Acknowledgment.—We wish to acknowledge the assistance of Mr. R. B. Shiflett in measuring the MCD and absorption spectra of $SbCl_6^-$. This work was supported in part by a grant from the National Science Foundation.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF HAWAII, HONOLULU, HAWAII 96822

Preparation and Basicity of Sodium Dimethylamidotrihydroborate(III)[1]

BY JOHN W. GILJE AND RICHARD J. RONAN

Received January 22, 1968

Although borane complexes of many nitrogen-containing Lewis bases have received extensive study over the past several decades, the literature contains remarkably few references to borane derivatives of amides. A sparsely characterized dioxanate of $NaH_3BN(CH_3)_2$, formed in the reaction of dimethylamine borane with sodium hydride, has been reported.[2] Shore and Parry[3] and Burg and Schlesinger[4] all have proposed, on the basis of hydrogen evolution, that NaH_2NBH_3 forms by the reaction of ammonia borane with sodium in liquid ammonia. However, neither group actually isolated or characterized a product. In this note we report an investigation of the reaction between dimethylamine borane and sodium, and the characterization and Brønsted–Lowry acid–base chemistry of sodium dimethylamidotrihydroborate(III), $Na(CH_3)_2NBH_3$.

Experimental Section

All manipulations were performed using standard vacuum-line and/or inert-atmosphere techniques. Ir, nmr, and mass spectra were run on Beckman IR-5, Varian A-60 with variable-temperature probe, and Perkin-Elmer Hitachi RMU-6D spectrometers, respectively.

Dimethylamine borane was prepared from the reaction of diborane with dimethylamine by a method analogous to that reported for the preparation of monomethylamine borane[5] except that diethyl ether was substituted for tetrahydrofuran. Diborane was prepared by the method of Weiss and Shapiro.[6] Ammonia and dimethylamine, obtained from Matheson Co., were dried over sodium from which they were distilled immediately before use.

Reaction of Dimethylamine and Sodium.—In a typical reaction 0.161 g (2.73 mmol) of $(CH_3)_2HNBH_3$ and a glass bulb containing about 0.06 g of sodium were placed in a reaction tube, which was then attached to the vacuum line and evacuated. Approximately 10 ml of anhydrous ammonia was distilled into the tube at −196°, the temperature was raised to −40°, and the ball containing the sodium was broken with a magnetic hammer. There was a rapid evolution of noncondensable gas which was periodically withdrawn using a Toepler pump. After 30 min the gas evolution had ceased, the excess sodium was amalgamated with a few drops of mercury, and the remaining traces of noncondensable gas were removed. The total noncondensable gas produced was measured as 1.31 mmol and identified as H_2 by its mass spectrum. In two similar runs 1.06 mmol of $(CH_3)_2HNBH_3$ produced 0.50 mmol of H_2, and 0.53 mmol of $(CH_3)_2HNBH_3$ produced 0.26 mmol of H_2.

The white, hygroscopic solid which remained in the reaction vessel after the solvent ammonia was distilled off analyzed as $Na(CH_3)_2NBH_3$. *Anal.* Calcd for $Na(CH_3)_2NBH_3$: B, 13.4; hydrolytic H, 3.7; equiv wt, 80.8. Found: B, 13.1; hydrolytic H, 3.6; equiv wt, 81.7.

Hydrolysis of $Na(CH_3)_2NBH_3$ with Strong Acid.—About 2 ml of 12 *N* HCl was frozen into a reaction tube containing 0.0125 g (0.155 mmol) of $Na(CH_3)_2NBH_3$. The tube was sealed and warmed to room temperature during which time gas evolution could be observed. After 15 min the contents of the tube were refrozen to −196°, the tube was opened to the vacuum line, and the noncondensable gas was removed. The tube was then heated to 70° for 1 hr during which period no further gas evolution could be detected. The total noncondensable gas obtained was measured as 0.455 mmol and was identified as H_2 as before. No further gaseous products were observed. An nmr spectrum of the solution remaining after hydrolysis indicated the presence of $(CH_3)_2NH_2^+$. $B(OH)_3$ (0.149 mmol) was detected by titration in the presence of mannitol as described elsewhere.[7]

In attempts to hydrolyze $(CH_3)_2NBH_3^-$ completely in neutral or basic solutions very slow hydrogen evolution was observed with complete hydrolysis requiring at least several days.

