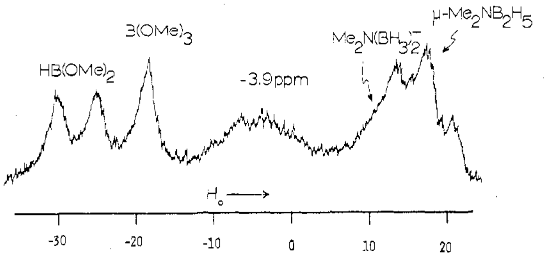

Figure 1. Boron-11 NMR spectrum of initial methanolysis products of $Na(CH_3)_2N{\cdot}2BH_3$ at -60 °C.

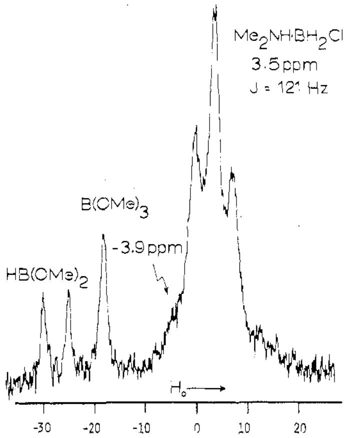

Figure 2. Boron-11 NMR spectrum of initial methanolysis products of $(CH_3)_2NH{\cdot}BH_2Cl$ at 5 °C.

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 disappearance 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.

$$(CH_3)_2N{\cdot}2BH_3^- + HCl \rightarrow H_2 + \mu\text{-}(CH_3)_2NB_2H_5 + Cl^- \quad (2)$$

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 consistent with our results.

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

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

$$(CH_3)_2NBH_2{\cdot}HOCH_3 \rightarrow (CH_3)_2NH{\cdot}BH_2OCH_3 \quad (5)$$

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

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terminal hydrogens.[2-4] At room temperature most complexes exhibit in the proton NMR a broad quartet (^{11}B, $I = {}^3/_2$), the broadness being dependent on the particular sample. Lowering the temperature of the sample results in collapse of the multiplet with the resonance eventually appearing as a singlet. The spectral collapse is attributed to rapid spin–lattice relaxation of the ^{11}B and ^{10}B nuclei and is not related to slowing of the fluxional process.[5,6] The effect described has been called "thermal decoupling"[5] or more recently "correlation time decoupling".[7]

A slowing of the fluxional behavior in borohydride–copper complexes to the point where individual environments could be distinguished with NMR was first observed in the complex $(Ph_3P)_2CuB_3H_8$.[8] At temperatures below −90 °C, several ^1H resonances could be observed which is consistent with effective "thermal" decoupling of the hydrogens from the boron nuclei and a slowed intramolecular exchange among the different hydrogen environments. Very recently, paramagnetic tetrahydroborate complexes have been studied in which, for a variety of reasons, the slowing of the bridge–terminal hydrogen exchange could be observed using the NMR technique.[9,10]

Slowing of the fluxional behavior of diamagnetic tetrahydroborate complexes such as $(Ph_3P)_2CuBH_4$ has not been reported to date. The problem appears to be that the solubility of $(Ph_3P)_2CuBH_4$ is too limited in solvent systems capable of reaching the low temperatures believed to be necessary to slow down the fluxional behavior relative to the NMR time scale. We wish to report the NMR behavior of a tetrahydroborate complex of copper(I) which shows for the first time a slowing of the fluxional behavior in a diamagnetic copper complex. The complex tetrahydroboratobis(trimethyl phosphite)copper(I) recently synthesized in our laboratory affords a compound which is much more soluble in halocarbon solvents than the corresponding triphenylphosphine complex. (For low-temperature studies an acceptable compromise between solubility and viscosity was found by using a 2:1 vinyl chloride–vinyl fluoride solution.) In addition, its lighter mass should contribute to better field homogeneity or less viscosity at lower temperatures. The methyl resonances from the phosphite do not interfere with the "thermally" decoupled tetrahydroborate ^1H resonance.

