# Ligand Derivatives of (3)-1,2-Dicarbadodecahydroundecaborate(−1)

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**Abstract:** Treatment of (3)-1,2-dicarbadodecahydroundecaborate(−1) and its C,C′-dimethyl derivative with ferric chloride in the presence of a ligand leads to the formal substitution of the ligand for a hydride ion. The resulting $B_9C_2H_{11}L$ species appears to carry the attached ligand on one of the three boron atoms associated with the open pentagonal face. In general, two isomers are formed in these reactions. Compounds containing tetrahydrofuran, diethyl sulfide, pyridine, and acetonitrile ligands were isolated and characterized.

The selective degradation of 1,2-dicarba-*closo*-dodecaborane(12), $B_{10}C_2H_{12}$, by methanolic potassium hydroxide to produce the (3)-1,2-dicarbadodecahydroundecaborate(−1) ion, (3)-1,2-$B_9C_2H_{12}^-$, has been reported, and the structure and properties of the (3)-1,2-$B_9C_2H_{12}^-$ anion and some of its carbon substituted derivatives have been described.[2,3] The (3)-1,2-$B_9C_2H_{12}^-$ anion is formally generated by the removal of a $B^+$ ion from one of the two equivalent positions (3 and 6) simultaneously adjacent to both carbon atoms. Previously presented evidence[2,3] indicates that the (3)-1,2-$B_9C_2H_{12}^-$ anion is an icosahedral fragment, isoelectronic with the hypothetical $B_{11}H_{12}^{3-}$. The accepted simplified structure of the (3)-1,2-$B_9C_2H_{12}^-$ anion is given in Figure 1.

## Results and Discussion

Oxidation of the (3)-1,2-dicarbadodecahydroundecaborate(−1) ion, (3)-1,2-$B_9C_2H_{12}^-$, and its carbon-substituted derivatives with ferric chloride in nonaqueous media and in the presence of a ligand, L, such as tetrahydrofuran, pyridine diethyl sulfide, or acetonitrile, results in the following general reaction.

$$\text{(3)-1,2-}B_9C_2H_{12}^- + 2FeCl_3 + L \longrightarrow \text{(3)-1,2-}B_9C_2H_{11}L + 2FeCl_2 + HCl + Cl^-$$

The reaction is formally a ligand substitution of a hydride ion on a boron atom to give a neutral species isoelectronic with the (3)-1,2-$B_9C_2H_{12}^-$ anion. This type of reaction may be generally designated as "oxidative-substitution." In contrast to these results, treatment of (3)-1,2-$B_9C_2H_{12}^-$ with ferric chloride in aqueous solution results in complete degradation of the (3)-1,2-$B_9C_2H_{12}^-$ anion, while in nonaqueous solution and in the absence of a ligand, no immediate reaction occurs between ferric chloride and the (3)-1,2-$B_9C_2H_{12}^-$ anion.

The site of the substitution reaction is apparently one of the three boron atoms forming (with the two carbon atoms) the open face of the icosahedral fragment shown in Figure 1. When substitution is conceptually limited to these three boron atoms, there are two possible isomers for (3)-1,2-$B_9C_2H_{11}L$ and its symmetrically carbon-substituted derivatives, and two such isomers were isolated in most cases. The proposed general structures of these isomers are shown in Figures 2 and 3. Figure 2 indicates the isomer obtained if substitution occurs on the unique boron atom of the ring forming the face of the icosahedral fragment, while Figure 3 indicates the isomer obtained if substitution takes place on either of the boron atoms on the open face of the icosahedral fragment adjacent to a carbon atom. The isomers shown in Figures 2 and 3 will hereafter be generally referred to as symmetric (3)-1,2-$B_9C_2H_{11}L$ and asymmetric (3)-1,2-$B_9C_2H_{11}L$, respectively. A structure similar to that of asymmetric (3)-1,2-$B_9C_2H_{11}L$ has been proposed for the (3)-1,2-$B_9C_2H_{11}X^-$ ion reported by Olsen and Hawthorne.[4] The published $^{11}B$ nmr spectrum of (3)-1,2-$B_9C_2H_{11}X^-$ closely resembles those of the asymmetric isomers described in this study.