Titration Experiments.—In order to minimize any decomposition of $(CH_3)_2NBH_3^-$, solutions of $Na(CH_3)_2NBH_3$ were prepared immediately before each titration by adding about 40 ml of cold (0°) CO_2-free water to a weighed sample of $Na(CH_3)_2NBH_3$ contained in a 50-ml volumetric flask which had also been cooled to 0°. The flask was then placed in a constant-temperature bath held at 20 ± 0.50° and allowed to equilibrate for 0.5 hr after which the solution was made to final volume. Typical solutions were in the range of 0.05–0.005 *M*.

Aliquots of these solutions were titrated with 0.0500 *N* HCl. The pH was recorded during these titrations with a Beckman Expandomatic pH meter equipped with a scale expander and Sargent S-30080-15C calomel and S-30050-15C glass electrodes.

Results and Discussion

In anhydrous liquid ammonia at −40° dimethylamine borane reacts rapidly with sodium to form hydrogen and $Na(CH_3)_2NBH_3$ by

$$(CH_3)_2HNBH_3 + Na \longrightarrow 0.5H_2 + Na(CH_3)_2NBH_3$$

Although infrared spectra taken of $Na(CH_3)_2NBH_3$ were always contaminated with $(CH_3)_2HNBH_3$ which formed through the reaction of $(CH_3)_2NBH_3^-$ with trace moisture in the KBr pellets or mulling agents, the strong- and medium-intensity peaks in the spectrum were determined by examination of a number of spectra from which the peaks due to the dimethylamine borane could be removed by inspection. The following bands (in cm^{-1}) were thus obtained: 3080 m, 2920 m, 2330 s, 2240 s, 1440 s, 1155 s, 1136 s, 882 s, 865 m, 694 w. The proton magnetic resonance spectrum of $Na(CH_3)_2NBH_3$ was recorded in liquid ammonia at −35°. The methyl

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(1) Acknowledgment is gratefully made to the Petroleum Research Fund administered by the American Chemical Society and American Cancer Society Grant 86A for partial support of this work. The nmr and mass spectrometers used in this work were obtained through Public Health Service Grant GM 10413 and NSF Instrument Grant GP 5813, respectively.

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resonance occurs at about δ −1.2 ppm. (Negative chemical shifts are downfield from the reference tetramethylsilane, TMS.) Since this peak nearly coincides with the center peak of the ammonia triplet, its assignment was confirmed by observing the spectrum at several $Na(CH_3)_2NBH_3$ concentrations. The relative intensity of the peak assigned to the $(CH_3)_2NBH_3^-$ methyl resonance increased with increasing $(CH_3)_2NBH_3^-$ concentration. No peaks attributable to the borane resonances could be resolved. The pmr spectra of the $(CH_3)_2HNBH_3$ and $(CH_3)_2NBH_3^-$ solutions were recorded periodically over a period of several weeks. During this time no $(CH_3)_2NH$ was ever detected and no evidence for the formation of species such as $H_2NBH_3^-$ or H_3NBH_3 could be obtained. These observations strongly imply that no transamination of either $(CH_3)_2HNBH_3$ or $(CH_3)_2NBH_3^-$ occurs with ammonia over extended periods under the conditions used in this study.

