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# The Preparation of Two New Alkenyl-Substituted Carboranes. Their Properties and Some Derivative Chemistry

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The dehydration of two β-hydroxyalkyl-substituted 1,2-$B_{10}C_2H_{12}$ carborane derivatives led to the formation of two new alkenyl-substituted derivatives: 1,2-(3′-cyclopentene)-1,2-dicarba-*closo*-dodecaborane(12) and 1,2-divinyl-1,2-dicarba-*closo*-dodecaborane(12). These products were degraded to the corresponding substituted (3)-1,2-$B_9C_2H_{12}^-$ dicarbollide anions and some representative transition metal derivatives prepared from them. The extent of alkenyl group participation in the derivative chemistry was investigated. It was found possible directly to observe an anionic π-allyl-substituted carborane derivative which was subsequently deuterated. Electronic spectra suggest the existence of conjugation in the alkenyl-substituted dicarbollide anions.

## Introduction

As part of a continuing investigation of the chemistry of substituted $B_{10}C_2H_{12}$ carboranes,[1,2] we have synthesized two new alkenyl-substituted carboranes, 1,2-(3′-cyclopentene)-1,2-dicarba-*closo*-dodecaborane(12) (I) and 1,2-divinyl-1,2-dicarba-*closo*-dodecaborane(12) (II). It has previously[1] been found that analogous 1-phenyl-substituted carboranes exhibit no ground-state effects attributable to conjugation of the ring with the 1,2-carborane icosahedron and it was of interest to learn if this would also be the situation with I and II.

The analogous monovinyl compound, 1-vinyl-1,2-dicarba-*closo*-dodecaborane(12), has been synthesized by two routes, acetic acid elimination from 1-(β-acetoxyethyl)-1,2-dicarba-*closo*-dodecaborane(12)[3] and the reaction of decaborane with vinylacetylene.[4]

Other reported alkenyl-substituted carboranes include 1,2-diisopropenyl-1,2-dicarba-*closo*-dodecaborane(12), synthesized from $(CH_3CN)_2B_{10}H_{12}$ and bis(isopropenyl)acetylene,[5] and 1,2-(3′,5′-cyclohexadiene)-1,2-dicarba-*closo*-dodecaborane(12), synthesized from 1,2-$B_{10}C_2H_{10}Li_2$ and *cis*-1,2-dichloro-2-butene followed by dehydrohalogenation.[6]

Both new alkenyl-substituted carboranes reported here were obtained by dehydration of the corresponding β-hydroxyalkyl derivatives (Figure 1).

## Experimental Section

**Physical Measurements.**—Infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer. Proton nmr spectra were obtained on a Varian Associates Model A-60D spectrometer at 60 Mc/sec and on a 250-Mc/sec instrument constructed by Professor F. A. L. Anet of this department. The $^{11}B$ nmr spectra were obtained at 80 Mc/sec on the latter instrument. Reported melting points are uncorrected. Elemental analyses were made by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Characterization and yield data are presented in Table I.

**Preparation of 1,2-(4′-Hydroxycyclopentane)-1,2-dicarba-*closo*-dodecaborane(12) (III).**—The alcohol III was prepared from the corresponding ketone, 1,2-(4′-cyclopentanone)-1,2-dicarba-*closo*-dedecaborane(12),[3,7] by reduction with $LiAlH_4$ in dry diethyl ether under nitrogen.

In a typical preparation, a solution of 47.4 g (0.24 mol) of ketone dissolved in 200 ml of dry diethyl ether was dripped slowly into 100 ml of dry diethyl ether containing 9.2 g of $LiAlH_4$ under nitrogen at 0°. The mixture was stirred 1.5 hr and then hydrolyzed slowly with cold water. The separated ether layer was washed with dilute HCl and water, dried over anhydrous $MgSO_4$, and evaporated to dryness. The solid product was then recrystallized three times from benzene and dried at 65° (0.1 mm) over $P_2O_5$. Analytical samples were then sublimed at 100° under high vacuum, yield 45.8 g, 96%.

**Preparation of (3′-Cyclopentene)-1,2-dicarba-*closo*-dodecaborane(12) (I).**—In a typical preparation, 7.00 g (0.035 mol) of III was ground together with 11.0 g of Wölem basic alumina, activity grade 1. The powder was then placed in the bottom of a reaction vessel consisting of a 100-ml round-bottom flask sealed to a 25-cm long, 22-mm diameter tube. Next a column of basic alumina, grade 1, about 20 cm high was added and held in place by glass wool. The upper end was then fitted with an ice-cooled sublimation cold finger. The alumina column was maintained at 350° under vacuum and the entire apparatus was placed in a 300° oven up to the bottom of the cold finger. After 9–10 hr the sublimate was collected giving a 4.80-g (75%) yield of crude product. The product was then crystallized from ethanol and sublimed at 100° under high vacuum.

