The Dimethylamidodiborane(1−) Anion

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Summary $Me_2N(BH_3)_2^-$ and $B_2H_7^-$ exist in equilibrium with μ-$Me_2NB_2H_5$ and BH_4^- in monoglyme; $NaMe_2N(BH_3)_2$ is prepared by the reaction of NaH with μ-$Me_2NB_2H_5$.

IN monoglyme solution $NaBH_4$ and μ-$Me_2NB_2H_5$ exchange hydrogen but not boron. The ^{11}B n.m.r. spectrum† of a monoglyme solution of $NaBH_4$ and μ-$Me_2NB_2H_5$ in 2:1 ratio shows a weak BH_4^- signal at +41·6 p.p.m., a signal characteristic of $B_2H_7^-$ at +25·3 p.p.m., and a quartet centred at +11·2 p.p.m. (see 0° portion of Figure). Addition of more μ-$Me_2NB_2H_5$ to this solution results in the appearance of a signal at +17·0 p.p.m., characteristic of μ-$Me_2NB_2H_5$. These observations imply the reaction shown by equation 1.

$$\mu\text{-}Me_2NB_2H_5 + 2BH_4^- \rightleftharpoons Me_2N(BH_3)_2^- + B_2H_7^- \quad (1)$$

This equilibrium lies to the right below room temperature, and is shifted to the left by removing all volatile materials. Warming the solution also drives the equilibrium to the left owing to the insolubility of $NaBH_4$ in monoglyme at elevated temperatures.[1] The Figure shows the progressive change with increasing temperature of the ^{11}B n.m.r. spectrum of the solution; at 40° most of the $NaBH_4$ has been precipitated and a broad single peak at +17·0 p.p.m. characteristic of μ-$Me_2NB_2H_5$ has appeared;[2] at 60° only the μ-$Me_2NB_2H_5$ signal remains.

The $Me_2N(BH_3)_2^-$ ion is related structurally to $H_2P(BH_3)_2^-$ [3,4] and $HS(BH_3)_2^-$,[5] and is the first example of a derivative of the unknown $H_2N(BH_3)_2^-$, the anion originally suggested for the diammoniate of diborane.[6]

Sodium dimethylamidodiborane is prepared directly by the room-temperature reaction of μ-$Me_2NB_2H_5$ with an excess of NaH in monoglyme (equation 2).

$$\mu\text{-}Me_2NB_2H_5 + NaH \rightarrow NaMe_2N(BH_3)_2 \quad (2)$$

Separation of unreacted NaH by filtration and concentration of the solution results only in a viscous oil. Treatment of the oil with anhydrous dioxan and subsequent vacuum evaporation of the solution gives colourless crystalline $NaMe_2N(BH_3)_2,0{\cdot}5C_4H_8O_2$ (I). The dioxan of crystallization can be recovered quantitatively by warming the solid to 70° under vacuum. The new compound (I) dissolves without reaction in glyme ethers, ethanol, and water; neutral aqueous solutions show only slight decomposition after two weeks at room temperature, although acidification results in rapid hydrolysis. The ^{11}B n.m.r. spectrum of a monoglyme solution of (I) shows a well resolved quartet at +11·2 p.p.m. (J 91 Hz) in agreement with that shown in the Figure. The ^1H n.m.r. spectrum in D_2O shows a sharp CH_3 singlet at τ 7·72 and a 1:1:1:1 $^{11}BH_3$ quartet at τ 8·50.

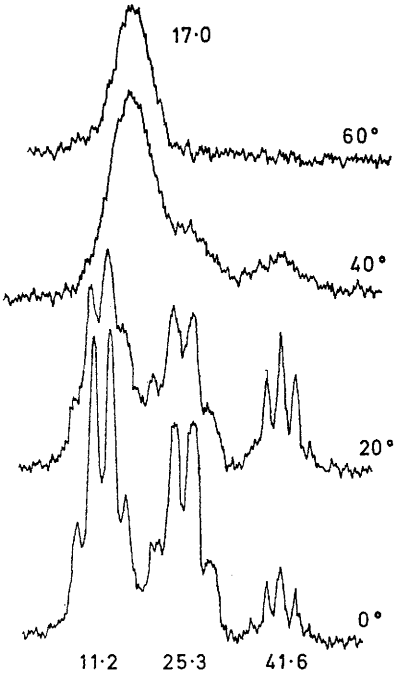

FIGURE. *Temperature variation of the* ^{11}B *n.m.r. spectrum of a monoglyme solution of* $NaBH_4$ *and* μ-$Me_2NB_2H_5$ *in* 2:1 *ratio.*

In diglyme solution, (I) reacts with B_2H_6 according to equation 3.

$$Me_2N(BH_3)_2^- + B_2H_6 \rightarrow \mu\text{-}Me_2NB_2H_5 + B_2H_7^- \quad (3)$$

The μ-Me_2NB_2H may be recovered in good yield by vacuum line fractionation.

I thank the National Science Foundation for support of this work.

(*Received, October* 13*th*, 1969; *Com.* 1556.)

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† The ^{11}B n.m.r. spectra reported were obtained using a Varian HA-100 spectrometer equipped with a 32·1 MHz probe and standard, temperature accessories. The ^{11}B chemical shifts are relative to Et_2OBF_3.

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