Assignment of the pmr spectrum of ion **3** at −70° is as follows: δ 8.13 (2 H), H_2, H_3; δ 4.18 (2 H), H_1, H_4; δ 2.64 (2 H) H_5 exo, H_6 exo; δ 1.92 (1 H), H_7 syn; δ 1.49 (3 H), H_7 anti, H_5 endo, H_6 endo. Due to the complexity of the spectrum and probable peak overlap $J_{^{199}Hg-^1H}$ coupling in ion **3** could not be assigned. The deshieldings observed for the H_1, H_4 and H_5 exo, H_6 exo protons are analogous to the deshieldings observed for the H_1 and H_6 exo protons in the 2-methyl and 2-halonorbornyl cations.[10] The singlets at δ 3.12 and 12.30 and 13.01 are assigned to protonated acetic acid.[11] The observation that all the acetate present had been converted to protonated acetic acid, combined with the considerable deshielding of the H_2 and H_3 protons, indicates that the charge on ion **3** and by analogy on ion **2**, is 2. It is also worth noting that a ^{13}C shift of +34.2 ppm (relative to CS_2) for C_2 and C_3, obtained by the indor method, is entirely consistent with the proposed structure.

It is interesting to note that if a solution of ion **3** is warmed to −30° all the pmr peaks between δ 4.18 and 1.49 coalesce into a single, broad adsorption centered at ∼2.7. An equilibration process such as the one shown would account for this spectral behavior. On
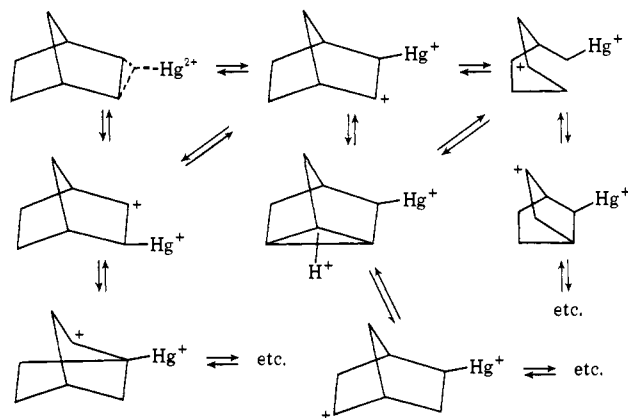
cooling back to −70°, ion **3** is regenerated.

Our studies are being extended to the preparation and investigation of other alkylene (cycloalkylene) mercurinium ions, including their preparation *via* direct mercuration of the olefins.

(10) G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Amer. Chem. Soc.*, **92**, 553 (1970).
(11) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967). At −30° the dehydration of protonated acetic acid to the methyloxocarbonium ion is observed.
(12) NIH Postdoctoral Fellow, 1969–1970.

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Two New *nido*-Carborane Families: $B_7C_2H_{11}$ and $B_8C_2H_{12}$. A New Isomer of $B_5C_2H_5(CH_3)_2$[1,2]

Sir:

Several years ago we reported that volatile white crystals were formed in the reaction of acetylene with

octaborane(12) in diethyl ether.[3] We now report these crystals to be *nido*-dicarbanonaborane(11) and *nido*-dicarbadecaborane(12), new members of the $B_nC_2H_{n+4}$ series of *nido*-carboranes. $B_7C_2H_{11}$ is isoelectronic with the Lewis acid B_9H_{13}, whereas $B_8C_2H_{12}$ is isoelectronic with $B_{10}H_{14}$. Numerous C-substituted B_7C_2-H_9RR' and $B_8C_2H_{10}RR'$ species have also been prepared.

In a typical preparation, 0.593 g of octaborane(12) (5.84 mmol) was allowed to react with 6.73 mmol of 2-butyne in a shielded trap containing 10 ml of diethyl ether. After 16 hr at 30°, the minor volatile products separated by high-vacuum fractional distillation and preparative vpc were 0.216 mmol of hydrogen, 0.400 mmol of ethane, a trace of diborane, 0.152 mmol of B_6H_{10} (2.6% yield), 0.088 mmol of the new $B_5C_2H_5$-$(CH_3)_2$ (1.5% yield), 0.050 mmol of unreacted 2-butyne, and excess diethyl ether. The major products were separated on a low-temperature fractionation column.[4] Pure $B_7C_2H_9(CH_3)_2$ (0.255 g, 29% yield) distilled from the column between −31 and −7°, and pure $B_8C_2H_{10}$-$(CH_3)_2$ (0.088 g, 10% yield) distilled between +3 and +11°. Repeated fractionation of the material distilling between −7 and +3° raised the yields to 58 and 20%, respectively. The overall conversion of B_8H_{12} to carboranes was 80%. Extraction and sublimation of the yellow oil remaining in the reactor trap afforded a trace of n-$B_{18}H_{22}$.