Figure 1 illustrates the changes occurring in the ^1H NMR spectrum of $[(MeO)_3P]_2CuBH_4$ with a decrease in temperature. The borane ^1H resonance for $[(MeO)_3P]_2CuBH_4$ is a somewhat broadened quartet at ambient temperature ($W_{1/2}$ = 14 Hz). The chemical shift for the quartet is +0.69 ppm compared to +0.3 ppm (J_{BH} = 83 Hz) for $[(MeO)_3P]_4Cu^+BH_4^-$ (−140 °C). This suggests a sizable average deshielding effect due to coordination to the copper and is the expected result based upon the presumed inductive effects of coordination to a positive center employing predominantly covalent dative bonding. At −65 °C the quartet is broadened considerably with relative increase in the intensity of the center two peaks. By −95 °C the resonance has collapsed to a broad doublet, and at −128 °C, thermal decoupling has progressed to an extent that the resonance appears as a broad singlet ($W_{1/2}$ = 92 Hz). The resonance sharpens somewhat at −147 °C ($W_{1/2}$ = 68 Hz) but begins to broaden again at −154 °C. By −159 °C the resonance has broadened and weakened considerably ($W_{1/2}$ = 80 Hz). At −165 °C the signal collapses to the baseline. Very little broadening of the phosphite methyl resonance (Figure 1) accompanied this collapse, which tends to rule out viscosity effects as the cause. Continued lowering of the temperature to approximately −180 °C, which appears to be the limit for the temperature apparatus, did not produce any new peaks assignable to BH hydrogens. The diamagnetic system is somewhat less complicated than the paramagnetic complexes which have been described, and the only process besides field inhomogeneities which seems capable of causing the collapse of the resonance involves slowing of the hydrogen permutation. According to Marks and Kolb[9] scalar relaxation of "the second kind" due to quadrupole-induced modulation of the ^{10}B–H and ^{11}B–H scalar interactions should not be important for anticipated ^{11}B spin–lattice relaxation times for these types of systems.

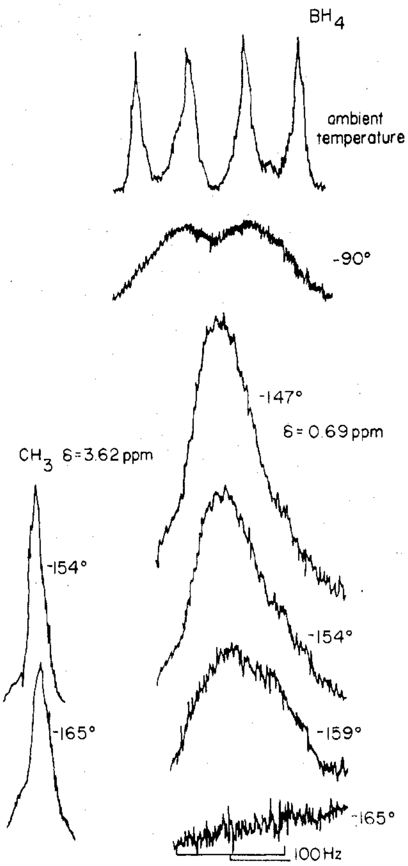

Figure 1. 100.1-MHz ^1H NMR of borane and methyl hydrogens of $[(MeO)_3P]_2CuBH_4$ in 2:1 CH_2CHCl–CH_2CHF showing peak collapse with temperature decrease.

Experimental Section

NMR spectra were obtained from a Varian XL-100 spectrometer; the low-temperature control device was calibrated using an independent thermocouple placed within the NMR tube situated in the probe. Vapor pressure osmometry was performed on a Mechrolab, Inc., Model 301A osmometer.