**Preparation of 1,2-Divinyl-1,2-dicarba-*closo*-dodecaborane(12) (II).**—The alcohol, 1,2-(bis-β-hydroxyethyl)-1,2-dicarba-*closo*-dodecaborane(12), was prepared as previously reported.[3] Dehydration of this bis alcohol was achieved in exactly the same manner as the preparation of I. The crude product was crystallized from ethanol and sublimed at 100° under high vacuum.

**Preparation of (3)-1,2-(3′-Cyclopentene)-1,2-dicarbadodecahydroundecaborate(−1) Ion (IV) and (3)-1,2-Divinyl-1,2-dicarbadodecahydrodecaborate(−1) Ion (V).**—The two carborane derivatives I and II were degraded to the corresponding substituted (3)-1,2-$B_9C_2H_{12}^-$ dicarbollide anions as previously reported[8] for the unsubstituted analog.

The products were isolated as the trimethylammonium and

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(1) M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *J. Amer. Chem. Soc.*, **87**, 4746 (1965).

(2) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **92**, 1157 (1970).

(3) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

(4) T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *ibid.*, **2**, 1089 (1963).

(5) M. M. Fein, D. Graftstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

(6) N. K. Hota and D. S. Matteson, *J. Amer. Chem. Soc.*, **90**, 3570 (1968).

(7) The conditions of preparation of the ketone, not stated in ref 3, are 70 mm of nitrogen pressure and 200°. It was found necessary to remove the corresponding acid anhydride coproduct by treating the mixture with dilute KOH in ethanol for a few minutes and then decanting the solution into water. The precipitated ketone was filtered off, washed with water, and recrystallized from ethanol.

(8) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 862 (1968).

TABLE I

MELTING POINTS, YIELDS, AND ELEMENTAL ANALYSES FOR THE 1,2-ALKENE-SUBSTITUTED CARBORANES AND DERIVATIVES

| No. | Compd | Mp,[a] °C | Yield, % | Analyses, % |
|---|---|---|---|---|
| I | $B_{10}C_5H_{14}$ | 203–204 | 75 | Calcd: B, 59.31; C, 32.95; H, 7.74 |
| | | | | Found: B, 57.64; C, 33.69; H, 8.95 |
| II | $B_{10}C_6H_{16}$ | 101.5–102 | 83 | Calcd: B, 55.07; C, 36.71; H, 8.22 |
| | | | | Found: B, 54.80; C, 36.61; H, 8.50 |
| III | $B_{10}C_5H_{15}OH$ | 143 | 96 | Calcd: B, 53.97; C, 29.98; H, 8.05; O, 7.98 |
| | | | | Found: B, 52.79; C, 29.15; H, 8.12; O, . . . |
| IV | $B_9C_5H_{14}^-(CH_3)_4N^+$ | >300 dec | 85 | Calcd: B, 39.61; C, 44.01; H, 10.67; N, 5.70 |
| | | | | Found: B, 39.43; C, 43.87; H, 10.45; N, 5.74 |
| V | $B_9C_6H_{16}^-(CH_3)_3NH^+$ | 86.5–87 | 71 | Calcd: B, 39.61; C, 44.01; H, 10.67; N, 5.70 |
| | | | | Found: B, 39.61; C, 44.38; H, 10.03; N, 6.00 |
| VI | $(B_9C_5H_{13})_2Co^-(C_6H_5)_4As^+$ | 203–204 | 53 | Calcd: B, 24.85; C, 52.14; H, 5.92; As, 9.57; Co, 7.52 |
| | | | | Found: B, 24.40; C, 52.64; H, 6.05; As, 9.29; Co, 7.94 |
| VII | $(B_9C_6H_{15})_2Co^-(CH_3)_4N^+$ | 272 dec | 51 | Calcd: B, 38.76; C, 38.29; H, 8.43; N, 2.79; Co, 11.74 |
| | | | | Found: B, 37.95; C, 39.27; H, 8.53; N, 2.84; Co, 11.81 |
| VIII | $(B_9C_6H_{15})Mn(CO)_3^-Cs^+$ | 230–232 dec | 20 | Calcd: B, 21.32; C, 23.69; H, 3.31; O, 10.52; Mn, 12.04; Cs, 29.12 |
| | | | | Found: B, 21.22; C, 24.30; H, 3.06; O, . . . ; Mn, 12.11 Cs, 29.15 |

[a] Melting points are uncorrected in a sealed capillary.

