is postulated to be due to protonation of the amino acid groups on the enzyme causing decomposition of the metal–enzyme complex.

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# The Preparation and Characterization of the (3)-1,2- and (3)-1,7-Dicarbadodecahydroundecaborate(−1) Ions

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**Abstract:** Treatment of the 1,2- or 1,7-dicarbaclovododecaborane(12) isomers and their carbon-substituted derivatives with alcoholic base leads to the selective removal of a single boron atom to give (3)-1,2- or (3)-1,7-dicarbadodecahydroundecaborate(−1) isomers in quantitative yield. These anions have the gross heavy atom structure of an icosahedron with one missing vertex. The resolution of the enantiomers of a representative 1-substituted (3)-1,2- and 1-substituted (3)-1,7-dicarbadodecahydroundecaborate(−1) ion are reported.

In 1963 it was reported[1–9] that decaborane(14) reacted with acetylenic compounds in the presence of Lewis bases to produce members of a new class of organoboranes. The parent compound 1,2-dicarbaclovododecaborane(12), $B_{10}C_2H_{12}$, and various carbon-substituted derivatives were reported.[10] The structure of this compound was shown to have the geometry of a regular icosahedron with two carbon atoms at adjacent vertices[11] as depicted in Figure 1.

Grafstein and Dvorak[12] reported the thermal rearrangement of 1,2-dicarbaclovododecaborane(12) at 400–500° to give a new isomer of $B_{10}C_2H_{12}$ with the carbon atoms located at the 1,7 position of the icosahedron. More recently Papetti and Heying[13] described the preparation of a third isomer of $B_{10}C_2H_{12}$ with the carbon atoms occupying the 1,12 positions of the icosahedron. The 1,12 isomer was prepared by thermal rearrangement of the 1,2 isomer at temperatures near 600°. Weisboeck and Hawthorne[14] have reported the selective degradation of 1,2-dicarbaclovododecaborane(12) and its derivatives by methanolic potassium hydroxide in accord with the equation

$$B_{10}C_2H_{12} + CH_3O^- + 2CH_3OH \longrightarrow B_9C_2H_{12}^- + B(OCH_3)_3 + H_2$$

The resulting (3)-1,2-dicarbadodecahydroundecaborate(−1) ion, (3)-1,2-$B_9C_2H_{12}^-$, and several of its carbon-substituted derivatives have been isolated as heavy cation salts.[15] Acidification of (3)-1,2-$B_9C_2H_{12}^-$ produced the neutral dicarbaundecaborane(13), $B_9C_2H_{13}$.[14] The (3)-1,2-$B_9C_2H_{12}^-$ anion is formally generated by removal of $B^+$ from $B_{10}C_2H_{12}$. Evidence was presented by Wiesboeck and Hawthorne[14] that the (3)-1,2-$B_9C_2H_{12}$ anion and the $B_9C_2H_{13}$ molecule are icosahedral fragments, isoelectronic with the hypothetical $B_{11}H_{12}^{-3}$ and the known $B_{11}H_{13}^{-2}$ anions,[16] respectively. The proposed structure of the (3)-1,2-$B_9C_2H_{12}^-$ ion is shown in Figure 2.

In this paper the details of the preparation and characterization of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions and their carbon-substituted derivatives are described along with the results of the investigation of the structure and chemistry of these unusual ions.

## Results and Discussion

The ethanolic base degradations of 1,2- and 1,7-dicarbaclovododecaborane(12) and their carbon-substituted derivatives produce, in very high yield, two isomeric series of anions having the general formula $B_9C_2H_{10}R,R'^-$ where R and R′ are substituents on the carbon atoms. The stoichiometry of these reactions is

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(5) R. P. Alexander and H. Schroeder, *ibid.*, 2, 1107 (1963).

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(12) D. Grafstein and J. Dvorak, *ibid.*, 2, 1128 (1963).

(13) S. Papetti and T. L. Heying. *J. Am. Chem. Soc.*, 86, 2295 (1964).

(14) R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, 86, 1642 (1964).

(15) In the case of the $B_9C_2H_{12}^-$ anions the numbering system is the same as that employed in numbering the parent carborane. The prefix number in parentheses designates the position of the B atom in the parent icosahedral carborane which was removed to generate the anion. The remaining prefix numbers denote the positions of the carbon atoms. The suffix number in parentheses is the formal charge on the anion.

(16) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1, 734 (1962).

Table I. Analysis and Characterization Data for (3)-1,2-Dicarbadodecahydroundecaborate(−1) Salts and Derivatives

| Compound | Mp, °C[a] | Yield, % | Calculated, % C | H | B | Cs | N | Found, % C | H | B | Cs | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[(CH_3)_3NH][B_9C_2H_{12}]$[b] | 308–309.5 | 97 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $Cs[B_9C_2H_{12}]$ | ... | 94 | 9.04 | 4.54 | 36.58 | 49.97 | ... | 9.02 | 4.60 | 36.45 | 49.61 | ... |
| $Cs[B_9C_2H_{11}(C_6H_5)]$ | 257–259 | 88 | 28.06 | 4.71 | 28.44 | 38.79 | ... | 28.40 | 4.74 | 28.04 | 38.36 | ... |
| $[(CH_3)_3NH][B_9C_2H_{10}(CH_3)_2]$[b] | 141.5–143 | 98 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $Cs[B_9C_2H_{10}(CH_3)_2]$ | ... | 95 | 16.31 | 5.47 | 33.06 | 45.16 | ... | 15.92 | 5.12 | 31.07 | 44.18 | |
| $[(CH_3)_4N][B_9C_2H_{10}(CH_3)(C_6H_5)]$ | ... | 98 | 52.45 | 10.16 | 32.74 | ... | 4.71 | 52.60 | 10.43 | 32.47 | ... | 4.60 |
| $Cs[B_9C_2H_{11}(p\text{-}BrC_6H_4)]$ | 277–279 | 91 | 22.72 | 3.69 | 22.92 | 32.30 | ... | 22.84 | 3.33 | 23.17 | 31.62 | ... |

[a] Melting points are uncorrected. [b] Analyzed as cesium salt.

identical with that described above[14] and has been verified through hydrogen evolution measurements and recovery of the borate ester produced. The resulting anions are initially recovered as air-stable and colorless crystalline potassium salts. Other salts such as cesium, rubidium, tetramethylammonium, and trimethylammonium were prepared by precipitation from aqueous solutions of the potassium salts. The analyses, yields, and melting points of several of the salts of various $B_9C_2H_{10}R,R'^-$ anions are presented in Table I. These anions are not degraded by nonoxidizing acids, are unaffected by aqueous base (except at very high concentrations or temperatures), and show unusually high thermal stabilities.