The first series of compounds which will be discussed are the asymmetric (3)-1,2-$B_9C_2H_{11}$(THF) and the symmetric (3)-1,2-$B_9C_2H_{11}$(THF) isomers (THF = tetrahydrofuran). These compounds were prepared in benzene according to the following reaction scheme.

$$KB_9C_2H_{12} + 2FeCl_3 + THF \longrightarrow B_9C_2H_{11}(THF) + 2FeCl_2 + KCl + HCl$$

The reaction was essentially quantitative. One mole of HCl, 2 moles of $FeCl_2$, and 1 mole of KCl were produced per mole of (3)-1,2-$B_9C_2H_{12}^-$ ion. The above reaction was also carried out using the trimethylammonium and cesium salts of (3)-1,2-$B_9C_2H_{12}^-$ with analogous results. The product, (3)-1,2-$B_9C_2H_{11}$(THF), was recovered as a white solid, which was found to be a mixture of two components. These were separated by liquid-phase chromatography.

The $^1H$ nmr spectrum ($CCl_3D$) of the first compound (I) to elute from the chromatographic column is presented in Figure 4a, while that of the second compound (II) is given in Figure 4b. Both spectra contain a low-field multiplet and a multiplet at approximately $\delta$ −2.3[5] which were assigned to the tetrahydrofuran moiety.[6] The two spectra differ in that the spectrum

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(1) National Science Foundation Trainee, 1965–1968.

(2) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(3) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

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

(5) All $^1H$ nmr resonances are given in parts per million relative to tetramethylsilane.

(6) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

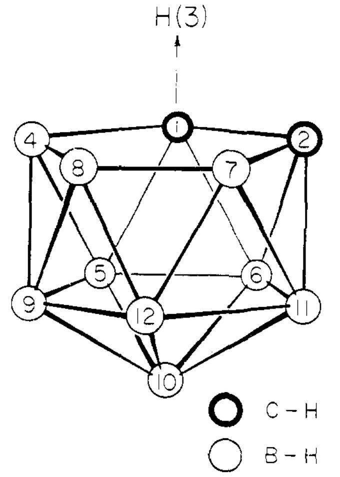

Figure 1. The accepted structure of the (3)-1,2-$B_9C_2H_{12}^-$ ion.

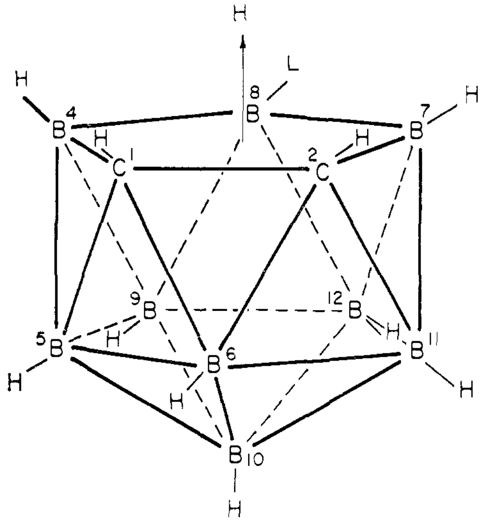

Figure 2. The proposed structure of the symmetric (3)-1,2-$B_9C_2H_{11}$ ligand derivatives.

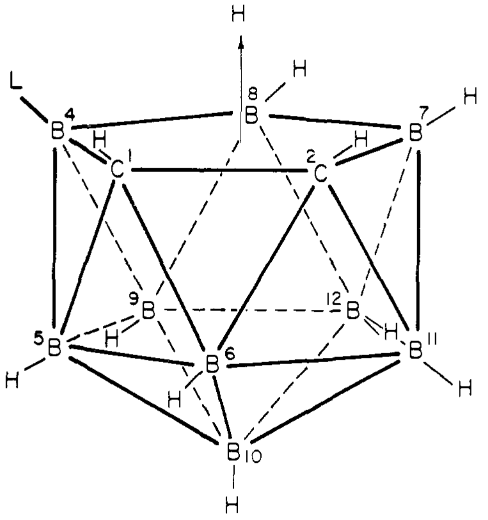

Figure 3. The proposed structure of the asymmetric (3)-1,2-$B_9C_2H_{11}$ ligand derivatives.