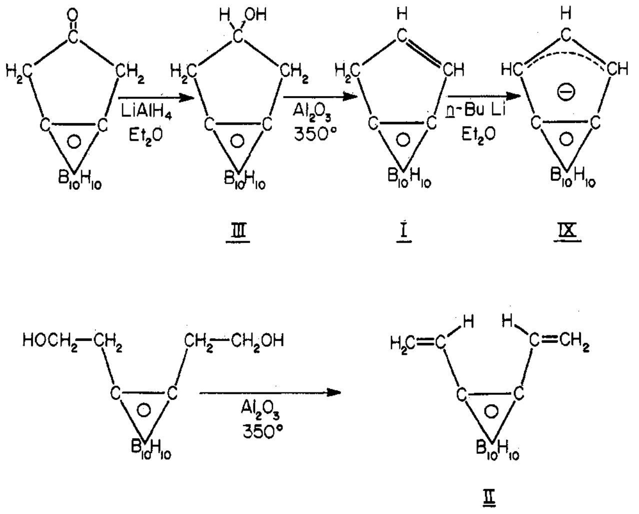

Figure 1.—Syntheses of the 1,2-substituted carboranes and formation of the anionic 1,2-$\pi$-allyl-substituted carborane IX.

tetramethylammonium salts, recrystallized from methanol–water, and dried over $P_2O_5$ at 65° (0.1 mm).

**Preparation of Bis[$\pi$-(3)-1,2-(3′-cyclopentene)-1,2-dicarbollyl]-cobalt(III) Anion (VI) and Bis[$\pi$-(3)-1,2-divinyl-1,2-dicarbollyl]-cobalt(III) Anion (VII).**—These two derivatives were prepared by the same procedure reported for the unsubstituted analog.[9]

Purification was achieved by chromatographing the crude product over silica gel with 20% methanol–80% chloroform by volume. VI was isolated as the tetraphenylarsonium salt, *dl* and meso mixture, and recrystallized twice from acetone–diethyl ether. VII was isolated as the tetramethylammonium salt and recrystallized twice from acetone–water.

**Preparation of $\pi$-(3)-1,2-Divinyl-1,2-dicarbollylmanganese Tricarbonylate Ion (VIII).**—This derivative was prepared in the same manner as the unsubstituted analog.[6] Purification was achieved in the same way as for VI and VII. The product was isolated as the cesium salt and recrystallized three times from hot water.

The characteristic spectroscopic data for the above compounds are given in Tables II–IV.

## Results and Discussion

The vapor-phase dehydration of $\beta$-hydroxyalkyl-substituted carboranes at low pressures has been shown to provide an excellent route to alkene-substituted derivatives. These carborane derivatives can be degraded, as expected, to form the substituted (3)-1,2-$B_9C_2H_{12}^-$ dicarbollide anions, Figure 2.

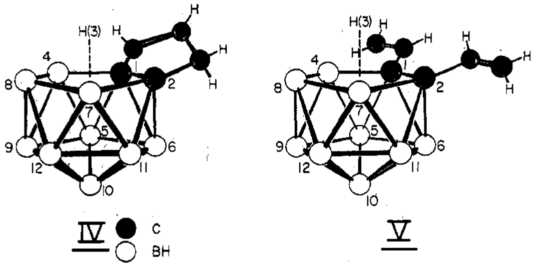

Figure 2.—The proposed structures of the (3)-1,2-$B_9C_5H_{14}^-$, IV, and (3)-1,2-$B_9C_6H_{16}^-$, V, dicarbollide anions. IV has two possible configurations of the alkenyl group which may give *d* and *l* stereoisomers. The orientation of the vinyl groups in V is unknown.

These substituted ions exhibit a derivative chemistry similar to that reported for the unsubstituted analog.[8] The proposed structures for the transition metal derivatives prepared are illustrated in Figure 3.

The extent of alkenyl group participation in the chemistry of these compounds was investigated. The question arose as to what extent I would display properties similar to cyclopentadiene and to what extent II would be similar to 1,3,5-hexatriene.

When I was treated with an equimolar amount of *n*-butyllithium in dry diethyl ether, the anionic $\pi$-allyl-substituted derivative IX was generated, Figure 1. Although direct nmr observation of this ion was possible, Table II, isolation was not attempted. Subsequent deuteration with $D_2O$ regenerated the carborane Id quantitatively deuterated with one deuterium atom in the methylene group as observed in its $^1H$ nmr spec-

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[9] 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. Amer. Chem. Soc.*, **90**, 879 (1968).

