proton nmr con-

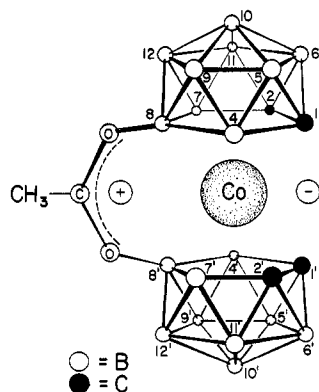
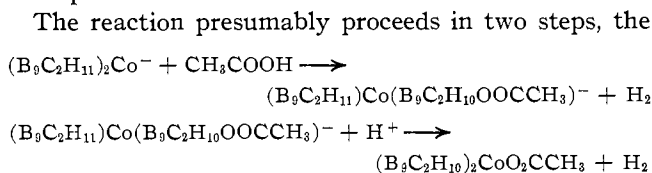


Figure 3.—Proposed structure of  $(1,2-B_9C_2H_{10})_2CoO_2C(CH_3)$  in schematic form with H atoms omitted.

tains a sharp 3H singlet and a single 4H carborane CH resonance; (iii) the  $^{11}B$  nmr spectrum exhibits a low-field singlet of weight 2, similar to that observed in the product obtained from  $CS_2$ . The carborane CH and boron resonances are rather broad, so that small differences in chemical shifts might be obscured, but the structure shown is the only reasonable structure with truly equivalent carborane CH and singlet boron nmr absorptions.



first an addition of acetic acid to give an acetate (similar to the reaction of alcohols with  $B_{12}H_{12}^{2-}$ , eq 3) and the second an intramolecular attack of the acetate group on the adjacent carborane cage. Two curious features of this reaction are that no hydrogen gas is evolved, in contrast to the reaction with  $CS_2$ , and that this reaction will not occur in the absence of acetic anhydride, even in carefully dried acetic acid. These facts are consistent with the hypothesis that some acetic acid is reduced, so that no hydrogen is evolved, and the water from the reduction stops the reaction unless it is continuously removed. We have also noted the absence of visible gas evolution when  $K^+(1,2-B_9C_2H_{11})_2Co^-$  reacted with 94%  $H_2SO_4$  at  $125^\circ$ . The complex dissolved over a 15-min period to yield a yellow solution with a strong odor of sulfur dioxide, which would be expected if sulfuric acid were reduced. This solution contained compounds which could not be precipitated with large cations, but still exhibited strong B-H stretching bands

in the infrared spectrum. We were unable to isolate any of these presumed sulfonic acid derivatives, however.

#### Further Transformations of Bridged Species.—

The carbonium ion centers of  $(1,2-B_9C_2H_{10})_2CoO_2CCH_3$  and  $(1,2-B_9C_2H_{10})_2CoS_2CH$  were rather unreactive toward protic solvents, probably due to the adjacent negative charge and delocalization of the positive charge onto the neighboring heteroatoms. The reaction with borohydride ion was much faster, so that a solution of this reagent in ethanol reduced  $(1,2-B_9C_2H_{10})_2CoS_2CH$  to  $(1,2-B_9C_2H_{10})_2CoS_2CH_2^-$  in excellent yields. The product presumably has an S- $CH_2$ -S bridge between the two carborane cages. Refluxing aqueous ethanol does eventually hydrolyze the positively charged bridges of  $(1,2-B_9C_2H_{10})_2CoS_2CH$  and  $(1,2-B_9C_2H_{10})_2CoO_2CCH_3$  to a dithiol and a diol, respectively. The diol shows the expected OH band in the infrared spectrum at  $3600\text{ cm}^{-1}$ , but the weak SH band of the dithiol is hidden by the strong B-H absorption. Recrystallization of the cesium salt of the dithiol from  $D_2O$  (conditions far too mild to effect B-H exchange) did yield a material with a weak absorption at  $1850\text{ cm}^{-1}$ , assigned to the S-D stretching vibration.

The fate of the carbon bridge fragments lost in these hydrolyses has not been studied; presumably the final product is formic or acetic acid. We have isolated an intermediate product by adding 0.98 equiv of hydroxide ion to  $(1,2-B_9C_2H_{10})_2CoS_2CH$  in ethanol. The crude ionic material so obtained contains a band in the infrared spectrum at  $1710\text{ cm}^{-1}$  and pmr resonances at  $\delta$  10.6 and 6; we believe it is the thiol thioformate  $(1,2-B_9C_2H_{10}SH)Co(1,2-B_9C_2H_{10}SCHO)^-$ , which would certainly yield formic acid upon further hydrolysis.

A very cursory examination of further reactions of the dithiol  $(1,2-B_9C_2H_{10}SH)_2Co^-$  has been made. It appears to behave generally as an aliphatic 1,3- or 1,4-dithiol (cyclic dithioketals and disulfide formed), except that the negative charge results in the ready formation of internal sulfonium salts in alkylation reactions. The monomeric disulfide is a deep purple color, in contrast to the yellow to orange color typical of these compounds. This may be due to a geometrical distortion of the complex due to the short S-S bridge between the carborane cages; the S-S distance in  $(1,2-B_9C_2H_{10})_2CoS_2CH$  is  $3.07 \pm 0.05\text{ \AA}$ , while in the disulfide it should be near the usual S-S bond length of  $2.04\text{ \AA}$ .

**Acknowledgment.**—This research was supported, in part, by the Office of Naval Research.