These authors have warned of possible line broadening resulting from metal ion promoted proton exchange.
(17) G. G. McDonald and J. S. Leigh, Jr., *J. Magn. Reson.*, **9**, 358 (1973).
(18) A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, **59**, 373 (1955).

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Degradative Substitution of 1,7-Dimethyl-1,7-dicarba-*closo*-dodecaborane to Form 3-Alkoxynonahydro-7,9-dimethyl-7,9-dicarba-*nido*-undecaborate(1−) Ions. Isomeric Anions

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The treatment of a wide variety of carbon-substituted 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ carboranes with alcoholic base has been shown to degrade them to the corresponding carbon-substituted 7,8- or 7,9-$C_2B_9H_{12}^-$ ions.[1] We have found that such treatment of 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ can result in degradative substitution to give alkoxy derivatives of 7,9-$(CH_3)_2$-7,9-$C_2B_9H_{10}^-$, e.g., 7,9-$(CH_3)_2$-7,9-$C_2B_9H_9OR$ (R = CH_3, C_2H_5, and *i*-C_3H_7), as briefly mentioned in a previous publication.[2] We report here a more complete characterization of these compounds which indicates that alkoxy substitution is in the 3 position rather than the previously suggested 2 position.[2]

Experimental Section

General Procedures. Infrared spectra were determined on a Perkin-Elmer 457 as KBr disks. The ^{11}B NMR spectra were recorded on Varian instruments operating at 32.1 and 70.6 MHz (Indiana University) and a Bruker 86.6-MHz instrument (University of Wisconsin); proton NMR spectra were recorded on Varian T-60, HA-100, and 220-MHz (Indiana) spectrometers.

All preparations were conducted under an atmosphere of nitrogen. The 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ was prepared as described in the literature[3] and all other reactants were reagent grade, *i*-C_3H_7OH being dried by percolation through molecular sieves.

General Procedure for Degradative Substitution. The procedure used for a typical preparation of $[(CH_3)_3NH^+][7,9\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_9H_9OC_2H_5^-]$ is described. The CH_3O and *i*-C_3H_7O derivatives can be prepared by substituting CH_3OH and *i*-C_3H_7OH, respectively, for C_2H_5OH.

A glass-lined autoclave was purged with N_2 and charged with a solution of 1.35 g of KOH in 40 ml of C_2H_5OH before adding 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$, 2.08 g, 12.1 mmol. The temperature in the autoclave was slowly raised until a surge in pressure was noted at 160° where it was maintained until no further increase in pressure was noted (usually 4–6 hr at 160° and a pressure of 300–400 psi in a 400-cm^3 autoclave). After cooling to 25°, 20 ml of C_2H_5OH was added to the reaction mixture and CO_2 was bubbled into it to precipitate the excess KOH as the carbonate, which was removed by filtration. The filtrate was taken to dryness on a rotary evaporator and the resulting potassium salt was then dissolved in water. If any unreacted carborane was detected at this point, it was removed by filtration and $(CH_3)_3NH^+Cl^-$ was added to the filtrate to give the crude product. Pure $[(CH_3)_3NH^+][7,9\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_9H_9OC_2H_5^-]$ was obtained by recrystallization from hot water; yield 1.29 g, 4.8 mmol, 40%.

In the case of the CH_3OH preparation a temperature of 140° was generally sufficient for reaction but 160° was required for the *i*-C_3H_7OH preparation.

Table I. ^{11}B and ^1H NMR Data[a]

$[Me_3NH^+][3\text{-}i\text{-}C_3H_7O\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_9H_9^-]^e$
^{11}B: 0.50 s, 1.34 d (J_{BH} = 140), 2.76 d (J_{BH} = 150), 5.98 d (J_{BH} = 145), 18.63 d (J_{BH} = 145), 22.34 d of d (J_{BH} = 130, J_{BH_μ} = 40), 26.04 d of d (J_{BH} = 135, J_{BH_μ} = 40), 33.51 d (J_{BH} = 137), 38.11 d (J_{BH} = 140)
^1H: 1.07 d (J_{HH} = 6, $(CNCH_3)_2$), 1.40^b s and 1.44^b s ($(C\text{–}CH_3)_2$), 3.13 s ($N(CH_3)_3$); 3.86 m, br (O–C–H?), NH not observed

$[Me_3NH^+][3\text{-}C_2H_5O\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_9H_9^-]^e$
^{11}B: 0.74 s, 1.42 d (J_{BH} = 160), 2.69 d (J_{BH} = 160), 6.15 d (J_{BH} = 148), 18.70 d (J_{BH} = 145), 22.24 d of d (J_{BH} = 140, J_{BH_μ} = 40), 25.96 d of d (J_{BH} = 135, J_{BH_μ} = 40), 33.81 d (J_{BH} = 135), 38.10 d (J_{BH} = 140)
^1H: 1.13 t (J_{HH} = 7, CH_3), 1.39^b s and 1.42^b s $(C\text{–}CH_3)_2$; 3.11 s ($N(CH_3)_3$); 3.63 q (J_{HH} = 7, $O\text{–}CH_2$), NH not observed