TABLE II

PROTON NMR DATA FOR THE 1,2-ALKENE-SUBSTITUTED CARBORANES AND DERIVATIVES (60 MC/SEC)

| No. | Compd | Features and coupling constants, Hz | τ, ppm | Rel area | Assignment |
|---|---|---|---|---|---|
| I | $B_{10}C_5H_{14}$ | Complex multiplet | 3.89[c] | 2.1 | Two vinyl protons |
| | | Overlapping doublets<br>$J$(vinyl) = 2.0 | 6.87 | 2.0 | Two methylene protons |
| Id | $B_{10}C_5H_{13}D$ | Doublet of doublets<br>$J$(cis) = 6.2<br>$J$(methylene) = 1.8 | 3.79[d] | 1.0 | One vinyl proton away from cage |
| | | Doublet of doublets<br>$J$(cis) = 6.2<br>$J$(methylene) = 2.1 | 4.05 | 1.0 | One vinyl proton adjacent to cage |
| | | Overlapping doublets | 6.87 | 1.1 | One methylene proton gem to deuteron |
| II | $B_{10}C_6H_{16}$ | Doublet of doublets[g]<br>$J$(cis) = 9.5<br>$J$(trans) = 16.0 | 4.00[c] | 2.0 | Two vinyl protons adjacent to cage |
| | | Doublet<br>$J$(trans) = 16.0<br>$J$(gem) < 0.5 | 4.25 | 2.0 | Two terminal vinyl protons trans to inner vinyl protons |
| | | Doublet<br>$J$(cis) = 9.5<br>$J$(gem) < 0.5 | 4.51 | 2.0 | Two terminal vinyl protons cis to inner vinyl protons |
| III | $B_{10}C_5H_{15}OH$ | Multiplet | 5.88[a] | 1.0 | Methine proton gem to hydroxyl |
| | | Doublet of doublets<br>$J$(gem) = 14.0<br>$J$(trans) = 8.0 | 7.65 | 2.0 | Two methylene protons trans to methine |
| | | Doublet of doublets<br>$J$(gem) = 14.0<br>$J$(cis) = 5.3 | 8.08 | 1.9 | Two methylene protons cis to methine |
| | | Doublet of doublets<br>$J$(methine) = 5.3<br>$J$(methylene) = 1.2 | 8.62 | 1.0 | Hydroxyl proton |
| IV | $B_9C_5H_{14}^-Cs^+$ | Doublet of triplets<br>$J$(cis) = 6.0<br>$J$(methylene) = 2.1 | 4.22[e] | 1.0 | One vinyl proton away from cage |
| | | Doublet of triplets<br>$J$(cis) = 6.0<br>$J$(methylene) = 2.2 | 4.66 | 1.1 | One vinyl proton adjacent to cage |
| | | AB pattern<br>$J$(AB) = 17 | 7.17<br>7.56 | 1.0<br>0.9 | Two methylene protons |
| V | $B_9C_6H_{16}^-(CH_3)_3NH^+$ | Broad singlet | 3.07[b] | 0.7 | $(CH_3)_3NH^+$ proton |
| | | Doublet of doublets<br>$J$(cis) = 10.0<br>$J$(trans) = 17.0 | 4.05 | 2.0 | Two vinyl protons adjacent to cage |
| | | Doublet of doublets<br>$J$(trans) = 17.0<br>$J$(gem) = 2.8 | 4.92 | 2.0 | Two terminal vinyl protons trans to inner vinyl protons |
| | | Doublet of doublets<br>$J$(cis) = 10.0<br>$J$(gem) = 2.8 | 5.30 | 2.0 | Two terminal vinyl protons cis to inner vinyl protons |
| | | Singlet | 6.85 | 9.2 | $(CH_3)_3NH^+$ methyl protons |
| VI | $(B_9C_5H_{13})_2Co^-(C_6H_5)_4As^+$ | Singlet | 2.09[b] | 20 | $(C_6H_5)_4As^+$ |
| | | Doublet of triplets<br>$J$(cis) = 6.0<br>$J$(methylene) = 2.0 | 3.55 | 2.0 | Two vinyl protons away from cage |
| | | Complex multiplet | 3.99 | 2.2 | Two vinyl protons adjacent to cage |
| | | Complex multiplet | 6.50 | 2.0 | Two methylene protons |
| | | Complex multiplet | 7.28 | 2.2 | Two methylene protons |
| VII | $(B_9C_6H_{15})_2Co^-(CH_3)_4N^+$ | Doublet of doublets<br>$J$(cis) = 10.5<br>$J$(trans) = 17.2 | 3.38[b] | 4.0 | Four vinyl protons adjacent to cage |
| | | Doublet of doublets<br>$J$(trans) = 17.2<br>$J$(gem) = 1.8 | 4.80 | 4.0 | Four terminal vinyl protons trans to inner vinyl protons |
| | | Doublet of doublets<br>$J$(cis) = 10.5<br>$J$(gem) = 1.8 | 4.83 | 4.0 | Four terminal vinyl protons cis to inner vinyl protons |
| | | Singlet | 6.58 | 12 | $(CH_3)_4N^+$ |