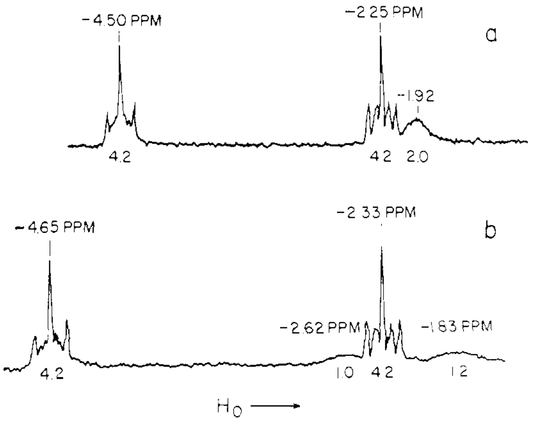

Figure 4. The 60-Mc/sec $^1H$ nmr spectrum of (a) symmetric (3)-1,2-$B_9C_2H_{11}$(THF) and (b) asymmetric (3)-1,2-$B_9C_2H_{11}$(THF) determined in $CDCl_3$ with $(CH_3)_4$ Si standard.

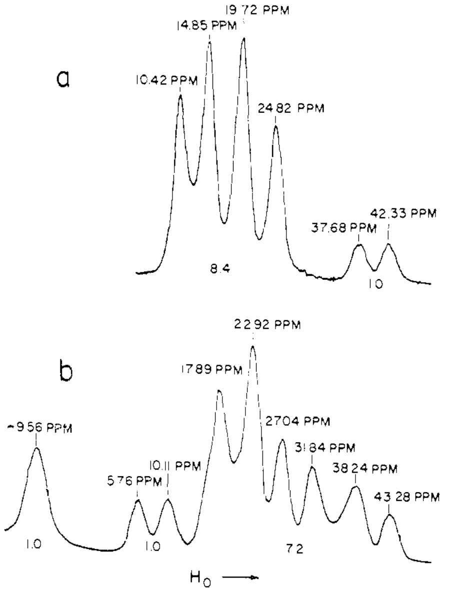

Figure 5. The 32-Mc/sec $^{11}B$ nmr spectrum of (a) symmetric (3)-1,2-$B_9C_2H_{11}$(THF) and (b) asymmetric (3)-1,2-$B_9C_2H_{11}$(THF) determined in acetone. All resonances are given relative to a $BF_3O(C_2H_5)_2$ standard.

of I shows a broad singlet at $\delta$ −1.92 while that of II shows two broad singlets at $\delta$ −2.62 and −1.83. Each of the singlets in the spectrum of compound II integrates for only one-half the relative intensity of the singlet in the spectrum of compound I when compared with the other resonances in the spectra. These broad resonances were assigned to the protons attached to the polyhedral carbon atoms. The observation of a single resonance in the spectrum of I indicates that this compound still contains the plane of molecular symmetry which has been lost in II.

The $^{11}B$ nmr at 32 Mc/sec of the two isomers I and II of (3)-1,2-$B_9C_2H_{11}$(THF) are given in Figures 5a and 5b, respectively. These $^{11}B$ and $^1H$ spectra are consistent with the structures shown in Figures 2 and 3 and are typical of the nmr spectra of all the ligand compounds. Using essentially the same procedure, two isomers of the (3)-1,2-dimethyl derivative, (3)-1,2-$B_9C_2H_9(CH_3)_2$(THF), were prepared and assigned structures.

The (3)-1,2-$B_9C_2H_{11}$(THF) isomers and their carbon-substituted derivatives are all white, crystalline, and high-melting compounds which decompose at, or just above, their melting points. They are not appreciably attacked by nonoxidizing acids and only slowly by base. These compounds are soluble in most organic solvents, insoluble in water and saturated hydrocarbons, and may be slowly sublimed under high vacuum at 100–150° without decomposition.

The pyridine derivative, (3)-1,2-$B_9C_2H_{11}$(py) (py = pyridine), and its carbon-substituted derivatives were prepared by a procedure similar to that described for the tetrahydrofuran series. The compound (3)-1,2-$B_9C_2H_{11}$(py) was obtained in essentially quantitative yield as a single isomer. The $^1$H nmr spectrum in the carborane proton region and the $^{11}$B nmr spectrum of this compound were similar to that of the asymmetric isomer of (3)-1,2-$B_9C_2H_{11}$(THF) and this compound was assigned the asymmetric structure.