$[Me_3NH^+][3\text{-}CH_3O\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_9H_9^-]^{c,e}$
^{11}B: 0.8 s, 2.7 d (J_{BH} = 130), 3.6 d (J_{BH} = 130), 8.0 d (J_{BH} = 140), 17.9 d (J_{BH} = 140), 22.3 d of d (J_{BH} = 135, J_{BH_μ} = 40), 27.3 d of d (J_{BH} = 135, J_{BH_μ} = 40), 34.7 d (J_{BH} = 140), 30.1 d (J_{BH} = 135)
^1H: 1.43 s $(C\text{–}CH_3)_2$, 3.12 s ($N(CH_3)_3$), 3.41 s ($O\text{–}CH_3$); NH not observed

$4\text{-}CH_3O\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_9H_8{}^{d,f}$
^{11}B: −13.0 s (1), −8.5 d (1) (J_{BH} = 166), 4.0 d (1) (J_{BH} = 150), 9.8 d (2) (J_{BH} = 155), 11.2 d (1) (J_{BH} = 156), 17.8 d (1) (J_{BH} = 147), 22.5 d (1) (J_{BH} = 166)
^1H: 2.03 s ($C\text{–}CH_3$), 2.53 s ($C\text{–}CH_3$), 3.67 s ($O\text{–}CH_3$)

[a] ^{11}B data are given in ppm upfield from a $(C_2H_5)_2O\cdot BF_3$ external standard; ^1H NMR data are given in ppm downfield from TMS internal standard. All chemical shifts are followed by a coupling constant where observed, given in Hz, with a description of the multiplet (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad) and an assignment which corresponds to the observed relative intensity. [b] These resonances were seen at 220 MHz but could not be resolved at 100 MHz. [c] These data were obtained at 32.1 MHz (^{11}B) and 60 MHz (^1H) while the preceding were obtained at 70.6 and 220 MHz, respectively. [d] Proton spectra were obtained at 60 MHz. [e] Solvent acetone-d_6. [f] Solvent chloroform-d_1.

4-CH_3O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_8$. NaH (85 mg, 3.54 mmol) was added under N_2 to 50 ml of benzene which had been dried over lithium aluminum hydride and distilled in vacuo to a 100-ml, three-neck flask. Then, 507 mg (1.62 mmol) of $[(CH_3)_3NH^+][3\text{-}CH_3O\text{-}7,9\text{-}C_2\text{-}(CH_3)_2B_9H_9^-]$ was added and the mixture was refluxed for 56 hr under N_2. Anhydrous $SnCl_2$ (308 mg, 1.62 mmol) was added and heating was continued for another 40 hr at which time the mixture had turned deep black. The mixture was cooled to 25° and filtered through a glass frit which was then washed with 30 ml of dry benzene. The combined filtrates were evaporated to an oil which was sublimed in vacuo at 40–45° to a −78° cold finger yielding the pure product (62 mg, 20%). Mass spectrum: cutoff at *m/e* 192 corresponding to $^{11}B_9{}^{12}C_5{}^1H_{17}{}^{16}O$.

Results and Discussion

Weissenberg photographs of a single crystal of the ethoxy congener showed that the trimethylammonium salt was triclinic with cell parameters of *a* = 9.80 Å, *b* = 10.42 Å, *c* = 11.42 Å, and α = 81° 10', β = 89° 19', γ = 47° 42'. The density calculated for two molecules of $(C_9B_9NOH_{30})$ per cell is 1.04 g/cm^3 and agrees well with that observed experimentally, 1.02 g/cm^3.

The ^{11}B NMR spectra of the three alkoxy derivatives prepared here are nearly superimposable; that of the ethoxy compound was published previously.[2] All of the NMR data are summarized in Table I; it is evident that they are consistent with asymmetric substitution of the boron cage. This is seen most dramatically in the ^{11}B spectra where all nine boron environments are evident. The singlet due to the substituted boron site (0.5–0.8 ppm) shows no bridge hydrogen coupling but two other B–H resonances do (∼22 and ∼26 ppm). Since bridge hydrogens have always been found between two boron atoms on the nontrigonal face of *nido*-carboranes (positions 10 and 11 here, Figure 1), lower belt substitution is indicated. The 2 and 3 positions provide the only alternatives consistent with a structure with no elements of symmetry. We previously chose the 2 position, but on the basis of the chemical evidence presented below, the 3 position is the better choice.