TABLE II (*Continued*)

| No. | Compd | Features and coupling constants, Hz | τ, ppm | Rel area | Assignment |
|---|---|---|---|---|---|
| VIII | $(B_9C_6H_{15})Mn(CO)_3^-Cs^+$ | Doublet of doublets<br>J(cis) = 10.5<br>J(trans) = 17.0 | 3.60[b] | 2.0 | Two vinyl protons adjacent to cage |
| | | Doublet of doublets<br>J(trans) = 17.0<br>J(gem) = 1.5 | 5.04 | 2.0 | Two terminal vinyl protons trans to inner vinyl protons |
| | | Doublet of doublets<br>J(cis) = 10.5<br>J(gem) = 1.5 | 5.36 | 2.0 | Two terminal vinyl protons cis to inner vinyl protons |
| IX | $B_{10}C_5H_{13}^-Li^+$ | Triplet<br>J(cis) = 3.8 | 3.37[f] | 0.9 | One central allyl proton |
| | | Doublet<br>J(cis) = 3.8 | 5.62 | 2.1 | Two outer allyl protons adjacent to cage |

[a] Benzene solution relative to internal TMS. [b] Acetone-$d_6$ solution relative to internal TMS. [c] $CCl_4$ solution relative to internal TMS. [d] $CDCl_3$ solution relative to internal TMS. [e] $CD_3CN$ solution relatve to internal TMS. [f] Diethyl ether–*n*-hexane solution relative to internal TMS. [g] Fully resolved at 250 Mc/sec.

TABLE III

BORON NMR SPECTRA OF THE 1,2-ALKENE-SUBSTITUTED CARBORANES AND (3)-1,2-DICARBOLLIDE ANIONS AT 80 MC/SEC

| No. | Compd | Chem shift, δ[a] | J, Hz | Rel intens |
|---|---|---|---|---|
| I | $B_{10}C_5H_{14}$ | 5.0 | 166 | 2.0 |
| | | 8.3 | 150 | 2.0 |
| | | 10.2 | 158 | 4.1 |
| | | 12.3 | 165 | 1.9 |
| II | $B_{10}C_6H_{16}$ | 4.8 | 150 | 2.0 |
| | | 11.0 | 158 | 8.0 |
| IV | $B_9C_5H_{14}^-(CH_3)_4N^+$ | 11.6–12.7[b] | 165, 154, 158 | 3.0 |
| | | 19.0–23.6[b] | 165, 154 | 4.2 |
| | | 33.9–35.8[b] | 158, 152 | 1.9 |
| V | $B_9C_6H_{16}^-(CH_3)_3NH^+$ | 14.2–16.3[b] | 150 | 3.0 |
| | | 22.4–23.7[b] | 140, 137 | 4.0 |
| | | 38.2–40.0[b] | 147 | 2.0 |

[a] Ppm of center of doublets relative to external $BF_3 \cdot O(C_2H_5)_2$, in acetone solution. [b] Overlapping doublets.

