Synthesis of the New 6-Carba-*nido*-dodecahydrodecaborate(−1) and 4-Carba-*nido*-nonaborane(14)

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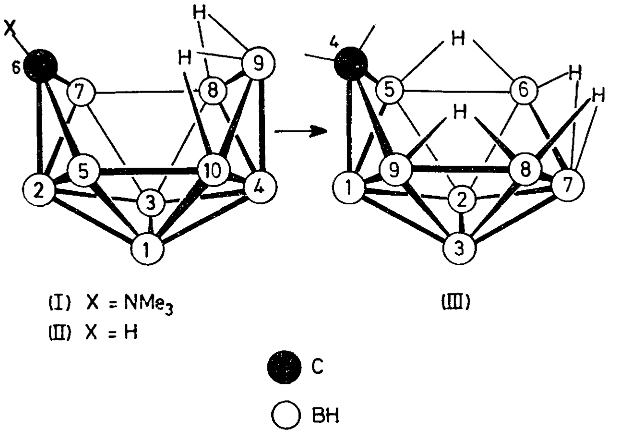
Summary Reduction of 6-Me_3N-6-CB_9H_{11} (I) to 6-$CB_9H_{12}^-$ (II) and hydrolytic degradation of (II) to 4-CB_8H_{14} (III), the first monocarbaborane belonging to the *arachno-series*, are described; structures for these compounds are proposed on the basis of their genesis and n.m.r. spectra.

UP to now, only two carba-*nido*-boranes, namely CB_5H_7 and CB_5H_9, have been isolated.[1] We now report on a high-yield synthesis of two further compounds of this series, the $CB_9H_{12}^-$ anion (II) and the CB_8H_{14} carbaborane (III).



(I) X = NMe_3
(II) X = H

(III)

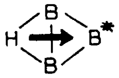
FIGURE. Formation and proposed structures of 6-$CB_9H_{12}^-$ and 4-CB_8H_{14}.

Knoth[2] showed that treatment of 6-Me_3N-6-CB_9H_{11} (I) in boiling tetrahydrofuran with 3 equiv. of Na, followed by subsequent hydrolysis, afforded the *closo*-1-$CB_9H_{10}^-$ anion. Under milder reduction conditions, *i.e.* in liquid ammonia followed by treatment with methanol, we have obtained a new $CB_9H_{12}^-$ anion which was isolated as white crystals of its Me_4N^+ salt in 80% yield based on (I) consumed, after crystallization from acetone–water.

The 32·1 MHz ^{11}B n.m.r. spectrum of (II) in $(CD_3)_2CO$ showed six doublets of relative area 2 : 1 : 2 : 2 : 1 : 1 centred at −1·7, 2·6, 4·3, 12·6, 30·7, and 38·6 p.p.m. relative to BF_3–OEt_2. The 100 MHz ^1H n.m.r. spectrum in $(CD_3)_2CO$ consisted of three signals at δ 5·40, 3·40, and −3·7 (v.br.) (relative to Me_4Si) of relative area 1 : 12 : 2 assigned to the skeletal CH group, NMe_4^+ protons, and two equivalent hydrogen bridges.

The similarity of the ^{11}B n.m.r. spectra of $CB_9H_{12}^-$ and 6-Me_3N-6-CB_9H_{11} [δ −1·0 (1B), 1·7 (2B), 5·9, 12·1 (2B), 29·9 (1B), and 38·0 (1B)] and the presence of a CH signal in the ^1H n.m.r. spectrum of the anion (II) indicate that during the reduction the Me_3N group was replaced by hydrogen in the starting carbaborane (I).

