Isomeric $B_{10}C_2H_{13}^-$ Ions Derived from the Direct Reduction of $B_{10}C_2H_{12}$

By GARY B. DUNKS, RICHARD J. WIERSEMA, and M. FREDERICK HAWTHORNE*
(*Department of Chemistry, University of California, Los Angeles, California* 90024)

Summary The direct reduction of 1,2-$B_{10}C_2H_{12}$ with sodium metal in tetrahydrofuran produced the $B_{10}C_2H_{12}^{2-}$ ion, treatment of $B_{10}C_2H_{12}^{2-}$ ion with water afforded two isomeric $B_{10}C_2H_{13}^-$ ions, the least stable of which could be thermally converted to the more stable; analysis of the n.m.r. spectra of these $B_{10}C_2H_{13}^-$ ions indicate that they may include a methylene type polyhedral carbon atom; pyrolysis of $[Me_4N][B_{10}C_2H_{13}]$ produced $Me_3N{\cdot}BH_2$-$B_{10}C_2H_{11}$ and $[Me_4N][7,9\text{-}B_9C_2H_{12}]$.

THE direct reduction of 1,2-$B_{10}C_2H_{12}$ with sodium metal in tetrahydrofuran (THF) produced the $B_{10}C_2H_{12}^{2-}$ ion[1-3] which has been shown to form mixed, neutral cobalt(III) complexes involving the $C_5H_5^-$ and $B_{10}C_2H_{12}^{2-}$ ligands.[4a] We now report that protonation of the $B_{10}C_2H_{12}^{2-}$ produced two isomeric $B_{10}C_2H_{13}^-$ ions, one of which was apparently undetected by Zakharkin, Kalinin, and Podvisotskaya.[2]

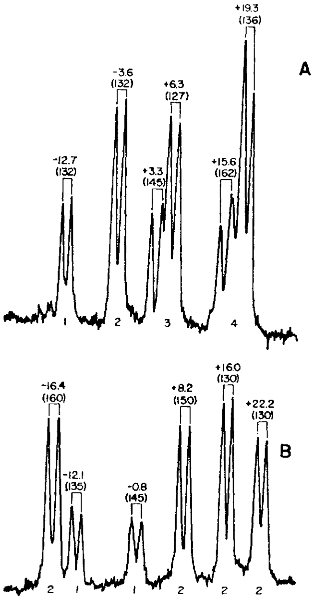

FIGURE 1. *The* 80·5 *MHz* ^{11}B *n.m.r. spectra of* (12)-7,8-$B_{10}C_2H_{13}^-$, (I), (*A*), *and* (12)-3,13-$B_{10}C_2H_{13}^-$, (II), (*B*), *measured in* CD_3COCD_3. *Chemical shifts* (*p.p.m.*) *relative to* $BF_3{\cdot}O(C_2H_5)_2$ *and coupling constants* (*Hz*) *are indicated. Relative areas appear beneath the peaks.*

The $B_{10}C_2H_{12}^{-2}$ ion reacts with 98% $BF_3{\cdot}OEt_2$ followed by degassed H_2O to produce the (12)-7,8-$B_{10}C_2H_{13}^-$ ion.[4b] The tetramethylammonium, (TMA+), salt of (12)-7,8-$B_{10}C_2H_{13}^-$,(I) (73%), was precipitated from water and recrystallized from water–acetone solutions. The 100 MHz ^1H n.m.r. spectrum of (I) consisted of a broad singlet of area 2 at τ 5·60 and a sharp singlet of area 12 at τ 6·55 which were assigned to the identical carborane C–H units and the methyl resonance of the cation, respectively. The 80·5 MHz ^{11}B n.m.r. spectrum (Figure 1A) consisted of six doublets of relative areas 1 : 2 : 1 : 2 : 1 : 2 : 1 which is consistent with a molecule containing 3 unique pairs and 4 unique boron atoms

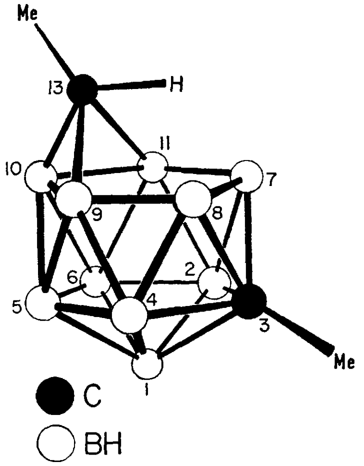

FIGURE 2. *The proposed molecular structure of the* (12)-3,13-$Me_2B_{10}C_2H_{11}^-$ *ion* (IV).[4b]