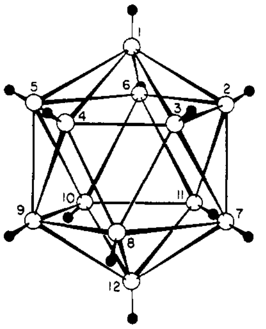

Figure 1. Structure of icosahedral $B_{10}C_2H_{12}$ isomers with numbering system.

The initial base degradation studies[14] were carried out with 1-phenyl-1,2-dicarbaclovododecaborane(12) to produce a single isomer of the anion having the composition $B_9C_2H_{11}(C_6H_5)^-$. Assuming that no motion of the carbon atoms relative to each other occurred during the degradation reaction, the absence of position isomers indicated that the boron atom removed is one of the four atoms at positions 3, 6, 8, and 10 (Figure 1) contained in a plane which bisects the carbon–carbon bond.

Degradation of 1-phenyl-1,2-dicarbaclovododecaborane(12) deuterated in the 8, 9, 10, and 12 positions proceeded at the same rate as with the undeuterated material, and 97% pure hydrogen was evolved.[17] Thus, the 8 and 10 boron atoms do not appear to be removed during the degradation reaction and the boron atom which is removed is undoubtedly one of the chemically equivalent 3- or 6-boron atoms. The 3- and 6-boron atoms would be expected to be most susceptible to base attack[18] since these atoms both have two relatively electropositive carbon atoms as nearest neighbors and hence are the most electropositive boron atoms in the icosahedral framework. The rate of degradation of 1-phenyl-1,2-dicarbaclovododecaborane(12) in aqueous ethanolic potassium hydroxide at 75° was followed by hydrogen evolution measurements and was observed[14] to be first order with respect to both carborane and hydroxide ion concentrations.

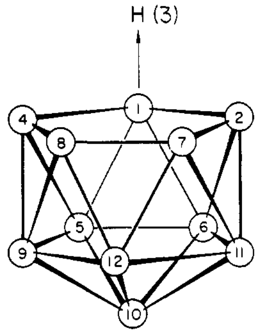

Figure 2. Schematic drawing of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions with numbering system.

A plausible mechanistic sequence involves the known (*vide infra*) $B_9C_2H_{11}^{-2}$ ion.

$$B_{10}C_2H_{12} + C_2H_5O^- \xrightarrow{\text{slow}} [B_{10}C_2H_{12}(C_2H_5O)]^-$$

$$[B_{10}C_2H_{12}(C_2H_5O)]^- + C_2H_5O^- \longrightarrow [B_{10}C_2H_{12}(C_2H_5O)_2]^{-2}$$

$$[B_{10}C_2H_{12}(C_2H_5O)_2]^{-2} \longrightarrow B_9C_2H_{11}^{-2} + HB(C_2H_5O)_2$$

$$HB(C_2H_5O)_2 + C_2H_5OH \longrightarrow H_2 + B(C_2H_5O)_3$$

$$B_9C_2H_{11}^{-2} + C_2H_5OH \longrightarrow B_9C_2H_{12}^- + C_2H_5O^-$$

The products of degradation of 1,2-dicarbaclovododecaborane(12) and its carbon-substituted derivatives are most likely (3)-1,2-$B_9C_2H_{12}^-$ anions having the geometry of an 11-particle icosahedral fragment (Figure 2) in which the carbon atoms occupy adjacent positions in the "open-face" of the icosahedral fragment. The 12th or "extra" hydrogen is most likely located in the "open-face" of the icosahedral fragment and is discussed below. It should be noted that Fritchie[19] has shown by X-ray crystallographic studies that the $B_{11}H_{13}^{-2}$ ion, isoelectronic with the $B_9C_2H_{13}$ molecule,[14] has a boron framework consisting of a nearly regular icosahedron missing one vertex. Two of the hydrogen atoms bridge nonadjacent edges of the open pentagonal face; the remainder appear as terminal B–H atoms at the vertices.

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[17] The deuterated phenylcarborane was prepared from 1,2,3,4-tetradeuteriodecaborane(14); see ref 14.

[18] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

[19] C. J. Fritchie, Jr., *Inorg. Chem.*, 6, 1199 (1967).

Table II. Analysis and Characterization Data for (3)-1,7-Dicarbadodecahydroundecaborate(−1) Salts and Derivatives

| Compound | Mp, °C[a] | Yield, % | Calculated, % C | H | B | Cs | N | Found, % C | H | B | Cs | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Cs[B_9C_2H_{12}]$ | 327–328.5 | 96[b] | 9.04 | 4.54 | 36.58 | 49.84 | ... | 9.02 | 4.31 | 36.30 | 49.95 | ... |
| $Cs[B_9C_2H_{11}(C_6H_5)]$ | 353–355 dec | 60,[b] 70[c] | 28.06 | 4.71 | 28.44 | 38.79 | ... | 27.97 | 4.78 | 28.15 | 38.62 | ... |
| $[(CH_3)_3NH][B_9C_2H_{10}(CH_3)_2]$ | 147–148 | 86[b] | 37.99 | 11.73 | 44.00 | ... | 6.28 | 37.95 | 11.78 | 44.57 | ... | 6.11 |

[a] Melting points are uncorrected. [b] Prepared by the alcoholic base degradation of the corresponding 1,7-carborane. [c] Prepared by the thermal isomerization of the (3)-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) ion.