$B_7C_2H_9(CH_3)_2$ is an air-sensitive, clear liquid (mp −9°) of moderate thermal stability at 20°. Even using a cold inlet, the mass spectrum at 70 eV contained intense B_6C_4 and B_7C_4 and weaker B_8C_4 and B_9C_4 envelopes. At 40 eV, the B_7C_4 envelope predominated with a maximum at m/e 137 and a cutoff at m/e 140, corresponding to the $^{11}B_7^{12}C_4^1H_{15}^+$ ion. At 40 eV, the relative intensities were characteristic of other known *nido*-carboranes.[5] The molecular weight was determined to be 140 (calcd for $B_7C_4H_{15}$: 138.8) by freezing point depression in cyclohexane. Infrared absorption peaks at 2965 (w), 2935 (m), 2870 (w), 2575 (vs b), 2470 (w sh), 1900 (w b), 1511 (w), 1455 (m), 1444 (m sh), 1382 (m), and 1371 cm^{-1} (m) suggest the presence of B–H, B–H–B, and two C–CH_3 groups. Lack of absorption between 3000 and 3060 cm^{-1} and at 1320 and 1250–1280 cm^{-1} diminishes the possibilities for >C–H and B–CH_3 units, respectively.[6] The 13 weak cage vibrations observed between 710 and 1168 cm^{-1} suggest a molecule of low symmetry. Degradation in propionic acid with Pd catalyst yielded 96% n-butane, providing evidence that the cage carbon atoms are vicinal in $B_7C_2H_9(CH_3)_2$.

The apparent 1:1:1:2:1:1 pattern in the 70.6-MHz [11]B nmr spectrum (Figure 1) requires at least six magnetically nonequivalent boron environments. The 220-MHz pmr spectrum contains methyl resonances at δ −2.32 and −1.28 ppm, bridge resonances at +1.17 and +2.56 ppm, and one sharp apical quartet at 0 ppm ($J = 150$ cps). The remaining six cage proton resonances overlap at δ −3.02 ($J \sim 150$), −2.78

National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.
(3) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).
(4) J. Dobson and R. Schaeffer, *ibid.*, **9**, 2183 (1970).
(5) R. E. Williams in "Progress in Boron Chemistry," Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, Elmsford, N. Y., 1967, pp 81–90.
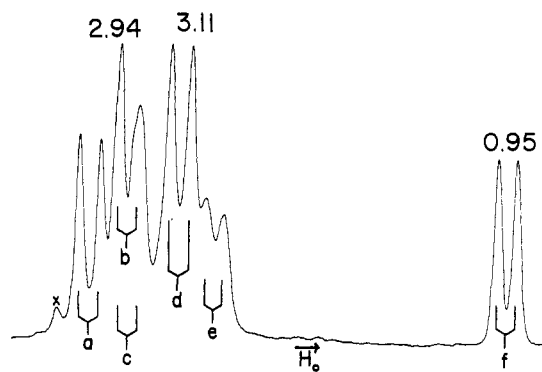(6) R. N. Grimes, *J. Organometal. Chem.*, **8**, 45 (1967).

(1) Studies of Boranes. XXXI. For paper XXX of this series see J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970).
(2) Presented in part before the Inorganic Division at the 160th

Figure 1. The 70.6-MHz ^{11}B nmr spectrum of neat $B_7C_2H_9(CH_3)_2$. Chemical shifts [ppm relative to external $BF_3 \cdot O(C_2H_5)_2$] and coupling constants (cps) are: (a) 0, 170; (b) +3.7, ~150; (c) +4.4, ~150; (d) +10.1 ~155; (e) +13.9, 135; and (f) +46.7, 148. Integrated areas are given above the peaks.

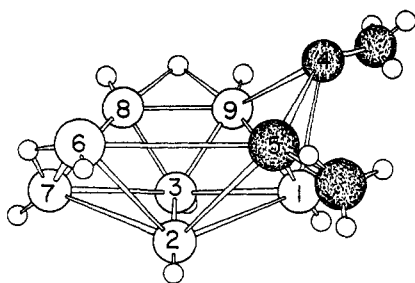Figure 3. The 70.6-MHz ^{11}B nmr spectrum of neat $B_8C_2H_{10}(CH_3)_2$. Chemical shifts [ppm relative to external $BF_3 \cdot O(C_2H_5)_2$] and coupling constants (cps) are: (a) −4.6, 145; (b) −2.6, 140; (c) −0.4, 165; (d) +4.0, ~140; (e) +5.7, ~150; (f) +20.3, 170; and (g) +40.2, 150. Integrated areas are given above the peaks.