The $B_{10}C_2H_{12}^{2-}$ ion reacts with aqueous 0·1N NaOH to produce the proposed (12)-3,13-$B_{10}C_2H_{13}^-$ ion, which was isolated from water as the TMA^+ salt, (II) (20%), and recrystallized from acetone–water. The 100 MHz ^1H n.m.r. spectrum of (II) consisted of a sharp singlet of area 12 at τ 6·58 and three broad singlets each of area 1 at τ 7·48, 7·19, and 6·79 which were assigned to the methyl resonance of the cation, carborane C-H, and the methylene type carborane CH_2 units respectively. The 80·5 MHz ^{11}B n.m.r. spectrum of (II) (Figure 1B) contained six doublets of relative areas 2 : 1 : 1 : 2 : 2 : 2 which is consistent with a molecule containing 4 unique pairs and 2 unique boron atoms.

Heating of crystalline (I) at 100° *in vacuo* for 6 h produced (II) in quantitative yield. Pyrolysis of (II) at 200° *in vacuo* for 3 h produced a neutral material which was recrystallized from ether–hexane solutions (31%, *m/e* 217, m.p. 213—216°) and was characterized as $Me_3N{\cdot}BH_2B_{10}C_2H_{11}$, (III) (identical to the product of the reaction of $Me_3N{\cdot}BH_2I$ and Li^+ 1,2-$B_{10}C_2H_{11}^-$) together with Me_4N^+(12)-7,9-$B_9C_2H_{12}^-$, (23%), methane and trimethylamine.

The $B_{10}C_2H_{10}Me_2^{2-}$ ion prepared from 1,2-$Me_2B_{10}C_2H_{10}$ reacts with 98% $BF_3{\cdot}OEt_2$ followed by degassed H_2O to produce the proposed (12)-3,13-$Me_2B_{10}C_2H_{11}^-$ ion. The TMA^+ salt of (12)-3,13-$Me_2B_{10}C_2H_{11}^-$ ion (IV) (85%) was precipitated from H_2O and recrystallized from acetone–water. The room temperature 100 MHz ^1H n.m.r. spectrum of Ph_4As[(12)-3,13-$Me_2B_{10}C_2H_{11}$], (V), consisted of a singlet of area 20 at τ 2·16 which was assigned to the phenyl protons of the cation, a broad quartet of area 1 centered at τ 6·45, a broad singlet of area 3 at τ 8·32 and a very broad singlet of area 3 at τ 8·67. The 100 MHz ^1H n.m.r. spectrum of (V) at −60° was virtually identical to the spectrum measured at room temperature with ^{11}B decoupling and consisted of a sharpened quartet at τ 6·45 (*J* 6·5 Hz), a very sharp singlet at τ 8·32 and a sharp doublet at τ 8·67 (*J* 6·5 Hz). The quartet and doublet were assigned respectively to the resonance of a single proton and a methyl group both bound to a polyhedral carbon atom. The singlet of area 3 was assigned to the resonance of a methyl group bound to a polyhedral carbon atom. In the spectra taken at room temperature without the use of ^{11}B decoupling, all of the resonances were broadened. The 80·5 MHz ^{11}B n.m.r. spectrum of (IV) consisted of six doublets of area 2 : 1 : 1 : 2 : 2 : 2 at −16·5 (184), −4·8 (130), +1·5 (137), +6·5 (161), +13·6 (130) and +21·7 (130). The chemical shifts are in p.p.m. relative to $BF_3{\cdot}OEt_2$ and the coupling constants, Hz, are in parentheses. The formulae assigned to (I), (II), (III), and (IV) are in agreement with the chemical analysis and equivalent weight measurements. Decomposition of (IV) with $PdCl_2$ and propionic acid produced ethane[5] (28%) which indicates that the polyhedral carbon atoms were non-adjacent. A structure of (IV) consistent with the data is presented in Figure 2. This system may represent only the second example of methylene type polyhedral carbon atoms in the carboranes.[6] The gross geometry of (I) is thought to be similar to (IV) with the exception of the positions of the polyhedral carbon atoms. The geometry of (II) is identical with (IV). However, the exact location of the "extra" hydrogen atom in (I) is not known but is expected to be associated with the open face.

Currently we are studying similar reactions with other C-substituted 1,2-$B_{10}C_2H_{12}$ derivatives to ascertain their generality together with reaction chemistry of (I), (II), and (III).

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[4] (a) G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1971, **93**, 2541; (b) in this reference position 12 was apparently occupied by the cobalt atom. The same numbering system has been retained with the number 12 in parentheses to denote the missing vertex.

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