The alcoholic base degradation of 1,7-dicarbaclovododecaborane(12) proceeds in the same manner as in the case of the 1,2 isomer albeit at a greatly reduced rate. As in the latter case, only a single position isomer is observed in the produced anion when the carbon atoms are symmetrically substituted which suggests that only the 2-, 3-, 9-, or 10-boron atoms (Figure 1) could have been removed. By analogy with the 1,2 isomers, those boron atoms nearest carbon would be expected to be most susceptible to base attack. Therefore, one of the equivalent 2- or 3-boron atoms is undoubtedly that which is removed. The lower reaction rate observed can be rationalized on the basis of the greater dispersal of positive charge associated with the position of the carbon atoms in the 1,7-dicarbaclovododecaborane(12). The isomer produced by the base degradation of 1,7-dicarbaclovododecaborane(12) is then the (3)-1,7-dicarbadodecahydroundecaborate(−1) ion. The chemical and thermal stability of carbon-substituted (3)-1,7-dicarbadodecahydroundecaborate(−1) ions are comparable to those of the corresponding 1,2 isomers. Analytical, melting point, and yield data for various salts and carbon-substituted derivatives of the (3)-1,7-dicarbadodecahydroundecaborate(−1) ion are presented in Table II.

Recently it has been reported[20] that (3)-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) ion may be thermally rearranged to the corresponding 1,7 isomer identical with that obtained from the degradation of 1-phenyl-1,7-dicarbaclovododecaborane(12). Thus, the cesium salt of (3)-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) when fused *in vacuo* at 300° for 3 hr produced (3)-1-phenyl-1,7-dicarbadodecahydroundecaborate(−1) in high yield.

Zakharin and Kalnin[21] recently described the facile degradation of 1,2-dicarbaclovododecaborane(12) with piperidine to produce a piperidinium salt of the corresponding (3)-1,2-dicarbadodecahydroundecaborate(−1) ion which contained an additional molecule of piperidine. When heated under vacuum, this product eliminated 1 mole of piperidine and produced the simple piperidinium salt. The Russian workers consequently suggested that the loosely bound piperidine molecule was attached to the (3)-1,2-dicarbadodecahydroundecaborate(−1) anion by a weak dative B–N bond.

In view of our studies of the degradation of 1,2-dicarbaclovododecaborane(12) with alcoholic potassium hydroxide, it appeared likely that the compound reported by the Russian workers actually contained a weakly bound piperidine molecule present in the crystalline phase as a hydrogen-bonded complex with piperidinium ion and not directly attached to the (3)-1,2-dicarbadodecahydroundecaborate(−1) ion. This was established[22] to be the case by comparison of the $^{11}B$ nmr spectra of authentic piperidinium (3)-1,2-dicarbododecahydroundecaborate(−1) in piperidine solution and in 95% ethanol solution with the trimethylammonium salt of (3)-1,2-dicarbadodecahydroundecaborate(−1) in 95% ethanol. The three spectra were found to be identical in all respects. It has been further observed that piperidine may be substituted for alcoholic base in the degradation of carbon-substituted 1,7-dicarbadodecaborane(12) derivatives to the corresponding (3)-1,7-dicarbadodecahydroundecaborate(−1) anions.

Although no position isomers are observed with unsymmetrically carbon-substituted (3)-1,2- or (3)-1,7-dicarbadodecahydroundecaborate(−1) ions, in certain cases one would expect the formation of enantiomeric anions. For example, the anion obtained by removal of the 6-boron atom of an unsymmetrically carbon-substituted 1,2-dicarbaclovododecaborane(12) should be the enantiomer of that obtained by the removal of the 3-boron atom. Unsymmetrically carbon-substituted (3)-1,2-dicarbadodecahydroundecaborate(−1) anions were prepared and resolved into their enantiomers with the *d*- and *l*-N,N,N-trimethyl-$\alpha$-phenylethylammonium cation.[23] As a control, the resolution of a symmetrically substituted anion was attempted using the same resolving agent and solvent system and no resolution was observed.

The specific rotations of the tetramethylammonium salts of *d*- and *l*-(3)-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) and *d*-(3)-1-phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate(−1) are shown in Table III.

Table III. Optical Rotations of Optically Active (3)-1,2- and (3)-1,7-Dicarbadodecahydroundecaborate(−1) Ions

| Tetramethylammonium dicarbadodecahydroundecaborate(−1) Salt | $[\alpha]^{25}$D, deg |
|---|---|
| *d*-1-Phenyl-(3)-1,2- | 9.8 |
| *l*-1-Phenyl-(3)-1,2- | −10.0 |
| *d*-1-Phenyl-2-methyl-(3)-1,2- | 28 |
| *d*-1-Phenyl-(3)-1,7-[a] | 14.6 |

[a] Cesium salt.

The fact that resolution was achieved is a further confirmation that the 3- or the chemically identical 6-boron atom is removed in the ethanolic potassium hydroxide degradation, as proposed. The plane optical rotary dispersion curves of both *d* salts have the same general

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(20) P. M. Garrett, F. N. Tebbe, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 5016 (1964).

(21) L. I. Zakharin and V. N. Kalnin, *Tetrahedron Letters*, 407 (1965).

(22) M. F. Hawthorne, P. A. Wegner, and R. C. Stafford, *Inorg. Chem.*, **4**, 1675 (1965).

(23) D. N. Kursanov and S. V. Vitt, *Dokl. Akad. Nauk SSSR*, **113**, 607 (1957).

Table IV. Infrared Spectra (Nujol Mull) of (3)-1,2- and (3)-1,7-Dicarbadodecahydroundecaborate(−1) Anions[a]

| (3)-1,2-Dicarbadodecahydroundecaborates(−1) | | | | |
|---|---|---|---|---|
| $[(CH_3)_3NH][B_9C_2H_{12}]$ | $Cs[B_9C_2H_{11}(C_6H_5)]$ | $[(CH_3)_3NH][B_9C_2H_{10}(CH_3)_2]$ | $Cs[B_9C_2H_{11}(P\text{-}BrC_6H_4)]$ | $RbB_9C_2H_{10}(C_6H_5)(CH_3)$ |
| 2512 s | 2506 s | 3175 m | 2544 s | 2520 s |
| 1412 w | 1590 m | 2519 s | 1602 w | 1610 m |
| 1374 m | 1209 w | 1418 w | 1211 w | 1379 m |
| 1285 w | 1078 w | 1208 w | 1074 m | 1078 w |
| 1070 w | 1027 m | 1027 m | 1008 m | 1035 m |
| 1024 m | 885 w | 978 m | 889 w | 1005 w |
| 951 s | 705 s | 816 w | 833 m | 927 w |
| 902 w | | 755 w | 726 w | 892 w |
| 846 w | | 738 w | | 766 s |
| | | 680 m | | 704 s |
| | | | | 696 s |