Preparation of Tetrahydroboratobis(trimethyl phosphite)copper(I). A 4-mmol sample of $[(MeO)_3P]_3CuCl$ (1.88 g), prepared by reaction of CuCl and $(CH_3O)_3P$ in $CHCl_3$, was dissolved in 20 mL of $CHCl_3$ and combined with 5.2 mmol of $NaBH_4$ (0.197 g) dissolved in 15 mL of absolute ethanol. The solution was stirred for 15 min and filtered, and the solvent was removed by flash evaporation. The complex was dissolved in 2 mL of methylene dichloride and 15 mL of pentane, and the solution was filtered and cooled to −78 °C until the product oiled out (10–15 min). The supernatant was decanted and the procedure repeated. The complex was then placed under high vacuum until the complex just began to darken from reduction. The product is a clear, fairly nonviscous liquid. Anal. Calcd for $C_6H_{22}P_2O_6BCu$: C, 22.07; H, 6.79; B, 3.31; Cu, 19.46. Found: C, 22.94; H, 6.45; B, 3.48; Cu, 18.49. Vapor pressure osmometric molecular weight values support the presence of the monomer in solution: calcd, 326.5; found, 320. Infrared data also support the bidentate mode of attachment based on similarity to $(Ph_3P)_2CuBH_4$[11] in multiplicity and position of the B–H stretching mode [absorption (cm^{-1}), relative intensity, assignment]: 2380 (s), 2345 (sh), ν(terminal B–H); 1995 (s), 1935 (s), ν(bridging B–H); 1390 (m), ν(bridge stretch); 1135 (s), $\delta(BH_2)$.

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Registry No. $[(MeO)_3P]_3CuCl$, 67784-65-0; $[(MeO)_3P]_2CuBH_4$, 67784-66-1.

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Reaction between Nitric and Sulfamic Acids in Aqueous Solution[1]

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The production of nitrous oxide when sulfamic acid is treated with nitric acid in the presence of sulfuric acid was first reported by Thiele and Lachman[2] and confirmed by Divers and Haga:[3]

$$HNO_3 + NH_2SO_3H \rightarrow N_2O + H_2SO_4 + H_2O \qquad (1)$$

Baumgarten[4] reported quantitative yields of N_2O upon treating solid sulfamic acid with HNO_3 of weight percent concentrations 73 and above. While the possible formation of nitramide (H_2NNO_2) was considered,[3] it was not detected as product in early investigations. Nitramide is known to decompose to N_2O and would appear to be a likely intermediate species in this reaction, however, and Heubel and Canis[5] detected formation of this species in a series of reactions between sulfamates and nitrates studied by thermogravimetry. In a subsequent study Canis[6] reported the production of H_2NNO_2 in low yield (<5%) upon treatment of solid NH_2SO_3H with 95% HNO_3 in the temperature range −50 to −20 °C and higher yields upon addition of $NaNO_3$. Because small changes in HNO_3 concentration between 93 and 100% have a large effect on the reaction rate, Canis postulated a mechanism involving attack of the species NO_2^+ on sulfamate. She also reported an increase in the rate and proportion of N_2O production upon addition of concentrated H_2SO_4.

In more recent studies,[7,8] the kinetics of the nitric acid–sulfamic acid reaction have been measured at somewhat elevated temperatures and over a broad range of HNO_3 concentrations. Hughes et al.[8] have made the surprising observation that the reaction proceeds through two initial stages, each involving apparent intermediate formation, and reported that nitrous oxide and sulfate products appear in a third (and slowest) stage which is first order in both sulfamate and nitrate concentrations and whose acidity function dependence indicates involvement of NO_2^+. These authors have suggested alternative schemes, in each of which H_2NNO_2 is postulated to be the immediate precursor to product N_2O. We report here experiments with ^{15}N tracer which bear on this point.