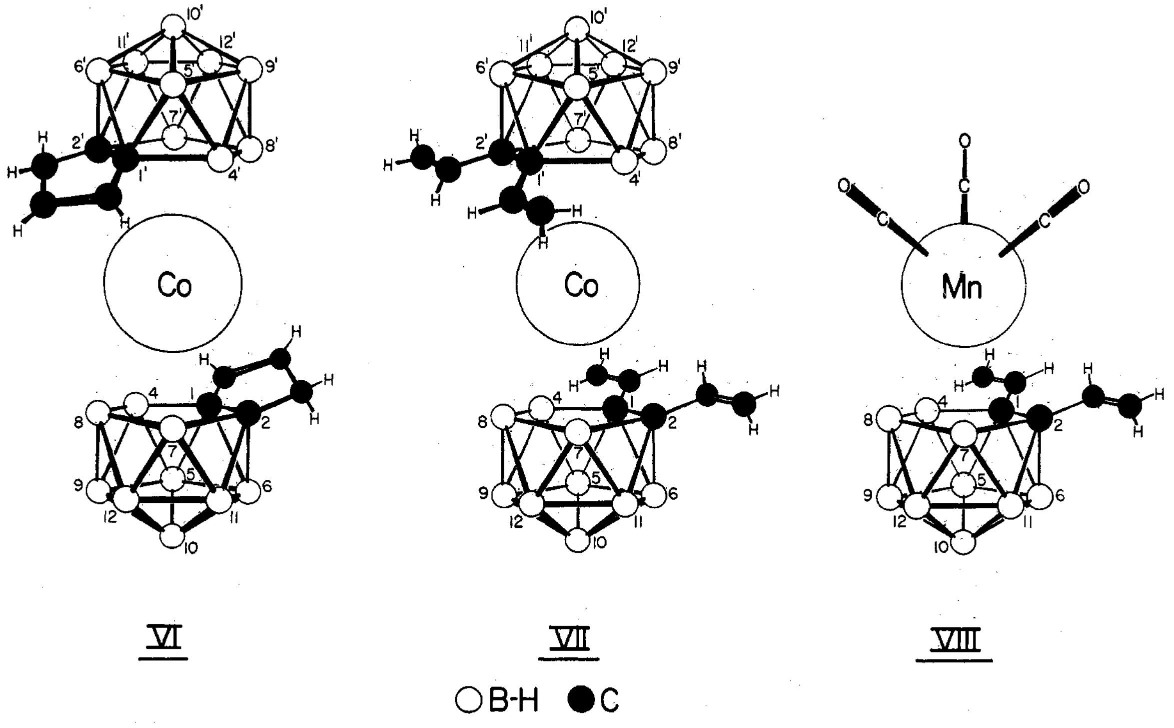

Figure 3.—The proposed structures of $(B_9C_5H_{13})_2Co^-$, VI, $(B_9C_6H_{15})_2Co^-$, VII, and $(B_9C_6H_{15})Mn(CO)_3^-$, VIII, ions. VI has two possible configurations of the alkenyl groups which may give *dl* and meso stereoisomers. The orientation of the vinyl groups in VII and VIII is unknown.

TABLE IV

INFRARED SPECTRA OF THE 1,2-ALKENE-SUBSTITUTED CARBORANES AND DERIVATIVES

| No. | Compd | | Absorptions,[c] cm$^{-1}$ |
|---|---|---|---|
| I | $B_{10}C_5H_{14}$ | *a* | 2590 vs, 1955 w, 1855 w, 1595 w, 1328 w, 1275 w, 1260 w, 1178 m, 1165 m, 1124 m, 1027 s, 977 m, 948 m, 937 m, 914 w, 844 s, 809 w, 762 m, 734 m, 720 m, 709 m, 690 m, 687 s |
| | | *b* | 3090 w, 2925 w, 2395 w, 2280 w, 1428 m |
| II | $B_{10}C_6H_{16}$ | *a* | 3108 w, 3032 w, 2588 vs, 2380 w, 1944 w, 1887 w, 1631 m, 1302 m, 1212 w, 1187 m, 1073 w, 1125 m, 999 s, 968 s, 942 s, 911 m, 847 w, 805 w, 783 w, 765 w, 726 s, 702 w, 666 w, 620 s |
| | | *b* | 2980 w, 2942 w, 2920 w, 1432 w, 1406 s, 1380 w |
| III | $B_{10}C_5H_{15}OH$ | *a* | 3320 s, 2633 w, 2570 vs, 2380 w, 1962 w, 1845 w, 1338 m, 1298 m, 1223 w, 1180 m, 1089 s, 1068 w, 1049 m, 1036 w, 1020 s, 998 w, 971 m, 954 w, 937 w, 910 w, 848 w, 825 s, 815 w, 775 m, 726 s, 671 s |
| | | *b* | 2925 w, 1440 s, 1420 w |
| IV | $B_9C_5H_{14}^-(CH_3)_4N^+$ | *a* | 2710 w, 2668 w, 2515 vs, 2480 vs, 2340 w, 1586 w, 1340 w, 1300 w, 1280 w, 1172 m, 1110 w, 1030 w, 1001 w, 972 w, 945 s, 935 w, 902 w, 886 w, 755 w, 720 m |
| | | *b* | 3040 w, 3020 w, 2882 w, 2828 w, 1472 s, 1450 w, 1433 w, 1404 w |
| V | $B_9C_6H_{16}^-(CH_3)_3NH^+$ | *a* | 3176 w, 3118 s, 3079 m, 3024 m, 2780 w, 2748 m, 2580 s, 2490 vs, 2360 w, 1819 w, 1776 w, 1618 s, 1413 m, 1397 m, 1382 m, 1296 w, 1244 m, 1171 m, 1079 w, 1033 m, 1022 m, 990 w, 981 s, 969 s, 948 w, 908 s, 884 s, 803 w, 781 w, 752 w, 725 w, 646 w |
| | | *b* | 2805 w, 1462 vs, 1450 m |
| VI | $(B_9C_5H_{13})_2Co^-(C_6H_5)_4As^+$ | *a* | 2720 w, 2604 m, 2552 s, 2520 s, 2500 s, 1880 w, 1818 w, 1574 w, 1334 w, 1324 w, 1307 w, 1267 w, 1190 w, 1179 w, 1147 w, 1103 w, 1077 m, 1016 s, 994 s, 926 w, 914 w, 856 w, 848 w, 785 w, 771 m, 743 s, 734 s, 715 w, 687 s |
| | | *b* | 3040 w, 2890 w, 1478 m, 1435 s |
| VII | $(B_9C_6H_{15})_2Co^-(CH_3)_4N^+$ | *a* | 2580 vs, 2555 vs, 1860 w, 1708 w, 1668 w, 1623 w, 1398 m, 1315 w, 1282 w, 1205 w, 1150 w, 1058 m, 1016 m, 1006 m, 979 w, 949 m, 932 m, 924 m, 913 w, 896 w, 865 w, 770 m, 738 m, 721 w, 688 m |
| | | *b* | 3045 w, 2980 w, 2265 w, 1475 s, 1438 w, 1396 m |
| VIII | $(B_9C_6H_{15})Mn(CO)_3^-Cs^+$ | *a* | 2705 w, 2555 s, 2505 vs, 2440 m, 2008 vs, 1929 vs, 1890 s, 1665 w, 1623 m, 1400 m, 1328 w, 1302 w, 1278 w, 1207 m, 1148 m, 1051 m, 1030 s, 1002 m, 987 m, 980 w, 917 s, 880 w, 847 w, 775 w, 743 m, 726 w, 791 m |
| | | *b* | 3060 w, 2295 w, 1402 m |

