Figure 2. (A) Total electron density plot for the ground state in the $B_2-H_b-B_3$ plane. Contour levels are 0.07, 0.09, 0.11, 0.14, 0.50, and 3.0 e/au^3. (B) Total electron density plot for the ground state in the $B_2-H_b-B_6$ plane. Contour levels are 0.07, 0.09, 0.11, 0.14, 0.50, and 0.30 e/au^3.
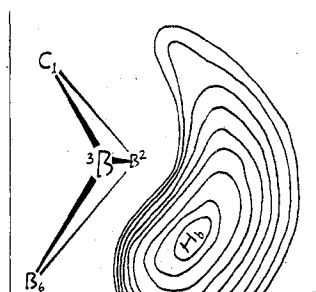

Figure 3. Energy surface for movement of H_b in the plane of symmetry. Contours are drawn with 10 kcal mol^{-1} spacing.

returned to a structure in essentially exact agreement with that obtained in microwave studies in order to remove any bias. The surface thus determined, shown in Figure 3, makes it extremely unlikely that such a structure is involved in the tautomerism.[6]

Our conclusions, therefore, are that the unique hydrogen is best described as an equatorial–equatorial bridge hydrogen in the static molecule and undergoes tautomerism at room temperature by passing through an equatorial–apical BHB bridge. While some small bonding interaction between the bridge hydrogen and boron 6 does occur, this interaction contributes very little to the ground-state valence structure.

Registry No. Monocarbahexaborane(7) (A), 25301-90-0; monocarbahexaborane(7) (B), 55188-36-8.

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A Boron-11 NMR Study of the Methanolysis of Sodium Dimethylamide–Bis(borane) and Some Related Boron–Nitrogen Compounds[1]

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Although the literature contains numerous studies on the solvolysis of diborane, alkali metal borohydrides, and amine–boranes,[2] little is known of the solvolytic behavior of derivatives of diborane and the borohydrides. This work is a qualitative boron-11 NMR study of the methanolysis of $Na(CH_3)_2N\cdot2BH_3$[3] and μ-$(CH_3)_2NB_2H_5$. In the course of this investigation it became of interest to examine the methanolysis of $K(CH_3)_2N\cdot BH_3$, $(CH_3)_2NH\cdot BH_3$, and $(CH_3)_2NH\cdot BH_2Cl$ under similar conditions; these observations are also included.

Results

$Na(CH_3)_2N\cdot2BH_3$. Solutions of $Na(CH_3)_2N\cdot2BH_3$ in methanol are stable at 25 °C for months, but acidification causes rapid solvolysis according to eq 1.[4] When the acid

$$Na(CH_3)_2N\cdot2BH_3 + 6CH_3OH + 2HCl \rightarrow$$
$$(CH_3)_2NH_2Cl + 2B(OCH_3)_3 + 6H_2 + NaCl \quad (1)$$

methanolysis is followed by boron NMR at −60 °C (the solutions were usually diluted with $(C_2H_5)_2O$ to overcome low-temperature viscosity problems), signals characteristic of starting material, μ-$(CH_3)_2NB_2H_5$, $HB(OCH_3)_2$, and $B(OCH_3)_3$ are readily detected. An additional weak resonance, barely resolvable as a triplet, is also found under these conditions at −3.9 ppm (Figure 1). We have tentatively assigned this signal to the unisolated compound $(CH_3)_2N$-$H\cdot BH_2OCH_3$ (see below). At −40 °C the $Na(CH_3)_2N\cdot2BH_3$ and μ-$(CH_3)_2NB_2H_5$ signals rapidly disappear. Warming to 25 °C causes the disappearance of all signals except that of the ultimate methanolysis product, $B(OCH_3)_3$, within ca. 2 min.

In separate parallel low-temperature boron NMR experiments genuine μ-$(CH_3)_2NB_2H_5$ was found to undergo acid methanolysis in exactly the above manner. As in Figure 1 the bridge hydrogen coupling was not resolved at −60 °C.