| (3)-1,7-Dicarbadodecahydroundecaborates(−1) | | |
|---|---|---|
| $[(CH_3)_3NH][B_9C_2H_{12}]$ | $CsB_9C_2H_{11}(C_6H_5)$ | $[(CH_3)_3NH][B_9C_2H_{10}(CH_3)_2]$ |
| 3125 s | 2512 s | 3125 s |
| 2506 s | 1261 m | 2506 s |
| 1241 w | 1116 m | 1244 w |
| 1106 m | 978 m | 1208 w |
| 1028 m | 843 m | 1016 m |
| 969 m | 746 w | 972 m |
| 867 w | 754 m | 907 w |
| 829 w | 720 m | 787 w |
| 757 w | 706 s | 738 m |
| 737 m | | |

[a] Values in cm$^{-1}$. s = strong, m = medium, w = weak.

shape, and this similarity strongly suggests that the two ions have the same absolute configuration.

Similarly, two enantiomers are obtained by the degradation of an unsymmetrically carbon-substituted 1,7-dicarbaclovododecaborane(12). Complete resolution has not been achieved in this series of ions. However, the *d*-1-phenyl-1,7-dicarbadodecahydroundecaborate(−1) ion has been isolated and characterized as its cesium salt (Tables II and III).

The infrared spectra of trimethylammonium and cesium salts of the 1,2- and 1,7-dicarbadodecahydroundecaborate(−1) ions and some of their carbon-substituted derivatives are given in Table IV. Each of these spectra exhibits a single sharp absorption between 2500 and 2550 cm$^{-1}$ which has been assigned to terminal boron–hydrogen stretching vibration. No bridge hydrogen (B–H–B) vibrations were observed. The infrared spectra of both series of isomeric dicarbadodecahydroundecaborate(−1) ions are qualitatively similar to that of the parent carboranes. The "extra" hydrogen atom in the $B_9C_2H_{12}^-$ isomers and their C-substituted derivatives may be viewed as rapidly tautomerizing between various B–H–B and C–H–B bridge positions and/or a $BH_2$ position about the open pentagonal face of the (3)-1,2- and (3)-1,7-dicarbadodecahydroundecaborate(−1) ions. An alternative view of this "extra" hydrogen atom suggests that it occupies the position previously held by the boron atom in the parent carboranes, and is bound in a six-center molecular orbital with the atoms forming the pentagonal face of the icosahedral fragment. However, the fact that no bridge hydrogen atom vibrations are clearly observed in the infrared spectra cannot be taken as proof that such an H atom is not present since bridge-hydrogen infrared absorptions are generally weak and are not observed in some instances in which their presence is actually known by other means.[18]

The $^{1}H$ nmr spectra of (3)-1,2- and (3)-1,7-dicarbadodecahydroundecaborate(−1) salts and some of their carbon-substituted derivatives are given in Table V. The observed $^{1}H$ nmr spectra are consistent with the proposed symmetry of the (3)-1,2- and (3)-1,7-dicarbadodecahydroundecaborate(−1) ions, in that symmetrically carbon-substituted derivatives show a single proton resonance representative of hydrogen atoms (unsubstituted ions) or equivalent substituent groups.

The $^{11}B$ nmr spectra (32 Mc/sec) of these same materials are listed in Table VI. Based upon the proposed structure, both the (3)-1,2- and (3)-1,7-dicarbadodecaborate(−1) ions should, at very high resolution, present a spectrum composed of three doublets of relative area one and three doublets of relative area two when the carbon atoms are symmetrically substituted, and nine doublets of relative area one when the carbon atoms are unsymmetrically substituted. While the spectra are too complex to accommodate complete interpretation, at least five distinctly different types of boron atoms were observed with the symmetrical carbon-substituted derivative, and seven distinctly different types of boron atoms are seen in the case of the unsymmetrically carbon-substituted derivatives. In all of the 32-Mc/sec $^{11}B$ nmr spectra, the observed boron resonances appeared as doublets and gave no evidence of spin–spin coupling with the "extra" hydrogen atom. However, the $^{11}B$ nmr spectrum of potassium (3)-1,2-dicarbadodecahydroundecaborate(−1) at 60 Mc/sec (Figure 3) shows an additional splitting of one of the high-field doublets of relative area 1.0. This observation may be taken as evidence for the interaction of the "extra" hydrogen with at least one of the boron atoms included in the open pentagonal face of the anion. Furthermore, this 60-Mc/sec $^{11}B$ nmr spectrum constitutes the only spec-

Table V. $^{1}H$ Nmr Spectra of (3)-1,2- and (3)-1,7-Dicarbadodecahydroundecaborate Salts

| Compound | Feature | δ, ppm[a] | Rel peak area | Assignment |
|---|---|---|---|---|
| $[1,2\text{-}B_9C_2H_{12}][(CH_3)_4N]$ | Sharp singlet | −3.43 | 12.0 | $4CH_3$[b] |
| | Broad singlet | −1.67 | 2.0 | 2H[c] |
| $[1,2\text{-}B_9C_2H_{11}(C_6H_5)][(CH_3)_4N]$ | Sharp singlet | −3.32 | 12.0 | $4CH_3$[b] |
| | Broad singlet | −2.08 | 0.9 | H[c] |
| | Multiplet | −7.12 | 5.0 | $H_5C_6$[c] |
| $[1,2\text{-}B_9C_2H_{10}(CH_3)_2][(CH_3)_4N]$ | Sharp singlet | −1.35 | 6.0 | $2CH_3$[c] |
| | Broad singlet | −3.42 | 12.0 | $4CH_3$[b] |
| $[1,2\text{-}B_9C_2H_{11}(p\text{-}BrC_6H_4)]Cs$ | Broad singlet | −2.10 | 1.1 | H[c] |
| | Sharp singlet | −7.22 | 4.0 | $H_4C_6Br$[c] |
| $[1,7\text{-}B_9C_2H_{12}][(CH_3)_3NH]$ | Broad singlet | −1.08 | 2.0 | 2H[c] |
| | Sharp singlet | −3.19 | 9.1 | $3\text{-}CH_3$[b] |
| $[1,7\text{-}B_9C_2H_{11}(C_6H_5)]Cs$ | Sharp singlet | −1.30 | 1.0 | H[c] |
| | Broad doublet | −7.22 | 4.9 | $H_5C_6$[c] |
| $[1,7\text{-}B_9C_2H_{10}(CH_3)_2][(CH_3)_3NH]$ | Broad singlet | −1.42 | 6.0 | $2CH_3$[c] |
| | Sharp singlet | −3.10 | 9.0 | $3CH_3$[b] |
| | Broad singlet | −7.28 | 1.0 | H–N[b] |