Figure 2. One enantiomorph of the possible structure for $B_7C_2H_9$-$(CH_3)_2$. Note that varying placement of the bridge protons is possible.

Figure 4. One enantiomorph of the possible structure for $B_8C_2H_{10}$-$(CH_3)_2$. Single-bridge pmr resonance mitigates against varying the placement of the bridge hydrogens.

($J \sim 160$), and −1.78 ppm ($J \sim 160$ cps). A possible structure (Figure 2) for $B_7C_2H_9(CH_3)_2$ could be based on the known $B_9H_{13} \cdot L$ framework.

$B_8C_2H_{10}(CH_3)_2$ is a thermally stable, clear liquid (mp +3°), unreactive in air for several hours. Mass spectra contain the most intense peak at m/e 147 and an exact mass match at the sharp cutoff m/e 152.20042 (calcd for $^{11}B_8{}^{12}C_4{}^1H_{16}{}^+$: 152.19965). The molecular weight was determined as 151 (calcd for $B_8C_4H_{16}$: 150.6) by vapor density measurements. Infrared absorption peaks at 2990 (w), 2973 (w), 2935 (w), 2871 (w), 2575 (s b), 1968 (w sh), 1895 (w), 1545 (m), 1457 (m), 1443 (m sh), 1388 (w), 1371 (w), and 1287 cm^{-1} (w) imply the presence of B–H–B and two C–CH$_3$ groups and the absence of ≯C–H and B–CH$_3$ groups.[6] The 16 cage vibrations between 661 and 1118 cm^{-1} suggest a molecule of very low symmetry. A 39% yield of n-butane from the propionic acid–Pd catalyst degradation of $B_8C_2H_{10}(CH_3)_2$ supports the presence of vicinal cage carbon atoms.

The 70.6-MHz ^{11}B nmr spectrum (Figure 3) of $B_8C_2H_{10}(CH_3)_2$ is an apparent 1:1:1:1:2:1:1 pattern, requiring at least seven distinct magnetic environments. The 220-MHz pmr spectrum displays methyl resonances at δ −2.05 and −2.00 ppm, apical quartets at −0.92 ($J \sim 165$) and −0.45 ppm ($J \sim 155$ cps), and one bridge resonance of intensity two at +2.52 ppm. The remaining six cage proton resonances overlap at −2.47 ppm ($J \sim 150$ cps). A possible decaborane(14)-like model structure with the carbon atoms in the 5,6 (6,7) positions (see Figure 4) is easily co: :d by
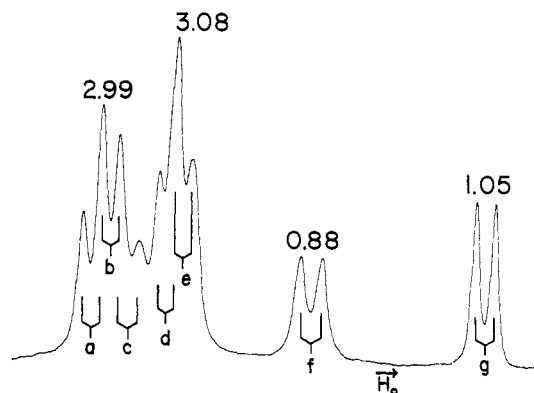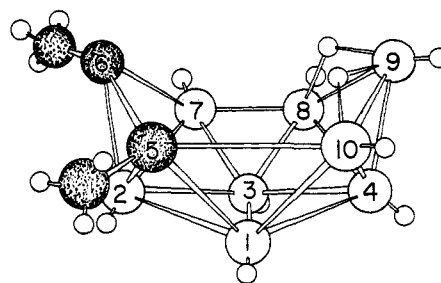
adding 2-butyne between the 3,8 and 6,7,8 atoms of octaborane(12).[7]