$K(CH_3)_2N\cdot BH_3$. The acid methanolysis of $K(CH_3)_2N\cdot BH_3$ is slower and requires higher temperature than $Na(CH_3)_2$-$N\cdot2BH_3$. At −20 °C boron NMR shows only the spectrum of the starting material. At 0 °C the coupling constant of the quartet increases from 85 to 99 Hz indicating protonation of the anion to form $(CH_3)_2NH\cdot BH_3$ (the chemical shifts of the two quartets differ by only 1.2 ppm).[5] Complete methanolysis requires 15–20 min at 25 °C. Parallel NMR experiments
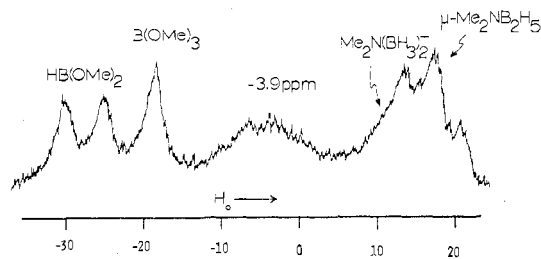
Figure 1. Boron-11 NMR spectrum of initial methanolysis products of $Na(CH_3)_2N\cdot 2BH_3$ at -60 °C.

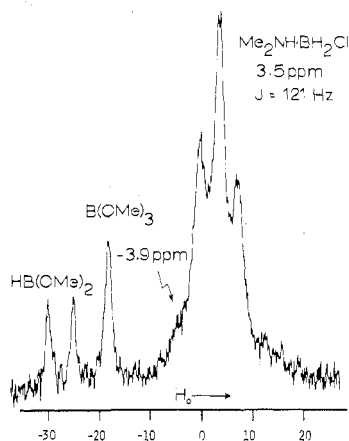**Figure 2.** Boron-11 NMR spectrum of initial methanolysis products of $(CH_3)_2NH\cdot BH_2Cl$ at 5 °C.

using genuine samples of $(CH_3)_2NH\cdot BH_3$ gave identical results.

$(CH_3)_2NH\cdot BH_2Cl$. Kinetic studies suggest that the rate-determining step in the hydrolysis of $(CH_3)_3N\cdot BH_2Cl$ is cleavage of the B–Cl bond.[6] We therefore monitored the methanolysis of $(CH_3)_2NH\cdot BH_2Cl$ with the hope of detecting the proposed intermediate, $(CH_3)_2NH\cdot BH_2OCH_3$. In neutral methanol $(CH_3)_2NH\cdot BH_2Cl$ undergoes complete solvolysis in ca. 10 min at 0 °C. Figure 2 shows a boron-11 NMR spectrum of a partially solvolyzed sample. The -3.9 ppm signal is clearly visible on the low-field side of the $(CH_3)_2NH\cdot BH_2Cl$ triplet.
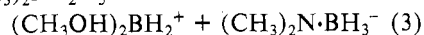
Discussion

The NMR studies show that the first detectable product of the acid methanolysis of $Na(CH_3)_2N\cdot 2BH_3$ is μ-$(CH_3)_2NB_2H_5$ (eq 2). Slight warming causes the disap-

$$(CH_3)_2N\cdot 2BH_3^- + HCl \rightarrow H_2 + \mu\text{-}(CH_3)_2NB_2H_5 + Cl^- \quad (2)$$
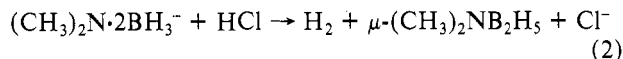
pearance of μ-$(CH_3)_2NB_2H_5$ leaving only signals due to $HB(OCH_3)_2$ and $B(OCH_3)_3$ and the weak triplet at -3.9 ppm. Since the latter is also observed in our methanolysis studies of $(CH_3)_2NH\cdot BH_2Cl$, it must be a monoboron compound, for which the most likely choice is $(CH_3)_2NH\cdot BH_2OCH_3$. The absence of other detectable species with a B–N–B framework suggests that B–N bond cleavage immediately follows reaction 2, rather than a succession of steps replacing hydrogens by methoxy groups on boron.