[a] δ relative to tetramethylsilane at 60 Mc/sec in deuterioacetone solvent. [b] Resonances arising from trimethyl- or tetramethylammonium cation. [c] Substituents on the polyhedral C atoms.

troscopic observation of the "extra" hydrogen atom thus far obtained.

Although the spectroscopic evidence for the "extra" hydrogen is sparse, its presence has been clearly established chemically. In addition to the precise determination of the stoichiometry of the reaction in which the $(3)\text{-}1,2\text{-}B_9C_2H_{12}^-$ ion is formed, it has been found that the "extra" hydrogen is very weakly acidic and can be removed with a strong base to generate a dianion, $B_9C_2H_{11}^{-2}$.

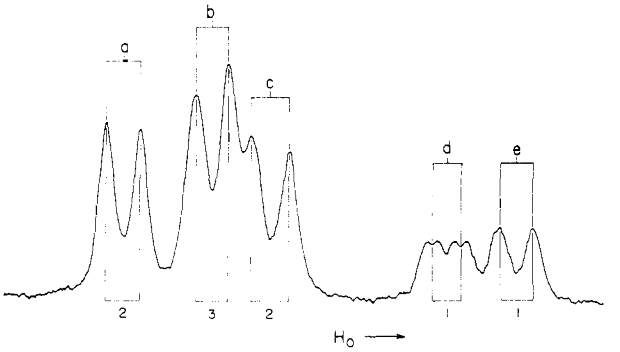

Figure 3. A 60-Mc/sec $^{11}B$ nmr spectrum of $(3)\text{-}1,2\text{-}B_9C_2H_{12}^-$ showing secondary splitting of doublet d. Chemical shifts are presented in Table VI. Relative integrated areas are beneath the peaks.

$$B_9C_2H_{12}^- + NaH \xrightarrow{\text{tetrahydrofuran}} B_9C_2H_{11}^{-2} + H_2 + Na^+$$

The above reaction is quantitative and proceeds with the liberation of exactly 1 mole of hydrogen.[24] The proton-abstraction reaction is reversible and the $(3)\text{-}1,2\text{-}B_9C_2H_{12}^-$ anion is regenerated when the $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{-2}$ dianion is exposed to protonic solvents, such as water and alcohols. The $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{-2}$ ion and its carbon-substituted derivatives have been shown to form a number of transition metal derivatives, in which the metal may be considered to be π-bonded to the open pentagonal face of an icosahedral fragment, as in the case of the formation of ferrocene from $C_5H_5^-$. In so

Table VI. $^{11}B$ Nmr Spectra (32 Mc/sec) of (3)-1,2- and (3)-1,7-Dicarbadodecahydroundecaborate Salts

| Compound | δ[a] (*J*, cps) | Rel peak area |
|---|---|---|
| $[1,2\text{-}B_9C_2H_{12}][(CH_3)_3NH]$ | 36.5 (131) | 1.0 |
| | 32.1 (128) | 1.0 |
| | 21.0 (138) | 2.1 |
| | 16.3 (140) | 3.0 |
| | 10.9 (141) | 2.0 |
| $[1,2\text{-}B_9C_2H_{11}(C_6H_5)][(CH_3)_4N]$ | 34.7 (137) | 1.0 |
| | 32.1 (127) | 1.0 |
| | 22.4 (121) | 1.0 |
| | 16.1 (125) | |
| | | 6.0[b] |
| | 7.8 (121) | |
| $[1,2\text{-}B_9C_2H_{10}(CH_3)_2][(CH_3)_4N]$ | 35.5 (123) | |
| | | 2.1[b] |
| | 32.7 (128) | |
| | 17.5 (136) | 4.0 |
| | 9.0 (127) | 3.0 |
| $[1,2\text{-}B_9C_2H_{11}(p\text{-}BrC_6H_4)]Cs$ | 34.3 (139) | |
| | | 2.0[b] |
| | 31.3 (121) | |
| | 16.9 (125) | 3.9 |
| | 9.7 (131) | 3.1 |
| $[1,7\text{-}B_9C_2H_{12}][(CH_3)_3NH]$ | 33.9 (134) | 2.0 |
| | 23.2 (123) | |
| | | 4.0[b] |
| | 21.6 (132) | |
| | 6.4 (130) | |
| | | 3.0[b] |
| | 5.6 (128) | |
| $[1,7\text{-}B_9C_2H_{11}(C_6H_5)]Cs$ | 37.2 (121) | 1.0 |
| | 33.7 (121) | 1.0 |
| | 23.2 (127) | 3.0 |
| | 19.7 (123) | 1.0 |
| | 6.3 (125) | |
| | 7.5 (131) | 3.1[b] |
| | 3.6 (125) | |
| $[1,7\text{-}B_9C_2H_{10}(CH_3)_2][(CH_3)_3NH]$ | 32.7 (136) | 2.0 |
| | 19.1 (124) | |
| | | 4.0[b] |
| | 17.5 (133) | |
| | 4.3 (131) | |
| | | 3.0[b] |
| | 3.7 (128) | |

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

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[24] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

doing, the metal simultaneously completes two icosahedra.[24–27] This general structure has been confirmed for several transition metal derivatives and may be taken as confirmation of the suggestion that (3)-1,2-$B_9C_2H_{12}^-$ ion has the same configuration as the (3)-1,2-$B_9C_2H_{11}^{-2}$ ligand. An extensive chemisty has developed around the (3)-1,2-$B_9C_2H_{11}^{-2}$ dianion which will be discussed in subsequent papers.