[a] Nujol mull. [b] Fluorolube mull. [c] Abbreviations: vs, very strong; s, strong; medium; w, weak.

trum. Thus, the methylene protons in I are acidic and resemble, at least qualitatively, the acidic protons of cyclopentadiene.

Attempts to produce similar $\pi$-allyl anionic species from IV and VI with *n*-butyllithium and sodium hydride failed.

Examination of the electronic spectra of these compounds provided insight into the question of alkenyl group conjugation. The alkenylcarboranes I and II exhibit only end absorption; no bands of wavelength longer than 2250 Å which could be attributed to electron delocalization with the cage were observed. The anions IV and V, however, exhibited bands with $\lambda_{max}$ at 2495 Å ($\epsilon$ 3100) and 2507 Å ($\epsilon$ 5600), respectively, which we are led to assign to transitions associated with a finite amount of conjugation of the alkene chromophores with the sp$^3$-like carbon orbitals in the face of the dicarbollide ion. It cannot be said at this time if these transitions are associated with charge transfer from the cage to the $\pi^*$ orbital of the alkene group or from the $\pi$-alkenyl orbital to the cage. The alkane analog of IV, (3)-1,2-(cyclopentane)-1,2-dicarbadodecahydroundecaborate(−1) ion,[2] did not display a similar band; only end absorption was observed. Moreover, the near additivity of $\epsilon_{max}$ for these absorptions, 3100 and 5600, and the absence of a large shift of the $\lambda_{max}$ of V to longer wavelengths relative to that of IV, lead us to conclude that there is little conjugation between the two vinyl groups in V.[10] This lack of conjugation is probably due to not only the poor overlap of the sp$^3$-like carbon orbitals in the face of the cage with the alkene carbon p orbitals but also, in part, to the presence of the proton bound to the face of the dicarbollide ion.

Although the cages of the carboranes I and II are apparently not conjugated with the alkenyl groups, these alkenes display a deactivated reactivity toward electrophilic attack. For example, bromination of I and II in methylene chloride or glacial acetic acid with aluminum chloride catalyst was extremely slow, monobromo products from cage bromination apparently being formed at about the same rate as dibromoalkene addition products. These alkenyl groups thus appear to be strongly deactivated by inductive electron withdrawal. Similar observations have been reported for isopropenylcarborane and vinylcarborane[11] and for 1,2-(3′,5′-cyclohexadiene)-1,2-dicarba-*closo*-dodecaborane(12).[6] Perhaps for this same reason, the ultraviolet photolysis of VIII in acetonitrile solution failed to displace CO and coordinate a vinyl group to the manganese atom. This

(10) For example, the following absorptions have been reported ($\lambda_{max}$ (m$\mu$), log $\epsilon$): cyclopentene:[10a] 165, 3.7; 187, 3.9; 210, 2.5; 1,3,5-hexatriene:[10b] 247.5, 4.75; 257.5, 4.90; 267.5, 4.83: (a) L. W. Pickett, M. Muntz, and E. M. McPherson, *J. Amer. Chem. Soc.*, **73**, 4862 (1951); (b) G. F. Woods and L. H. Schwartzman, *ibid.*, **70**, 3394 (1948).