Preparative gas chromatography of the products more volatile than $B_7C_2H_9(CH_3)_2$ afforded B_6H_{10} and a clear liquid. Mass spectra of this liquid resembled those of known $closo$-carboranes.[5] The most intense peak was m/e 113 and the exact mass match cutoff was m/e 114.13246 (calcd for $^{11}B_5{}^{12}C_4{}^1H_{11}{}^+$: 114.13261). Infrared spectra suggested only B–H units and one type of C–CH$_3$ group in a molecule of high symmetry. The 70.6-MHz ^{11}B nmr spectrum consisted of doublets [relative to $BF_3 \cdot O(C_2H_5)_2$] at δ −10.6 ($J = 150$), −5.2 ($J = 150$), and +12.1 ppm ($J = 170$ cps) in relative intensity 2:1:2. The single methyl resonance at δ −0.67 ppm in the 100-MHz pmr spectrum established this liquid as 4,5-$(CH_3)_2$-$B_5C_2H_5(CH_3)_2$, a new isomer of the known 3,6-$B_5C_2H_5(CH_3)_2$.[8–10]

The parent members of these new $nido$-carborane families, $B_7C_2H_{11}$ and $B_8C_2H_{12}$, are formed in 65%

(7) All boron cage nomenclature and numbering orders are those set forth under the new rules which appeared in *Inorg. Chem.*, 7, 1945 (1968).

(8) (a) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Amer. Chem. Soc.*, 85, 3378 (1963); (b) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *ibid.*, 88, 4622 (1966).

(9) Under the new boron nomenclature rules (ref 7), the $B_5C_2H_7$ species containing adjacent carbon atoms in the belt of the pentagonal bipyramid is the 4,5 isomer. The $B_5C_2H_7$ species with nonadjacent carbon atoms in the belt is the 3,6 isomer. This isomer has formerly been numbered 2,4 (ref 8). Numbering for the unknown 1,2 and 1,7 isomers remains unchanged.

(10) The 32.1-MHz ^{11}B nmr spectrum of neat 3,6-$B_5C_2H_5(CH_3)_2$ prepared as in ref 8a consisted of doublets at δ −8.5 ($J = 178$), −5.9 ($J = 169$), and +17.3 ppm ($J = 178$ cps) in relative intensity 1:2:2, in good agreement with the values reported by R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, 92, 5072 (1970).

yield. $B_7C_2H_{11}$ has never been fully purified owing to its thermal and hydrolytic instability; however, $B_8C_2H_{12}$ has been characterized. Infrared and pmr spectra are consistent with a decaborane(14)-like structure. The ^{11}B nmr spectra are nearly superimposable on those of $B_8C_2H_{10}(CH_3)_2$, and an exact mass match gave 124.16818 (calcd for $^{11}B_8{}^{12}C_2{}^1H_{12}{}^+$: 124.16835). To our knowledge, this species and a new $B_8C_2H_{12}$ containing nonadjacent carbon atoms[11] represent the first cases of skeletal isomers in *nido*-carboranes.

Pyrolysis products of $B_7C_2H_9(CH_3)_2$ include 15 volatile carboranes, of which 4,5-$B_5C_2H_5(CH_3)_2$, 1,6-$B_6C_2H_6(CH_3)_2$, *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$, 1,2-$B_8C_2H_8$-$(CH_3)_2$, 1,8-$B_9C_2H_9(CH_3)_2$, and 1,7-$B_{10}C_2H_{10}(CH_3)_2$ have been identified.[2] Evidence supporting other new *closo*-carborane isomers is being pursued.

(11) P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 1265 (1971).

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Preparation and Reactions of a Dicarba-*nido*-decaborane(12)

Sir:

The carboranes $B_4C_2H_8$,[1] $B_9C_2H_{13}$,[2] and $B_8C_2H_{12}$[3] have been reported as representative members of the $B_nC_2H_{n+4}$ *nido*-carborane family. We wish to report the preparation of yet another *nido*-$B_8C_2H_{12}$ carborane system and at the same time propose the possible existence of a new bonding feature present in this *nido*-$B_8C_2H_{12}$. The $B_8C_2H_{12}$ isomer reported here is markedly different from that of the $B_8C_2H_{12}$ species reported by Rietz[3,4] and appears as a moderately stable intermediate in the hydroboration route[5] leading from 1,3-$B_7C_2H_{13}$ to 1,6-$B_8C_2H_{10}$.

Treatment of 1,3-$B_7C_2H_{13}$ (I) with NaH in a 1:1 molar ratio in diethyl ether solvent followed by the slow addition of B_2H_6 produced 1,3-$B_7C_2H_{13}$, $NaBH_4$, 1,6-$B_8C_2H_{10}$, and the air- and moisture-sensitive product $B_8C_2H_{12}$ (II, mp 139–140°). Thermal decomposition of II *in vacuo* at 150° produced 1,6-$B_8C_2H_{10}$ and H_2 in quantitative yield. Attempts to further characterize II by mass spectroscopy and elemental analyses were complicated by the instability of II.