Monohalogenated derivatives of (3)-1,2-dicarbadodecahydroundecaborate(-1) anions have been prepared.[28] Addition of $I_2$ to an aqueous ethanol solution of (3)-1,2-$B_9C_2H_{12}^-$ salts precipitated iodide ion and produced the $H_3O^+$ salt of $B_9C_2H_{11}I^-$. The anion was recovered and characterized as the crystalline tetramethylammonium salt. Iodinated derivatives of the C-substituted anions were obtained in an analogous manner.[28] Protonation of the $B_9C_2H_{11}I^-$ anion produced the neutral sublimable acid $B_9C_2H_{12}I$. Replacement of $I_2$ by $Br_2$ gave analogous monobrominated materials.

Further reactions of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions will be presented in subsequent papers.

## Experimental Section

**Materials.** Decaborane(14) was sublimed before use. Tetrahydrofuran was freshly distilled from lithium aluminum hydride and collected under nitrogen. Sodium hydride, as a 60% dispersion in mineral oil, was obtained from Metal Hydrides, Inc. All other chemicals were reagent grade and were used without further purification. The preparations of the 1,2- and 1,7-dicarbaclovododecaboranes were based on procedures described in the literature.[1–9]

Infrared spectra were obtained as Nujol mulls with a Beckman IR-5 infrared spectrophotometer. Proton and $^{11}B$ nmr spectra were obtained with a Varian HA-100 spectrometer. The $^{11}B$ nmr spectrum at 60 Mc/sec was obtained using an experimental nmr spectrometer which employed a cryogenic solenoid.[29]

Optical rotations were taken on an O. C. Rudolf and Sons, Inc. manual spectropolarimeter. Elemental analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**1-*p*-Bromophenyl-1,2-dicarbaclovododecaborane(12).** In a 1-l., three-necked flask equipped with a mechanical stirrer, condenser, pressure equalized addition funnel, and nitrogen inlet was placed 50 g (0.41 mole) of sublimed decaborane, 22 ml (0.41 mole) of acetonitrile, and 500 ml of benzene. This solution was refluxed for 2 hr, 74 g (0.41 mole) of *p*-bromophenylacetylene was added dropwise, and the resulting mixture was refluxed for 30 hr. The solvent was then removed under reduced pressure using a rotary evaporator. The residue was extracted into 1 l. of pentane and the pentane solution washed four times with 100-ml portions of 10% sodium hydroxide solution. The pentane solution was then dried over anhydrous magnesium sulfate and the solvent removed with a rotary evaporator at reduced pressure to give a crystalline product, of mp 135–136°, yield 80.4 g (68%). *Anal.* Calcd for $B_{10}C_8H_{15}Br$: B, 36.13; C, 32.11; H, 5.05. Found: B, 36.08; C, 32.11; H, 5.14.

**1-Phenyl-1,7-dicarbaclovododecaborane(12)** was prepared by thermal rearrangement of 1-phenyl-1,2-dicarbaclovododecaborane-(12).[1] Five grams (0.023 mole) of 1-phenyl-1,2-dicarbaclovododecaborane(12) was charged into a 100-ml stainless steel autoclave at room temperature. The autoclave was evacuated with a mechanical vacuum pump and then heated electrically to a temperature of 420° for 24 hr. After cooling, the contents of the autoclave were dissolved in 30 ml of pentane.

The pentane solution was applied to a 4 ft × 1.5 in. column of Davidson Code 62 silica gel partially deactivated with 4% water in an upflow liquid phase chromatographic apparatus. The column was prewet with 200 ml of pentane and the sample eluted with pentane. The separation was monitored by measuring the ultraviolet absorbance of samples of 100-ml cuts taken from the column. A clean separation of the components was obtained. Evaporation of the solvent from combined cuts 5–8 yielded 3.4 g (69.4%) of 1-phenyl-1,7-dicarbaclovododecaborane(12), mp 55.1–55.7°. *Anal.* Calcd for $B_{10}C_8H_{18}$: B, 49.14; C, 43.60; H, 7.27. Found: B, 49.32; C, 43.65; H, 7.19.

**Preparation of 1,7-Dimethyl-1,7-dicarbaclovododecaborane(12).** In a 250-ml, three-necked flask was placed 2.00 g (0.013 mole) of 1-methyl-1,7-dicarbaclovododecaborane(12),[12] 50 ml of anhydrous ethyl ether, and a magnetic stirring bar. The flask was equipped with a pressure-equalized addition funnel containing 14.5 ml of *n*-butyllithium (0.023 mole). The second neck of the flask was equipped with a Dry Ice–2-propanol condenser and a nitrogen outlet. The third neck of the flask was stoppered and the system was flushed with nitrogen. The butyllithium solution was added over a 10-min period under a positive pressure of nitrogen. The solution was stirred for 2 hr, methyl iodide (5.72 g, 0.040 mole) was added with stirring, and the solution was refluxed for 18 hr under nitrogen. The reaction mixture was cooled and evaporated to dryness on a rotary evaporator and the solid product sublimed at 90° under high vacuum. The sublimate was condensed on an ice–salt cooled surface. The residue from the sublimation was discarded. The yield of sublimed product was 2.11 g (96%), mp 161–162°. *Anal.* Calcd for $B_{10}C_4H_{16}$: B, 62.75; C, 27.89; H, 9.36. Found: B, 62.61; C, 27.80; H, 9.21.