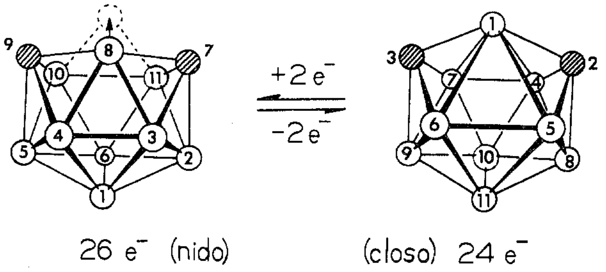

Figure 1. Interconversion of closo and nido 11-atom frameworks and the numbering convention for each.

Oxidative closure of *nido*-7,9-$C_2B_9H_{11}^{2-}$ by $SnCl_2$ has been shown to give *closo*-2,3-$C_2B_9H_{11}$.[2] The suggested mechanism of closure (a least motion mechanism—see Figure 1) would place a 2 substituent at the B(8) position on the mirror plane containing the carbon atoms of the 2,3-$C_2B_9H_{11}$ cage;[2,4] however, a 3 substituent would give a B(5 or the equivalent 4)-substituted product which contains no elements of symmetry. When closure of 7,9-$(CH_3)_2$-7,9-$C_2B_9H_8OCH_3{}^{2-}$ was effected with $SnCl_2$ in benzene, a completely asymmetrically substituted product was obtained as shown by ^1H and ^{11}B NMR. The ^1H spectrum (Table I) showed three peaks of equal intensity at 2.03 (*C*-CH_3), 2.53 (*C*-CH_3), and 3.67 (*O*-CH_3) ppm downfield from internal TMS, respectively. The ^{11}B spectrum (Table I) at 32.1 MHz displayed seven resolvable resonances, and at 70.6 MHz eight were discernible at −13.0, −8.5, 4.0, 5.6, 9.8, 11.2, 17.8, and 22.5 ppm from external $BF_3\cdot OEt_2$. All signals were doublets except for the lowest field signal which was confirmed to be a singlet by $\{^1H\}$–^{11}B decoupling and which can be assigned to the methoxy-substituted boron. The more symmetric B(8)-substituted isomer would give a much simpler spectrum with resonances of relative intensities of 1:1:1:2:2:2. Clearly, despite accidental coincidence at 9.8 ppm, the resolution of seven signals of unit intensity indicates completely asymmetric substitution. Based on the suggested mechanism of closure, we feel that the product is 4-CH_3O-2,3-$(CH_3)_2$-2,3-$C_2B_9H_8$ and that the starting material is 3-CH_3O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$.

On the basis of our results there appears to be a delicate balance of conditions dictating the results when 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ is treated with alcoholic base. The literature suggests that autoclave degradation occurs without substitution.[1] When treatment is done with KOH in *tert*-butyl alcohol at 170° in an autoclave for 6 hr we find that complete degradation results. Yet, under similar conditions with KOH in either CH_3OH, C_2H_5OH, or *i*-C_3H_7OH, degradative substitution predominates; on occasion, when methanolic KOH was used, a low yield of the previously reported[1] unsubstituted degradation product, 7,9-$(CH_3)_2$-7,9-$C_2B_9H_{10}{}^-$, was obtained. The latter can also be obtained under milder conditions following the procedure used for the degradation of unsubstituted 1,7-$C_2B_{10}H_{12}$, however employing longer reaction times (4–5 days).[5]

Ions isomeric with 3-RO-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$ can be prepared by direct interaction of 2,3-$(CH_3)_2$-$C_2B_9H_9$ and alcoholic KOH.[2] In fact, the original investigation suggested that the latter reaction gave 3-substituted anions and that the degradative route (vide supra) afforded 2 substitution.[2] However, in view of the present investigation and new NMR data, we must conclude that 10 substitution results when 2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$ is treated with alcoholic KOH. Selective $\{^1H_\mu\}$–^{11}B experiments are possible at high field strength (86.6 MHz for ^{11}B) and show that the "singlet" at −0.3 ppm is attached to a bridge hydrogen. The signal of relative intensity 2 at 23.9 ppm is now reassigned to the coincidental overlap of two signals of unit intensity only one of which shows bridge hydrogen coupling. Since bridging hydrogens are generally found on the open, nontriangular face and since the rest of the spectrum is indicative of asymmetric substitution, the alkoxy substituent must be at the 10 position. These results are also consistent with a recent assignment of closely related molecules.[6] In retrospect, the previous misassignment was due to undue reliance on line-narrowed spectra and hence a caveat is issued regarding their interpretation without supporting data. In view of the present results and other recent studies,[6] it is also probable that the suggested 3-Me_3N-7,9-$C_2B_9H_{11}$ and 3-[$(C_6H_5)_3P$]-7,9-$C_2B_9H_{11}$[2] are actually 10-L-7,9-$C_2B_9H_{11}$ species although we have not been able to confirm this with $\{^1H\}$–^{11}B experiments. Thus it appears that ligand adducts formed from $C_2B_9H_{11}$ and its C-substituted derivatives generally are formed by an "open-away" mechanism[2] to give 10 substitution.