(11) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, **2**, 1120 (1963); L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 937 (1967).

result may have been due in part to steric factors, however.

The $^1H$ nmr chemical shifts of the vinyl protons in carboranes I and II are found to be intermediate between normal benzenoid and olefinic regions. This effect can now most probably be attributed to deshielding due to the inductive electron withdrawal of the cage.[1,12]

Thus, even though there is some evidence of alkene group delocalization into the face of the substituted (3)-1,2-$B_9C_2H_{12}^-$ ions, these compounds have so far largely paralleled other substituted carboranes in their derivative chemistry.

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[12] K. M. Harmon, A. B. Harmon, and B. C. Thompson, *J. Amer. Chem. Soc.*, **89**, 5309 (1967).

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# The Structon Theory, Applied to Crystalline Borates[1]

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Principles and generalizations, previously applied to crystalline silicates and related compounds, are now applied to crystalline anhydrous borates. Many of these contain boron atoms with only three oxygen neighbors; some contain oxygen atoms with three boron neighbors. The types of *structons* and the relative numbers of these types are presented for the compounds of known crystal structure. It is shown how these data are related to the oxygen : boron ratio, the effective charges on the oxygen atoms, and equilibria between sets of structon types.

## Introduction

This is one of a series of papers[2-4] dealing with principles of the structure of crystals and glasses. The present contribution is concerned with anhydrous crystalline borates.

In the structon theory[5-7] emphasis is placed on the closest neighbor arrangements, *i.e.*, on the types of structons present, the relative numbers of these types, and their properties: their contributions to the overall properties of the substance and their effects on the arrangements of nonclosest-neighbor atoms.

It is useful to express the composition of a substance or an anion by a normalized formula, giving the numbers of the component atoms per *G-type atom* (in this case, per B). Thus, boric oxide, $B_2O_3$, is represented by the normalized formula $BO_{1.5}$ and the compound $CdB_4O_7$ is represented by the normalized formula $Cd_{0.25}BO_{1.75}$. The anion in that compound has the normalized formula $BO_{1.75}^{0.50-}$. The general formula for this and other borate anions can be written $BO_\sigma^{\rho-}$, with $\sigma$ designating the number of oxygen atoms per boron atom and $\rho$ designating the number of units of negative charge per boron atom. In an alkali borate, $M_2O \cdot B_2O_3$, $\rho$ is also the number of moles of alkali oxide per mole of boric oxide. The number of metal cations (M) per boron atom is $\rho$ in an alkali borate and $\rho/2$ in an alkaline earth borate. Neutrality for the whole substance requires that

$$\rho = 2\sigma - 3 \qquad \sigma = \frac{3}{2} + \frac{\rho}{2} \tag{1}$$

## Structon Types

The types of structons and the relative numbers of these types in a crystalline compound can be deduced from the locations of the atoms, as determined by crystal analysis. Table I lists the structon types for boric oxide and all borates of known structure. Each structon type is represented by a *structon formula*, in which the symbol for the structon atom is given first, followed in parentheses by symbols and numbers indicating the environment of closest neighbors. The structon formulas are enclosed in angular brackets (⟨⟩) to distinguish them from ordinary chemical formulas. The metal cations are all represented by the symbol M. The numbers, per boron atom, of each structon type are given before the structon formulas.

Table I also gives the normalized formulas for the borate anions (or the macromolecules in the case of boric oxide), with references to the literature, to the bond diagrams for the motifs of the anion structures (Table II), and to the appropriate sets of structon types in Table VII.

Each motif in Table II shows the unit of the pattern of interatomic bonds in the anion (or polymer molecule, in $B_2O_3$) but not the arrangement of atoms and bonds in space. Only half of each O″ oxygen represented as

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[1] Presented at the Buffalo Meeting of the American Crystallographic Association, Aug 15, 1968.

[2] M. L. Huggins, *Macromolecules*, **1**, 184 (1968).

[3] M. L. Huggins, *Inorg. Chem.*, **7**, 2108 (1968).

[4] M. L. Huggins, *Acta Crystallogr., Sect. B*, **26**, 219 (1970).

[5] M. L. Huggins, *J. Phys. Chem.*, **58**, 1141 (1954).

[6] M. L. Huggins, *J. Amer. Ceram. Soc.*, **38**, 172 (1955).

[7] M. L. Huggins, *Bull. Chem. Soc. Jap.*, **28**, 606 (1927).