**Preparation of 1-Phenyl-2-methyl-(3)-1,2-dicarbaclovododecaborane(12).** To 28.0 g (0.126 mole) of 1-phenyl-1,2-dicarbaclovododecaborane(12)[1] in 100 ml of dry ether at 0° was added 90 ml (0.126 mole) of *n*-butyllithium. The mixture was stirred for 1 hr in an ice bath, allowed to stand overnight at room temperature, and heated to reflux for 4 hr. After 36 g (0.25 mole) of methyl iodide was added dropwise, the solution was again refluxed for 4 hr and cooled. Water was added dropwise, and the ether layer was separated. The aqueous layer was washed twice with ether. The combined ether phases were dried overnight with sodium sulfate and filtered. After the solvents were removed on a rotary evaporator, the resulting oil crystallized. The material was placed in a 250-ml flask and sublimed under vacuum onto a Dry Ice trap, yielding 7.8 g of $C_6H_5(CH_3)C_2B_{10}H_{10}$, mp 86–96°. Resublimation using a 0° trap failed to improve the melting point. Two recrystallizations from methanol brought the melting point to 100.2–101.2°. The yield was 5.3 g (18%). *Anal.* Calcd for $C_6H_5(CH_3)C_2B_{10}H_{10}$: H, 7.74; C, 46.17; B, 46.09. Found: H, 7.83; C, 46.28; B, 46.04.

**Preparation of the (3)-1,2-Dicarbadodecahydroundecaborate(−1) Ion. General Procedure for Degradation Reactions.** A solution of 20 g (0.36 mole, 100% excess) of potassium hydroxide in 300 ml of absolute ethanol was placed in a 500-ml, three-necked flask equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet. After the solution had been cooled to room temperature, 1,2-dicarbaclovododecaborane(12)[1] (28 g, 0.175 mole) was added and the resulting solution stirred for 1 hr at room temperature, then heated to reflux temperature until hydrogen evolution ceased (2 hr).

After cooling, an additional 100 ml of absolute ethanol was added. The excess potassium hydroxide was precipitated as potassium carbonate by saturating the solution with a stream of carbon dioxide. The precipitate was removed by filtration and washed with five 50-ml portions of ethanol. The combined filtrate and washings were evaporated to dryness to yield a crude potassium salt, $KB_9C_2H_{12}$. At this point, the potassium salt was either further purified or was dissolved in water and the monoanion precipitated with other cations such as trimethylammonium, cesium, etc. An example of each procedure is described below.

The crude potassium salt was mixed with 700 ml of benzene in a 1-l., three-necked flask equipped with a mechanical stirrer and an efficient distillation column. The solution was stirred under a nitrogen atmosphere and residual ethanol and water distilled overhead as a benzene azeotrope. When no additional water was observed in the distillate, the mixture was filtered to recover most of the product. The remainder was recovered as a residue by evaporating the solvent from the filtrate under reduced pressure.

An extraction apparatus consisting of a 1-l. three-necked flask, fitted with a mechanical stirrer, nitrogen inlet, and two Soxhlet extractors was used for further purification of the potassium salt. One Soxhlet thimble was filled with calcium hydride and the other with the combined, partially purified, potassium salt of $B_9C_2H_{12}^-$. The flask was charged with 700 ml of benzene which had been dried over sodium ribbon. The system was then brought to the reflux

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(25) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965).

(26) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

(27) M. F. Hawthorne and D. T. Andrews, *Chem. Commun.*, 443 (1965).

(28) F. P. Olsen and M. F. Hawthorne, *Inorg. Chem.*, **4**, 1839 (1965).

(29) F. A. Nelson and H. E. Weaver, *Science*, **146**, 223 (1964).

temperature and the extraction continued for about 40 hr. As the potassium salt of (3)-1,2-dicarbadodecahydroundecaborate(−1) was slowly extracted, it crystallized in the flask. The solution was cooled to 4° and the crystalline anhydrous potassium salt recovered by filtration, yield 29.8 g or 98%.

The crude potassium salt of $B_9C_2H_{12}^-$ prepared from 28 g (0.175 mole) of carborane was converted to the trimethylammonium salt by the addition of a solution of 22 g (0.24 mole) of trimethylamine hydrochloride in 100 ml of water to a solution of the crude potassium salt of (3)-1,2-dicarbadodecahydroundecaborate(−1) in 150 ml of water. The precipitated trimethylammonium salt was isolated by filtration, washed with 50 ml of cold water, and dried *in vacuo* over phosphorus pentoxide, yield 37.8 g (98%). The trimethylammonium salt was further purified by recrystallization from water, *e.g.*, 38 g of trimethylammonium (3)-1,2-dicarbadodecahydroundecaborate was dissolved in 2 l. of boiling water. When the aqueous solution was cooled to 0°, 80% of the trimethylammonium salt crystallized.

**Preparation of (3)-1,7-Dicarbadodecahydroundecaborate(−1) Ion.** 1,7-Dicarbaclovododecaborane(12)[12] was degraded to the (3)-1,7-$B_9C_2H_{12}$ anion in essentially the same manner as described for the 1,2 isomer with the exception that the reaction was carried out in an autoclave at 150° for 4 hr under autogenous pressure. The isolation and purification procedure was identical with that used for the 1,2 isomer.

**(3)-1-Phenyl-1,2-dicarbadodecahydroundecaborate(−1) ion** was prepared and isolated according to the general procedure given for the unsubstituted analog by treating the 1-phenyl-1,2-dicarbaclovododecaborane(12)[1] with a refluxing ethanolic potassium hydroxide solution for 4 hr.

**The (3)-1-Phenyl-1,7-dicarbadodecahydroundecaborate(−1) ion** was prepared by the general degradation procedure using 1-phenyl-1,7-dicarbaclovododecaborane(12) with ethanolic potassium hydroxide in an autoclave for 6 hr at 200° under autogenous pressure.

**(3)-1,2-Dimethyl-1,2-dicarbadodecahydroundecaborate(−1) ion** was prepared by the general degradation procedure using 1,2-dimethyl-1,2-dicarbaclovododecaborane(12)[1] with ethanolic potassium hydroxide at the reflux temperature for 14 hr.

**(3)-1,7-Dimethyl-1,7-dicarbadodecahydroundecaborate(−1) ion** was prepared by the general degradation procedure using 1,7-dimethyl-1,7-dicarbaclovododecaborane(12) with ethanolic potassium hydroxide in an autoclave for 9 hr at 160°.

**(3)-1-*p*-Bromophenyl-1,2-dicarbadodecahydroundecaborate(−1) ion** was prepared by the general degradation procedure using the corresponding carborane with ethanolic potassium hydroxide at reflux temperature for 6 hr.