The 80-MHz ^{11}B nmr spectrum of II (Figure 1) consisted of six doublets of relative intensities 1:2:1:

(1) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964), and references cited therein.
(2) R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1642 (1964).
(3) R. R. Rietz, Abstracts of Papers, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14–18, 1970, No. INOR 17.
(4) R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, **93**, 1263 (1971).
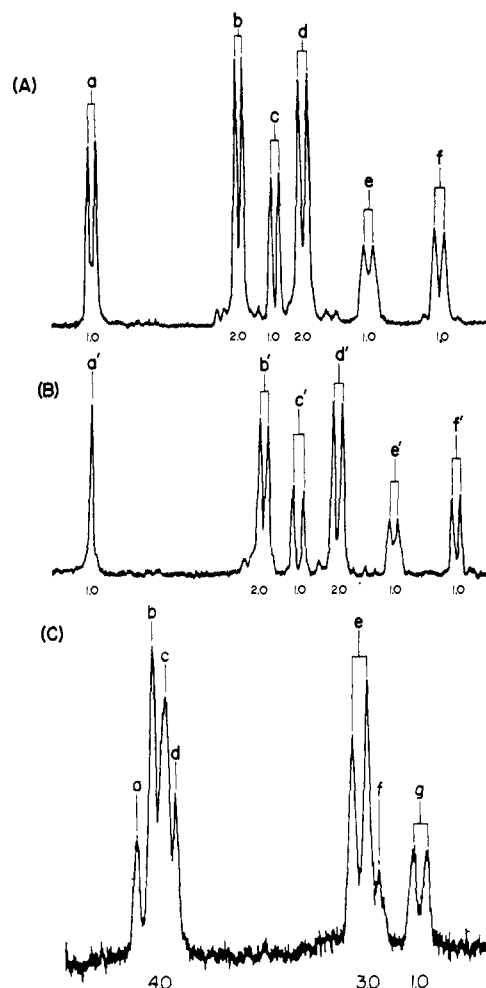(5) P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **9**, 1947 (1970).

Figure 1. The 80.52-MHz ^{11}B nmr spectra of (A) $B_8C_2H_{12}$ and (B) $ClB_8C_2H_{11}$ in carbon disulfide solvent and (C) $B_8C_2H_{12}N(CH_3)_3$ in toluene. Chemical shifts (ppm, with reference to $BF_3O(C_2H_5)_2$) and coupling constants (Hz) are for (A): (a) -36.3, 175; (b) -1.0, 155; (c) $+7.9$, 157; (d) $+13.7$, 154; (e) $+27.8$, 150; and (f) $+44.7$, 155. (B): (a') -37.2; (b') $+1.4$, 158; (c') $+9.1$, 155; (d') $+17.8$, 156; (e') $+30.6$, 151; and (f') $+44.5$, 161. (C): (a) $+2.9$; (b) $+4.9$; (c) $+6.7$; (d) $+8.1$; (e) $+32.5$; (f) $+35.0$; and (g) 40.2, 151.

2:1:1, while the ^1H nmr spectrum (60 MHz) exhibited a broad singlet at τ 7.04. These spectra, when considered along with the presence of a B–H–B bridge band at 2050 cm^{-1} in the infrared, lead us to propose the structure of this $B_8C_2H_{12}$ isomer to be that shown in Figure 2. Reaction of crude II with trimethylamine led to the formation of a ligand adduct derivative, $B_8C_2H_{12}N(CH_3)_3$ (III, mp 142–144°). *Anal.* Calcd for $B_8C_5H_{21}N$: B, 47.59; C, 33.05; H, 11.65; N, 7.71. Found: B, 45.93; C, 33.01; H, 12.42; N, 7.44. Thermal decomposition of III at 150° *in vacuo* afforded quantitative yields of 1,6-$B_8C_2H_{10}$, $N(CH_3)_3$, and H_2. The 60-MHz ^1H nmr spectrum of III consisted of a broad singlet identified as a carborane CH resonance of relative intensity 2 at τ 9.61 and an amine CH$_3$ resonance of relative intensity 9 at τ 8.25. The 80-MHz ^{11}B nmr spectrum of III is shown in Figure 1. The presence of B–H–B bridge bands in the infrared spectrum of III (2075 cm^{-1}) is in accord with its proposed structure (Figure 3).

Reaction of III with anhydrous HCl in a 3:1 ratio in CH$_2$Cl$_2$ solvent at $-80°$ gave pure II in moderate