In 12 *N* HCl $Na(CH_3)_2NBH_3$ hydrolyzes in a few minutes

$$Na(CH_3)_2NBH_3 + 3H_2O + H^+ \longrightarrow 3H_2 + B(OH)_3 + (CH_3)_2NH + Na^+$$

Titrations of aqueous solutions of $Na(CH_3)_2NBH_3$ with 0.05 *N* HCl, however, yield typical weak base–strong acid titration curves which indicate that the equilibrium

$$(CH_3)_2NBH_3^- + H_2O \rightleftharpoons (CH_3)_2HNBH_3 + OH^-$$

is established prior to the hydrolysis of the BH_3 group. The pmr chemical shift of the methyl protons in aqueous $(CH_3)_2NBH_3^-$ solutions is nearly identical with the chemical shift of the methyl groups in neutral aqueous solutions of $(CH_3)_2HNBH_3$ demonstrating that the equilibrium lies far to the right. Further supportive evidence for this reaction is the fact that $(CH_3)_2HNBH_3$ can be isolated from and seen in the mass and infrared spectra of $Na(CH_3)_2NBH_3$ which has been placed in contact with moist air. In these mass spectra, peaks which could have arisen from the hydrolysis of $H_2NBH_3^-$ were either completely absent or present in trace amounts (under 2% of the most intense peak) lending further evidence to the supposition that transamination did not occur during the preparation of $(CH_3)_2NBH_3^-$.

The hydrolysis of the borane group is too rapid at 25° to allow the base dissociation constant, K_b, to be conveniently determined from potentiometric titration data. However, at 20° this hydrolysis is slow enough to permit reproducible data to be obtained. A K_b of $1.76\ (\pm 0.33) \times 10^{-4}$ was obtained as the average of 24 values calculated[8] from data taken on four potentiometric titrations of solutions 0.05–0.005 *M* in $Na(CH_3)_2NBH_3$. The error is expressed to a 95% confidence level.

It is interesting to compare the properties of $(CH_3)_2NBH_3^-$ and $(CH_3)_2HNBH_3$ with those of similar alkylamines and alkylammonium ions. The aqueous equilibrium of $(CH_3)_2NBH_3^-$ and its formation from $(CH_3)_2HNBH_3$ are analogous to the well-known amine hydrolysis reaction and characteristic reduction of ammonium ions with sodium in liquid ammonia.[9] The methyl pmr signals of $(CH_3)_2NBH_3^-$ (δ −1.2 ppm) and $(CH_3)_2HNBH_3$ (δ −2.5 ppm)[10] appear at a higher field than those of trimethylamine (δ −2.2 ppm)[11] and trimethylammonium ion (δ −2.9 ppm),[11] respectively, compounds in which the BH_3 moiety has formally been replaced by an isoelectronic CH_3^+ group. This may well reflect a greater electron density about the methyl groups in the borane compounds than in the compounds containing the CH_3^+ group with its higher nuclear charge and consequent greater electron-withdrawing ability. Smilarly the base dissociation constants at 20° for $(CH_3)_2NBH_3^-$ and $(CH_3)_3N$[12] of 1.76×10^{-4} and 5.50×10^{-5}, respectively, also may reflect the relative electron-withdrawing power of the BH_3 and CH_3^+ groups since the electron density about and, thus, basicity of the nitrogen should be related inversely to the electron-withdrawing power of the groups attached to it.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA 32306

The Preparation of a Technetium Iron Carbonyl Anion

BY MAURICE W. LINDAUER,[1] GEORGE O. EVANS,
AND RAYMOND K. SHELINE

Received January 29, 1968

A technetium diiron dodecacarbonyl anion has been prepared that is analogous to the manganese compound reported by Anders and Graham[2] and the rhenium compound reported by Evans, Hargaden, and Sheline.[3] Ditechnetium decacarbonyl[4] (119 mg, 0.25 mmol; Pressure Chemical Co., Pittsburgh, Pa.) and 196 mg (1.0 mmol) of iron pentacarbonyl were dissolved in 150 ml of freshly distilled (over lithium aluminum hydride) tetrahydrofuran (THF) under a dry nitrogen atmosphere, and the solution was irradiated for 1 hr by an A-H6 high-pressure mercury (General Electric Co.) arc lamp at a distance of about 1 ft. During the first few minutes of irradiation, the

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(1) Chemistry Department, Valdosta State College, Valdosta, Ga. 31601

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