The ^{11}B n.m.r. spectra of both compounds (I) and (II) correspond best to a decaborane-like skeleton with the C–X group (X = NMe_3 or H) in the plane of symmetry, *i.e.* in positions 1(=3), 2(=4), or 6(=9). Of these possibilities, only the last is probable, which has the C atom in the lowest co-ordination position[3] and requires no rearrangement of skeletal atoms during the reduction. We recently reported[4] that the atom (B*) which is opposite the hydrogen bridge in the arrangement (A) is strongly shielded by the hydrogen atom and gives the highest field signal in the spectrum of a particular compound. Since in 6-$CB_9H_{12}^-$ there are two hydrogen bridges but the highest field signal in the ^{11}B n.m.r. spectrum is of relative intensity 1 we assume that both hydrogen bridges strongly shield the same B atom, *i.e.* B(4), and are therefore located between B(8) and B(9) and B(9) and B(10) [see (I) and (II), Figure]. In this respect our description of 6-Me_3N-6-CB_9H_{11} differs from that proposed by Knoth[2] who located the hydrogen bridges between the B(5) and B(10) and B(7) and B(8) atoms; in this case B(1) and B(3) would be strongly shielded, *i.e.* the highest field signal should be of relative intensity 2. Knoth's proposed structure is also unlikely since it cannot be expressed by a *styx*[5] topological formula.



(A)

Treatment of (II) with HCl or better $FeCl_3$–10% HCl solution afforded in 90% yield [based on (I) consumed] a white, crystalline, volatile, air-sensitive compound (III) readily soluble in organic solvents and quite stable under nitrogen. Compound (III), after purification by repeated sublimation at 40—50 °C, and 10^{-2} Torr had m.p. 45—46 °C.

The 32·1 MHz ^{11}B n.m.r. spectrum of (III) in C_6D_6 contained five doublets of relative area 1:1:2:2:2 centred at δ $-17{\cdot}0$ (160), $+3{\cdot}7$ (170), 6·3 (160), 34·9 (155), and 41·1 (155) p.p.m., relative to BF_3–OEt_2 (coupling constant in Hz in parentheses). The doublet at δ 6·3 p.p.m. shows a splitting of 35 Hz, which is typical of the presence of one hydrogen bridge, and that of 34·9 p.p.m. shows a splitting which is typical of a boron atom connected with two hydrogen bridges.

The 100 MHz ^1H n.m.r. spectrum of (III) in C_6D_6 showed two singlets at δ $+0{\cdot}10$ (1H) and $-1{\cdot}75$ (1H) attributable to equatorial and axial CH groups and two very broad singlets at δ $-0{\cdot}45$ (2H) and $-3{\cdot}52$ (2H) (relative to Me_4Si) attributable to two types of hydrogen bridges. All these signals are unchanged in position after ^{11}B decoupling, but the last two are narrowed substantially.

From these spectral data, we suggest the 4-CB_8H_{14} structure [(III) in Figure] with a CH_2 group and four hydrogen bridges in a hexagonal open face. This structure is strongly supported by the fact that the ^{11}B n.m.r. spectrum of (III) is similar to that of 4-NB_8H_{13}, which has been shown by *X*-ray diffraction[6] to possess the same arrangement of B and H atoms as in (III) with the NH group in position 4.

The carbaborane (III) undergoes very easy dehydrogenation during mass spectral analysis showing an intense peak at *m/e* 112 ($^{12}C^{11}B_8H_{12}$; calc.: 112·1683, found: 112·1685) and very small peak at *m/e* 114 corresponding to the parent $^{12}C^{11}B_8{}^1H_{14}$ carborane.

The formation of (III) from (II) can be explained easily by hydrolytic removal of the B(9) atom (Figure) from the 6-$CB_9H_{12}^-$ molecule. The carbaborane (III) is isoelectronic with the $B_9H_{14}^-$ anion, representing the first example of an *arachno*-carbaborane.

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[1] T. D. Onak, R. Drake, and G. B. Dunks, *J. Amer. Chem. Soc.*, 1965, **87**, 2505; G. B. Dunks and M. F. Hawthorne, *ibid.*, **1968**, **90**, 7355; S. R. Prince and R. Schaeffer, *Chem. Comm.*, 1968, 451.

[2] W. H. Knoth, *J. Amer. Chem. Soc.*, 1967, **89**, 1274; *Inorg. Chem.*, 1971, **10**, 598.

[3] R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210.

[4] S. Heřmánek and J. Plešek, *Z. anorg. Chem.*, 1974, **409**, 115.

[5] W. N. Lipscomb, 'Boron Hydrides', Benjamin, New York–Amsterdam, 1963.

[6] K. Baše, J. Plešek, S. Heřmánek, J. Huffman, P. Ragatz, and R. Schaeffer, *J.C.S. Chem. Comm.*, 1975, 934.