Table I. Mass Spectra of N_2O Product in the $H^{15}NO_3$-NH_2SO_3H Reaction

mass	$t = 7$ days[a]	$t = 21$ days[a]	$t = 19$ days[b]
46	0.0038	0.0039	0.0037
45	0.164	0.164	0.107
44	1.00	1.00	1.00
31	0.0113	0.0105	0.0064
30	0.0794	0.0734	0.0823
44-46[c]	7.35	7.36	5.15
30 + 31[c]	12.5	12.5	7.2

[a] $[HNO_3] = 12.7 \pm 0.5$ M, $[NH_2SO_3H] = 0.091 \pm 0.003$ M, % $^{15}N(HNO_3) = 12.8 \pm 0.5$. [b] $[HNO_3] = 5.9 \pm 0.2$ M, $[NH_2SO_3H] = 0.50 \pm 0.02$ M, % $^{15}N(HNO_3) = 6.9 \pm 0.3$. [c] % ^{15}N.

Experiments were carried out on degassed solutions in Y-shaped reaction vessels at room temperature (25 ± 2 °C), employing vacuum-line techniques. Gas products were collected by Toepler pump and analyzed by gas chromatography (Varian Aerograph 920 with a 12-ft Porapak Q column and a Varian A-25 integrator/recorder) or, in the cases of isotopic analyses and gas analyses at very low pressure, on an AEI MS-30 mass spectrometer. Extremely small quantities of gas product were found after extended reaction periods, indicating low rates consistent with the rate constants and activation energy reported by Hughes et al.[8] Yields of <2 μmol were produced in 10 mL of solution at $[NH_2SO_3H] = 0.50$ M and $[HNO_3]$ in the range 0.50–4.5 M, with reaction times between 2.5 and 21 days. Increasing quantities were obtained at higher nitric acid concentrations, up to 114 μmol with $[HNO_3] = 12.5$ M, $[NH_2SO_3H] = 0.091$ M, and reaction time 7 days. In each of these cases, the gas proved to be a mixture of N_2 and N_2O, the latter predominating. With a reaction mixture at $[HNO_3] = 12.7$ M and $[NH_2SO_3H] = 0.088$ M, product gas samples were withdrawn at intervals over a 2-week period, revealing a gradual increase of N_2 content from 1.0% of total gas product at 24 h to 4.7% at 2 weeks. Vacuum line conditions were such that we are confident the observed N_2 was not of atmospheric origin.

Tracer experiments were carried out at two different $H^{15}NO_3$ concentration levels, and the mass spectra of resulting separated N_2O product gases are shown in Table I. The unchanging isotopic composition at $[HNO_3] = 12.7$ M between 7 and 21 days of reaction time indicates that no shift of pathway occurred within this period. At both concentration levels the percentage of ^{15}N observed at masses 30 and 31, i.e., in NO produced by electron impact cracking in the mass spectrometer, is the same as its initial abundance in reactant HNO_3, within the error of measurement. This is the result that would be expected for N_2O produced by decomposition of an asymmetric, bound intermediate, e.g., nitramide:

$$H_2N^*NO_2 \rightarrow N^*NO + H_2O \qquad (2)$$

Clusius[9] has shown that nitramide decomposes to N_2O without rearrangement, and with all ^{15}N above natural abundance arising from HNO_3, the decay product at mass 45 should be almost entirely $^{14}N^{15}N^{16}O$ for reaction 2. However, the data in Table I show mass 45 abundances at both HNO_3 concentrations that are substantially greater than predicted for a nitramide precursor; this is reflected in the fact that the percentage of ^{15}N in N_2O (masses 44–46) is significantly greater than half the isotopic content of reactant HNO_3. In addition, N_2O of mass 46, largely $^{15}N^{15}N^{16}O$, is present in both experiments at levels that are small but unmistakably greater than predicted on the basis of reaction 2.

The only way that the apparent contradictions posed by these data can be reconciled is to assume that the observed N_2O is a mixture of two kinds, one arising from the asym-

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