Boron–nitrogen bond breaking giving the unsymmetrical cleavage products[7] of eq 3 must be ruled out on the basis of our observation of the slow methanolysis of $K(CH_3)_2N\cdot BH_3$. Equations 4 and 5 represent a possible sequence which is

$$2CH_3OH + \mu\text{-}(CH_3)_2NB_2H_5 \rightarrow$$
$$(CH_3OH)_2BH_2^+ + (CH_3)_2N\cdot BH_3^- \quad (3)$$

$$2CH_3OH + \mu\text{-}(CH_3)_2NB_2H_5 \rightarrow$$
$$CH_3OH\cdot BH_3 + (CH_3)_2NBH_2\cdot HOCH_3 \quad (4)$$

$$(CH_3)_2NBH_2\cdot HOCH_3 \rightarrow (CH_3)_2NH\cdot BH_2OCH_3 \quad (5)$$
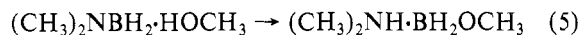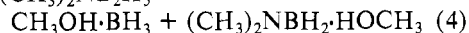
consistent with our results. The $CH_3OH\cdot BH_3$ should rapidly produce $HB(OCH_3)_2$ and $B(OCH_3)_3$.[8,9] The fast proton tautomerization in eq 5 is reasonable considering the greater basicity expected for the tertiary-amine-like nitrogen compared to the ether-like oxygen.

Experimental Section

General Data. Conventional high-vacuum and inert-atmosphere glovebag techniques were used in this work.[10] Boron-11 NMR spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz and equipped with a standard variable-temperature control. Boron-11 chemical shifts were determined by the substitution method and are given in ppm relative to $(C_2H_5)_2O\cdot BF_3$.

Reagents. All solvents were reagent grade and were dried or further purified by standard methods when necessary. The compounds $Na(CH_3)_2N\cdot 2BH_3\cdot 0.5C_4H_8O_2$,[4] μ-$(CH_3)_2NB_2H_5$,[11] $(CH_3)_2NH\cdot BH_2Cl$,[12] and $K(CH_3)_2N\cdot BH_3$[11] were prepared by literature methods. The $(CH_3)_2NH\cdot BH_3$ was purchased from Alfa Inorganics. Hydrogen chloride was generated on the vacuum line as needed by reacting sodium chloride with 98% sulfuric acid.

Experimental Method. In a typical experiment an NMR tube reaction vessel[13] was charged with 1–2 mmol of substrate, and 0.5 mL of CH_3OH, 0.5 mL of $(C_2H_5)_2O$ (a diluent for some low-temperature experiments), and 1–2 mmol of hydrogen chloride were added by vacuum transfer. For low-temperature studies the vessel was warmed to -78 °C by immersion in a dry ice slush and then quickly inserted into the precooled NMR probe. At the conclusion of the NMR study the vessel was returned to the vacuum line and opened to measure hydrogen, identify products, etc.

Registry No. $Na(CH_3)_2N\cdot 2BH_3$, 26601-80-9; μ-$(CH_3)_2NB_2H_5$, 23273-02-1; $K(CH_3)_2N\cdot BH_3$, 43210-87-3; $(CH_3)_2NH\cdot BH_3$, 74-94-2; $(CH_3)_2NH\cdot BH_2Cl$, 52920-74-8.

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Slowing of the Fluxional Process in a Diamagnetic Copper(I) Tetrahydroborate Complex

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Recent studies of covalent metal tetrahydroborates have demonstrated that almost all of these complexes exhibit magnetic equivalence of bridge and terminal hydrogen atoms at ambient temperatures. This equivalence has been attributed to rapid (on the NMR time scale) interchange of bridge and