**Preparation of (3)-1-Phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate (−1) Ion.** To 5.1 g (0.0218 mole) of 1-phenyl-2-methyl-1,2-dicarbaclovododecaborane(12) in 100 ml of absolute ethanol was added 2.6 g (0.046 mole) of potassium hydroxide in 40 ml of absolute ethanol. The solution was heated to reflux for 20 hr on a steam bath and then cooled. Carbon dioxide was bubbled through the solution in order to precipitate the excess potassium hydroxide as potassium carbonate. The filtered ethanol solutions were combined, and the ethanol was removed on a rotary evaporator. The salt was too hygroscopic for melting point determination. The tetramethylammonium salt was prepared for analysis by the usual method.

**Resolution of *dl*-(3)-1-Phenyl-1,2-dicarbadodecahydroundecaborate(−1).** Aqueous solutions of 14 g (0.05 mole) of crude potassium 1-phenyl-1,2-dicarbadodecahydroundecaborate and 14.6 g (0.050 mole) of *d*-N,N,N-trimethyl-α-phenylethylammonium iodide[23] were mixed. The resulting solid was crushed, washed with three portions of water, and dried over phosphorus pentoxide in a vacuum desiccator for several hours, yielding 16.4 g (0.044 mole) of *d*-N,N,N-trimethyl-α-phenylethylammonium *dl*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1), $[\alpha]^{23}\mathrm{D}$ 5.8°. The product was recrystallized from 60% ethanol–water and dried under vacuum over phosphorus pentoxide. Subsequent recrystallizations were carried out in the same manner. All rotations were taken in dry acetonitrile, and the samples were recovered to be returned to the original crop. Second and third crops were obtained by evaporating the mother liquor of the first and second crops, respectively, to two-thirds volume. The second crop was recrystallized from the mother liquor of the first, and the third crop recrystallized from the mother liquor of the second crop of each recrystallization. After the eighth recrystallization the solvent was changed to 95% ethanol. The total amount recovered was 2.8 g (34%) of *d*-N,N,N-trimethyl-α-phenylethylammonium *d*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1), mp 113.5–114.5°.

"Ionex" cation-exchange resin was washed with two 50-ml portions of 30% hydrochloric acid and four 50-ml portions of saturated potassium chloride solution and placed in a 1 in. × 20 in. column. The column was rinsed with several portions of distilled water and finally with a 53% (by volume) acetonitrile solution. The first crop of *d*-N,N,N-trimethyl-α-phenylethylammonium *d*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) crystals (mp 113.7–114.5°, 1.8 g, 0.0597 mole) was dissolved in 100 ml of 53% acetonitrile–water solution and passed through the column. The column was then washed with 150 ml of the same solvent. The combined solution and washings were placed on a rotary evaporator and the acetonitrile was removed. The small amount of precipitate was redissolved in 50 ml of solvent and rerun through the column. The negligible amount of unexchanged material remaining after the acetonitrile was removed the second time was removed from the solution by filtration.

The aqueous solutions were combined, and 5 ml of 50% tetramethylammonium chloride was added. The tetramethylammonium *d*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) was collected by filtration and dried overnight in a vacuum desiccator over phosphorus pentoxide. The yield was 1.32 g (0.00467 mole). After recrystallization from ethanol, the salt had a melting point of 214.1–215.0° and $[\alpha]^{23}\mathrm{D}$ 10.0°. The optical rotatory dispersion curve was determined over the range 290–600 mμ.

By the above method of recrystallization, 4.3 g (24.8% of theoretical) of *l*-N,N,N-trimethyl-α-phenylethylammonium *l*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) was obtained from 18.1 g of *dl*-potassium salt. The rotations and melting points are shown in Table III. Using a similarly prepared ion-exchange column and the same solvent mixture used in the above exchange, 1.473 g (0.01923 mole) of tetramethylammonium *l*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) $[\alpha]^{23}\mathrm{D}$ −9.8°, mp 213.5–215.2°, was obtained from 2.50 g of *l*-N,N,N-trimethyl-α-phenylethylammonium *l*-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) using only the first crop of crystals. The optical rotatory dispersion curve was obtained over the range 290–600 mμ.

**Resolution of *dl*-(3)-1-Phenyl-1,7-dicarbadodecahydroundecaborate(−1).** Using the same procedure as described for the 1,2 isomer, *d*-N,N,N-trimethyl-α-phenylethylammonium *d*-1-phenyl-1,7-dicarbadodecahydroundecaborate(−1) was isolated. After acid ion exchange the *d*-1-phenyl-1,7-dicarbadodecahydroundecaborate(−1) ion was precipitated as the $Cs^+$ salt, which was recrystallized from water, $[\alpha]^{25}\mathrm{D}$ 14.6°. The *l* enantiomer was not isolated.

**Resolution of *dl*-(3)-1-Phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate(−1).** From an aqueous solution of 6.1 g (∼0.0218 mole) of crude potassium 1-phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate(−1) and 6.5 g (0.022 mole) of *d*-N,N,N-trimethyl-α-phenylethylammonium iodide was obtained 8.4 g of *d*-N,N,N-trimethyl-α-phenylethylammonium *dl*-1-phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate(−1), mp 79–88°, $[\alpha]\mathrm{D}$ 10.65°. The resolution of the *d* form was carried out by the same recrystallization procedure used for the above salts. The solvent was changed from 60% ethanol (by volume) to 95% ethanol on the fourth recrystallization. Only 0.16 g (3.8%) of *d*-N,N,N-trimethyl-α-phenylethylammonium *d*-1-phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate(−1) was obtained in three crops.

The ion-exchange resin was prepared in the same manner as in the preceding section, but a 1 in. × 4 in. column was used for the exchange. After the ion-exchange procedure, 0.0342 g of tetramethylammonium *d*-1-phenyl-2-methyl-1,2-dicarbadodecahydroundecaborate(−1), $[\alpha]^{22}\mathrm{D}$ 28°, was obtained by precipitation with the tetramethylammonium chloride. The tetramethylammonium salt did not melt below 280°. The optical rotatory dispersion curve was determined over the range of 290–565 mμ.

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