Table II. Infrared Spectra[a]

[$(CH_3)_3NH^+$][3-*i*-C_3H_7-7,9-$(CH_3)_2$7,9-$C_2B_9H_9{}^-$]: 3030 m, 2964 s, 2945 s, 2920 s, 2860 s, 2707 s, br, 2515 vvs, 2480 vvs, 1895 vvw, 1482 s, 1456 m, 1417 vvw, 1384 m, 1372 m, 1226 m, 1202 s, 1183 vs, 1114 vs, 1080 w, 1056 w, 1009 s, 981 vs. 945 vvw, 932 m, 875 m, 838 m, 806 m, 780 vvw, 750 vw, 730 vw, 695 w, 642 vw, 620 vvw, 585 vvw, 569 vw, 532 vw, 488 vw, 455 vvw, 447 w, 360 vvw

[$(CH_3)_3NH^+$][3-C_2H_5O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$]: 303 m, 2950 s, 2920 s, 2860 s, 2715 s, br, 2525 vvs, 2475 vvs, 1900 vvw, 1480 s, 1452 m, 1416 vw, 1390 w, 1375 w, 1368 w, 1298 vw, 1225 m, 1187 vs, 1151 m, 1115 w, 1099 m, 1063 m, 1041 s, 1003 s, 977vs, 947 vvw, 932 w, 920 vvw, 895 w, 862 m, 839 m, 800 vw, 780 vvw, 749 vw, 730 vw, 693 w, 640 vw, 620 vvw, 585 vvw, 568 vw, 525 vvw, 485 vvw, 446 w, 320 vvw

[$(CH_3)_3NH^+$][3-CH_3O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$]: 3010 vw, 2940 s, 2920 s, 2862 m, 2840 vw, 2687 m, br, 2510 vvs, 1900 vvw, 1480 s, 1455 m, 1417 vw, 1377 vw, 1210 vs, 1161 s, 1120 w, 1080 vvw, 1067 vw, 1022 vs, 1000 s, 983 s, 966 m, 937 w, 869 m, 838 m, 798 vw, 780 vvw, 741 vw, 730 vw, 692 vw, 641 vvw, 620 vvw, 570 vvw, 523 vvw, 502 vvw, 490 vvw, 462 vvw, 455 vw, 447 vw, 345 vvw

4-CH_3O-2,3-$(CH_3)_2$-2,3-$C_2B_9H_8$: 2985 s, 2935 vs, 2857 s, 2565 vvs, 1464 vs, 1388 vs, 1327 vvs, br, 1269 s, 1244 vs, 1179 w, 1122 m, 1010 s, 990 m, 945 w, 926 m, 907 vw, 878 w, 864 w, 837 m, 782 m, 751 m, 736 w, 700 m, 682 vw, 604 vvw, 572 w, 523 w, 487 w, 467 vw, 420 vvw

[a] Band positions are reported in cm^{-1} with relative intensities: s, strong; m, medium; w, weak; v, very; br, broad.

The infrared spectra for the compounds prepared here are summarized in Table II.

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Registry No. [$(CH_3)_3NH^+$][3-*i*-C_3H_7-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$], 56030-42-3; [$(CH_3)_3NH^+$][3-C_2H_5O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$], 56030-44-5; [$(CH_3)_3NH^+$][3-CH_3O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9{}^-$], 56195-93-8; 4-CH_3O-2,3-$(CH_3)_2$-2,3-$C_2B_9H_8$, 55871-80-2; 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$, 17499-00-2; *i*-C_3H_7OH, 67-63-0; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; $SnCl_2$, 7772-99-8.

References and Notes

(1) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).
(2) V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *J. Am. Chem. Soc.*, **95**, 4560 (1973).
(3) L. I. Zakharkin, and A. V. Kazantsev, *Zh. Obshch. Khim.*, **37**, 1211 (1967).
(4) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Lett.*, 715 (1965).
(5) P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2008 (1969); M. F. Hawthorne, private communication.
(6) L. J. Todd, A. R. Siedle, F. Sato, A. R. Garber, F. R. Scholer, and G. D. Mercer, *Inorg. Chem.*, **14**, 1249 (1975).