A single isomer of the (3)-1,2-dimethyl derivative, $B_9C_2H_9(CH_3)_2$(py), was prepared. The $^1$H and $^{11}$B nmr spectra of (3)-1,2-$B_9C_2H_9(CH_3)_2$(py) clearly indicate that this too is the asymmetric isomer.

The compound, (3)-1,2-$B_9C_2H_{11}$(py), and its carbon-substituted derivatives are bright yellow to orange crystalline solids. Their solubility properties are very similar to the analogous tetrahydrofuran derivatives, but the pyridine derivatives are thermally more stable and melt without decomposition.

In addition to the tetrahydrofuran and pyridine derivatives, two other ligand systems have been studied. These are the acetonitrile and diethyl sulfide ligands.

The analogous acetonitrile compounds presented a unique situation in that the $^1$H nmr spectra indicated that each derivative formed at least two isomers which could not be separated by chromatography. For example, in the $^1$H nmr spectrum (acetone-$d_6$) of the dimethyl derivative, (3)-1,2-$B_9C_2H_9(CH_3)_2(CH_3CN)$, the resonances at $\delta$ $-2.95$ and $-3.10$ can be assigned to the acetonitrile protons of the two isomers. The polyhedral methyl resonances of the two isomers are not fully resolved. However, the over-all intensity ratio of the polyhedral methyl resonance to the acetonitrile resonance has the required value of 2:1. Based on the relative intensities of the two types of acetonitrile resonances, it can be estimated that one isomer comprises about 66% of the mixture. It is not possible to distinguish with certainty which peak represents the symmetric isomer and which peak represents the asymmetric isomer. Approximately the same type of mixture of isomers is seen in the $^1$H nmr spectra of (3)-1,2-$B_9C_2H_{11}(CH_3CN)$.

In the case of (3)-1,2-$B_9C_2H_{11}(CH_3CN)$ it was observed that even though the isomers could not be separated by chromatography, the asymmetric isomers could be selectively destroyed by allowing the mixture to stand for long periods of time on a silica gel chromatographic column. The $^1$H and $^{11}$B nmr spectra of the remaining compound indicate that it is the symmetric (3)-1,2-$B_9C_2H_{11}(CH_3CN)$.

A single derivative of diethyl sulfide, (3)-1,2-$B_9C_2H_9(CH_3)_2[S(C_2H_5)_2]$, was prepared and characterized. Chromatographic analysis showed one major component constituted approximately 90% of the crude yield in the reaction product. The near-coincidence of the resonances of the methyl groups of diethyl sulfide with the carborane methyl group resonances precluded a definite isomer assignment based on the $^1$H nmr spectrum, but since the $^{11}$B nmr spectrum of the compound resembled that of asymmetric (3)-1,2-$B_9C_2H_{11}$(THF), it was assigned the asymmetric structure.

The structures proposed for the ligand derivatives are consistent with their $^1$H nmr and $^{11}$B nmr spectra. However, the nmr data cannot rule out the possibility of substitution on boron atoms other than those forming the open face of the icosahedral fragment. The fact that not more than two isomers have been generally observed in any system thus far studied suggests that substitution is limited to the three boron atoms of the open face of the icosahedral fragment. An extreme possibility is that during the course of the oxidative substitution reaction a rearrangement has taken place within the icosahedral fragment which moves the carbon atoms to the 1,7 positions. Such a rearrangement is observed in (3)-1-$(C_6H_5)$-1,2-$B_9C_2H_{11}^-$, but temperatures in excess of 300° are required.[7] The reaction temperatures never exceeded 100° during the preparation of the ligand derivatives described in this study. However, the nmr spectral data would be equally consistent if the carbon atoms were in the 1,7 positions.

The proposed structures of the (3)-1,2-$B_9C_2H_{11}L$ derivatives are isoelectronic and isostructural with the parent (3)-1,2-$B_9C_2H_{12}^-$ ion. Since a proton can be removed from (3)-1,2-$B_9C_2H_{12}^-$ to produce the dianion (3)-1,2-$B_9C_2H_{11}^{2-}$,[2] it appeared probable that the same "extra hydrogen" could be removed from (3)-1,2-$B_9C_2H_{11}L$ to produce the corresponding (3)-1,2-$B_9C_2H_{10}L^-$ ion. It was observed that when tetrahydrofuran solutions of several of the (3)-1,2-$B_9C_2H_{11}L$ derivatives were treated with sodium hydride, 1 mole of hydrogen was evolved per mole of ligand, thus confirming the reaction

$$\text{(3)-1,2-}B_9C_2H_{11}L + NaH \longrightarrow Na^+ + \text{(3)-1,2-}B_9C_2H_{10}L^- + H_2$$

In the case of the (3)-1,2-$B_9C_2H_{11}$(py) and its carbon-substituted derivatives, the color of the solution changed from a light yellow to a very intense red. Exposure of this solution to protonic solvents regenerated the original yellow color.

