The Reaction of Dimethylamidotrihydroborate(1−) with Diborane. A New Synthesis of μ-Dimethylaminodiborane

Sir:

The recent study of the basicity of sodium dimethylamidotrihydroborate(1−), $Na(CH_3)_2NBH_3$, by Gilje and Ronan[1] prompts us to report our findings on the chemistry of this material. We have compared $(CH_3)_2NBH_3^-$ and its isoelectronic counterpart trimethylamine in their behavior toward diborane. It is well known that trimethylamine reacts with diborane to produce trimethylamine–borane,[2] a symmetrical cleavage product;[3] unlike trimethylamine, $Na(CH_3)_2NBH_3$ reacts with diborane in diglyme (diethylene glycol dimethyl ether) to generate the unsymmetrical cleavage products μ-dimethylaminodiborane and sodium tetrahydroborate in good yield.

$$(CH_3)_2NBH_3^- + B_2H_6 \rightarrow \mu\text{-}(CH_3)_2NB_2H_5 + BH_4^-$$

The $Na(CH_3)_2NBH_3$ was prepared by the reaction of dimethylamine–borane with sodium hydride in monoglyme (ethylene glycol dimethyl ether) and isolated by precipitation with dioxane to form $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$.[4] In a typical experiment a 500-ml reaction vessel was charged in a dry nitrogen atmosphere with 1.328 g (10.60 mmoles) of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ and 8 ml of dry diglyme, transferred to the vacuum line, and evacuated. The vessel was cooled to −196° and a 17.50-mmole sample of diborane was condensed in. The bulb was sealed, removed from the vacuum line, and warmed to room temperature with intermittent swirling of the solution. After 20 min, the vessel was opened to the vacuum line, and all volatile materials were distilled through a trap maintained at −45° into a trap at −196°. Complete separation of the more volatile products from diglyme required repeated fractionation through the −45° trap, and for this reason the amount of solvent employed should be kept to a minimum. The μ-dimethylaminodiborane was separated from the liberated dioxane by fractionation through a −78° trap and from the excess diborane by distillation into a −112° trap. The μ-dimethylaminodiborane was identified by comparison of its gas-phase infrared spectrum with that reported in the literature[5] and by its characteristic vapor pressure of 101 mm at 0°.[6] The presence of sodium tetrahydroborate was confirmed by an ${}^{11}B$ nmr spectrum[7] of a monoglyme solution of the solid material remaining in the reaction vessel. Recovered in this experiment were 8.72 mmoles of diborane, implying a loss of 8.78 mmoles, and 6.65 mmoles of μ-dimethylaminodiborane, a yield of 63% based upon $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$.

Yields of pure μ-dimethylaminodiborane as high as 80% can be attained when more diglyme is used, but this is offset by the tedious separation of the product from the solvent. Yields are generally higher if at least a 50% excess of diborane is employed. For preparative purposes the actual isolation of $Na(CH_3)_2NBH_3$ is unnecessary, and a diglyme solution of this material, separated from excess sodium hydride, may be directly treated with diborane to give satisfactory yields of μ-dimethylaminodiborane.

We have also compared the ${}^{11}B$ nmr spectra of $(CH_3)_2NBH_3^-$ and dimethylamine–borane to determine the effect of removing the NH proton on the chemical shift and coupling constant. The spectrum of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ in monoglyme consists of a quartet with $J = 84$ Hz and δ +14.7 ppm relative to $(C_2H_5)_2OBF_3$ (internal capillary). The spectrum of dimethylamine–borane in monoglyme obtained under identical conditions shows a quartet with $J = 95$ Hz and δ +13.5 ppm. Although the chemical shift of dimethylamine–borane determined in this work is not in exact agreement with the published value of +14.2 ppm,[8] there is no doubt concerning the coupling constants and the relative upfield shift of the $(CH_3)_2NBH_3^-$ quartet compared to dimethylamine–borane. The removal of the NH proton from dimethylamine–borane causes a redistribution of electronic charge resulting in a slight increase in shielding at the boron nucleus and the CH protons, which is reflected in a similar upfield shift of 1.3 ppm[1] for the methyl resonance in the proton spectrum. It is interesting to note that the decrease in ${}^{11}B$–H coupling upon removal of the NH proton from dimethylamine–borane is paralleled by a similar decrease in ${}^{13}C$–H coupling when the NH proton is removed from the trimethylammonium ion. The ${}^{13}C$–H coupling constants for trimethylammonium ion and trimethylamine are 144[9] and 131 Hz,[10] respectively.

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(1) J. W. Gilje and R. J. Ronan, *Inorg. Chem.*, **7**, 1248 (1968).

(2) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

(3) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3554 (1959).

(4) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *ibid.*, **83**, 2471 (1961).

(5) D. E. Mann, *J. Chem. Phys.*, **22**, 70 (1954).

(6) A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **71**, 3451 (1949).

(7) The ${}^{11}B$ nmr spectra discussed in this paper were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz.

(8) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **86**, 1505 (1964).

(9) Determined from ${}^{13}C$ satellites in the proton spectrum of trimethylammonium chloride in D_2O.

(10) E. A. V. Ebsworth and N. Sheppard, *J. Inorg. Nucl. Chem.*, **9**, 95 (1959).

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The Supposed Reduction of Nitrogenpentaammineruthenium(II) Salts by Sodium Borohydride

Sir:

We have reported[1,2] that nitrogenpentaammineruthenium(II) salts, $[Ru^{II}(NH_3)_5N_2]X_2$, are reduced by sodium borohydride, yielding up to one molecule of ammonia per molecule of nitrogen in the complex. Recent experiments by Shilov and coworkers[3] and by Chatt and coworkers[4] using N^{15}-labeled nitrogen have indicated that no reduction takes place. Further experi-

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(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(2) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

(3) Yu. G. Borodko, A. K. Shilova, and A. E. Shilov, private communication.

(4) J. Chatt, R. L. Richards, J. E. Fergussen, and J. L. Love, private communication.