The range of ligand derivatives prepared establishes the generality of the oxidative-substitution reaction. The properties of these compounds are varied and offer an entry into additional new chemistry. Further studies of both the preparation and reactions of these interesting compounds are in progress and will be reported in subsequent papers.

## Experimental Section

**Materials.** The preparation of (3)-1,2-dicarbadodecahydroundecaborate($-1$) ion and its carbon-substituted derivatives have been previously described.[3] Sublimed anhydrous ferric chloride was obtained from Matheson Coleman and Bell. Tetrahydrofuran was freshly distilled from lithium aluminum hydride. Pyridine, acetonitrile, and diethyl sulfide were freshly distilled before use. Benzene was dried by distillation from sodium ribbon. Deuterated solvents used in the $^1$H nmr studies were obtained from NMR Specialties Co. Davidson, Code 62 silica gel, calcined at 250° and partially deactivated with 4% water, was used for all column chromatographic separations. Proton nmr spectra were obtained with a Varian A-60 spectrometer, and $^{11}$B nmr spectra were obtained with a Varian HA-100 spectrometer at 32 Mc/sec.

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

Infrared spectra were determined with a Perkin-Elmer 221 infrared spectrometer, and molecular weights were measured with a Mecrolab Model 201A osmometer. Potentiometric measurements were made with a Leeds and Northrup Model 7664 pH meter with a saturated calomel reference electrode and a Beckman Model 1126-3 glass electrode. Reported melting points are uncorrected. Elemental analyses were made by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. All reactions were carried out under an inert atmosphere.

**(3)-1,2-$B_9C_2H_{11}$(THF). General Procedure.** A solution of 6.2 g (0.10 mole) of sublimed anhydrous ferric chloride in 200 ml of dry benzene and 40 ml (0.4 mole) of freshly distilled tetrahydrofuran was added dropwise over a period of 1 hr to a refluxing solution of 8.6 g (0.05 mol) of K[(3)-1,2-$B_9C_2H_{12}$] in 500 ml of dry benzene and 20 ml (0.2 mole) of freshly distilled tetrahydrofuran. As the ferric chloride solution contacted the solution in the flask, the ferric chloride was decolorized, HCl was evolved, and a precipitate of ferrous chloride and potassium chloride was formed. The HCl was removed from the reaction mixture by sweeping nitrogen through the solution. After the ferric chloride solution had been added, the excess tetrahydrofuran was removed by distillation, the reaction mixture cooled and filtered, and the precipitate washed with 100 ml of hot benzene. The combined colorless to light yellow filtrates were washed with 200-ml portions of distilled water until the aqueous phase was neutral. The washed benzene solution was dried over anhydrous magnesium sulfate, evaporated *in vacuo* at 50° to a volume of 200 ml, treated with 100 ml of heptane, and then chilled at −15°. A white solid (6.1 g) separated and was collected by filtration. Upon further concentration of the mother liquor, an additional 4.0 g of product was obtained: total yield, 10.1 g, 98.5%.

A 9.0-g sample of the reaction product was dissolved in about 75 ml of benzene, applied to a 2 in. × 4 ft liquid phase chromatographic column packed with silica gel, and eluted with benzene. The separation was monitored by periodic thin layer chromatographic analysis of the effluent phase. The less polar symmetric (3)-1,2-$B_9C_2H_{11}$(THF) was eluted before the asymmetric isomer. The benzene solution of the first component was evaporated to dryness *in vacuo* at room temperature to give 3.8 g of white crystalline symmetric (3)-1,2-$B_9C_2H_{11}$(THF): mp 153°; ir (Nujol mull) 2544 (s), 1475 (m), 1366 (m), 1186 (m), 1089 (m), 1010 (s), 1000 (sh), 920 (m), 839 $cm^{-1}$ (m). *Anal.* Calcd for $C_6H_{19}B_9O$: C, 35.24; H, 9.29; B, 47.62; mol wt, 205. Found: C, 35.08; H, 9.36; B, 47.51; mol wt, 201. The benzene solution of the second component was evaporated to dryness under the same conditions to give 4.3 g of white crystalline asymmetric (3)-1,2-$B_9C_2H_{11}$(THF): mp 148° (dec); ir (Nujol mull) 2532 (s), 1475 (m), 1357 (w), 1269 (w), 1192 (w), 1105 (w), 1066 (w), 1028 (m), 1007 (s), 998 $cm^{-1}$ (sh). *Anal.* Calcd for $C_6H_{19}B_9O$: C, 35.24; H, 9.29; B, 47.62; mol wt, 205. Found: C, 35.51; H, 9.75; B, 47.46; mol wt, 208.

The chromatographic separation was carried out as rapidly as possible since there was evidence of some degradation of the product on the column. Both (3)-1,2-$B_9C_2H_{12}$(THF) isomers can be recrystallized from benzene–heptane mixtures. Equivalent results were obtained when the trimethylammonium or cesium salts of (3)-1,2-$B_9C_2H_{12}^-$ were substituted for the potassium salt.

**(3)-1,2-$B_9C_2H_9(CH_3)_2$(THF).** Using the procedure described above, a 95% yield of the mixed isomers of (3)-1,2-$B_9C_2H_9(CH_3)_2$(THF) was obtained. Chromatographic separation in benzene of a 7-g sample of mixed isomers yielded 3.9 g of the asymmetric isomer [mp 158°; ir (Nujol mull) 2500 (s), 1445 (s), 1351 (m), 1186 (m), 1048 (m), 995 (s), 888 (m), 8091 (m), 740 $cm^{-1}$ (w). *Anal.* Calcd for $C_8H_{23}B_9O$: C, 41.33; H, 9.97; B, 41.88; mol wt, 233. Found: C, 41.36; H, 10.02; B, 41.58; mol wt, 228] and 2.1 g of the symmetric isomer [mp 150°; ir (Nujol mull) 2557 (s), 1367 (m), 1356 (m), 1191 (m), 1058 (w), 1005 (m), 984 (m), 836 (w), 759 (w), 745 $cm^{-1}$ (w). *Anal.* Calcd for $C_8H_{23}B_9O$: C, 41.33; H, 9.97; B, 41.88; mol wt, 233. Found: C, 41.36; H, 10.05; B, 41.69; mol wt, 228].

**(3)-1,2-$B_9C_2H_{11}$(py) and Its 1,2-Dimethyl Derivatives.** The procedures for the preparation of the pyridine-substituted products are the same as those described above; pyridine was substituted for tetrahydrofuran and the excess pyridine was removed during the water wash.

**(a) (3)-1 2-$B_9C_2H_{11}$(py).** A 98.5% yield of a single isomer, the bright yellow, crystalline asymmetric (3)-1,2-$B_9C_2H_{11}$(py), was obtained: mp 160°; ir (Nujol mull) 2551 (s), 2512 (sh), 1634 (w), 1499 (w), 1163 (m), 1028 (w), 764 (m), 684 $cm^{-1}$ (s). *Anal.* Calcd for $C_7H_{16}B_9N$: C, 39.74; H, 7.62; B, 46.02; N, 6.62; mol wt, 212. Found: C, 39.78; H, 7.56; B, 45.95; N, 6.37; mol wt, 227. This compound was readily recrystallized from benzene–heptane mixtures.

**(b) (3)-1,2-$B_9C_2H_9(CH_3)_2$(py).** With the same procedure, a 97.5% yield of yellow, crystalline asymmetric (3)-1,2-$B_9C_2H_9(CH_3)_2$(py) was obtained: mp 158°, ir (Nujol mull) 2512 (s), 1626 (w), 1208 (w), 1180 (m), 1020 (w), 1008 (w), 868 (sh), 863 (w), 847 (w), 768 (m), 683 (s), 674 $cm^{-1}$ (sh). *Anal.* Calcd for $C_9H_{20}B_9N$: C, 45.11; H, 8.41; B, 40.63; N, 4.84; mol wt, 240. Found: C, 44.87; H, 9.20; B, 40.36; N, 5.58; mol wt, 255.

**(3)-1,2-$B_9C_2H_{11}(CH_3CN)$ and Its 1,2-Dimethyl Derivatives. (a) (3)-1,2-$B_9C_2H_{11}(CH_3CN)$.** The preparation of this compound was the same as that of the corresponding tetrahydrofuran derivative except that acetonitrile was substituted for tetrahydrofuran. A 98% yield of white crystalline (3)-1,2-$B_9C_2H_{11}(CH_3CN)$ was obtained. Thin layer chromatographic analyses in a variety of solvents gave only a single broad band with no separation of isomers although the $^1H$ nmr spectrum of the product indicated the presence of at least two isomers. In an attempt to separate 2 g of this mixture on a 1 in. × 24 ft liquid phase chromatographic column packed with silica gel using a solvent mixture of 25% acetonitrile–75% ethyl acetate, 0.61 g of the symmetric isomer of (3)-1,2-$B_9C_2H_{11}(CH_3CN)$ was obtained (recovery 30%): mp 212° (dec); ir (Nujol mull) 2551 (s), 2364 (w), 1361 (w), 1099 (w), 1020 (m), 966 $cm^{-1}$ (w). *Anal.* Calcd for $C_4H_{14}B_9N$: C, 27.68; H, 8.13; B, 56.08; N, 8.07. Found: C, 28.04; H, 8.48; B, 55.79; N, 7.97. This apparently occurred not through separation but rather by selective degradation on the column of the asymmetric isomer.

**(b) (3)-1,2-$B_9C_2H_9(CH_3)_2(CH_3CN)$.** With the same procedure a 98% yield of white crystalline (3)-1,2-$B_9C_2H_9(CH_3)_2(CH_3CN)$ was obtained: mp 152–157°; ir (Nujol mull) 2551 (s), 2352 (w), 1364 (w), 1198 (w), 1010 (m), 1000 $cm^{-1}$ (sh). *Anal.* Calcd for $C_6H_{18}B_9N$: C, 35.75; H, 9.00; B, 48.31; N, 6.95. Found: C, 35.27; H, 9.55; B, 47.76; N, 6.58. No isomer separation could be obtained by liquid phase chromatography although the $^1H$ nmr spectrum indicated the presence of more than one isomer.

**(3)-1,2-$B_9C_2H_9(CH_3)_2[S(C_2H_5)_2]$.** The diethyl sulfide ligand derivative was prepared by the same procedure as the tetrahydrofuran derivatives by substitution of diethyl sulfide for tetrahydrofuran. Since the diethyl sulfide could not be removed by distillation or washing with water, the initial reaction product was obtained as an oil. The oil was dissolved in benzene, applied to a liquid phase chromatograph column packed with silica gel and rapidly eluted with a mixture of 60% benzene–40% pentane. By this procedure an 89% yield of white, crystalline (3)-1,2-$B_9C_2H_9(CH_3)_2[S(C_2H_5)_2]$ was obtained. This product was rechromatographed using the same type of column and solvent mixture to give a 95% recovery of the asymmetric isomer of (3)-1,2-$B_9C_2H_9(CH_3)_2[(S(C_2H_5)_2]$: mp 96°; ir (Nujol mull) 2512 (s), 1418 (w), 1077 (w), 1003 (m), 980 (m), 963 (m), 845 (m), 786 (m), 763 (m), 740 $cm^{-1}$ (w). *Anal.* Calcd for $C_8H_{25}B_9S$: C, 38.32; H, 10.05; B, 38.84; S, 12.79. Found: C, 38.16; H, 10.02; B, 38.65; S, 13.08. No symmetric isomer was observed.

**Acid–Base Chemistry of the (3)-1,2-$B_9C_2H_{11}$L Derivatives. Reaction of (3)-1,2-$B_9C_2H_{11}$L Derivatives with NaH.** A two- to threefold excess of sodium hydride suspended in THF was allowed to react with THF solutions of symmetric and asymmetric (3)-1,2-$B_9C_2H_9(CH_3)_2$(THF) and asymmetric (3)-1,2-$B_9C_2H_9(CH_3)_2$(py). The evolved gas was measured using a gas burret. In all cases 1 mole of gas was evolved per mole of ligand compound.

**Acknowledgment.** The authors are indebted to the Army Research Office (Durham) for partial support of this research.