$$B_{10}H_{12}\cdot 2DMF + 2DMF\text{-}d_7 \xrightarrow{\text{stepwise}} B_{10}H_{12}\cdot 2DMF\text{-}d_7 + 2DMF$$

At 85°, the methyl resonance peaks of $B_{10}H_{12}\cdot 2DMF$ decreased to a constant low intensity, but the positions remained unchanged. There was gradual formation of a solid phase.[5] When a sample of $B_{10}H_{12}\cdot 2DMF$ and DMF-d_7 was inserted into an n.m.r. probe preheated to 120°, the methyl resonances corresponding to the released DMF rapidly collapsed whereas the methyl resonances corresponding to $B_{10}H_{12}\cdot 2DMF$ did not.

The most reasonable conclusion to be drawn from this study is that the barrier to rotation about the C–N-$(CH_3)_2$ bond of $B_{10}H_{12}\cdot 2DMF$ is relatively large,[7] consistent with the B–O-bonded structure of type A. Structure B is not consistent with a large rotational barrier. The peak assigned to a C═O stretching frequency[5] in the infrared spectrum of $B_{10}H_{12}\cdot 2DMF$ can be just as well assigned to C═N stretching.

(7) The rate of rotation must be less than 18 sec.$^{-1}$ at 120°.

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Boroxine. A New Route to Borane Carbonyl[1]

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The most common method for the preparation of borane carbonyl, BH_3CO (also referred to as carbon monoxide borane), was first developed by Burg and Schlesinger[2] through a high-pressure reaction of CO(g) with diborane. We have recently observed that BH_3CO can be obtained from a rapid reaction of boroxine ($H_3B_3O_3$) and CO(g) at comparatively low pressures and temperatures. Under suitable conditions, this procedure gives yields of BH_3CO somewhat higher than that expected from an equilibrium reaction between B_2H_6 and CO.[3]

Experimental Section

Samples of solid boroxine were prepared by passing $H_2O(g)$ over a mixture of B(s) and $B_2O_3(l)$ at a temperature of approximately 1100°. The apparatus and procedure have been described previously.[4] An alternate procedure is to pass $H_2(g)$ over B–B_2O_3 mixtures.[5] Solid boroxine was warmed to a temperature between −34 and 23°, and $B_2H_6(g)$, which is produced by the partial decomposition of the solid, was removed. Carbon monoxide at a known pressure was added to the reaction bulb, and the vessel was warmed to the final temperature. Additional $B_2H_6(g)$ is produced by the further decomposition of the solid as it is heated. An infrared spectrum of the product mixture, taken a few minutes later, indicated that BH_3CO was formed (strong band at ~2170 cm.$^{-1}$)[6] and that the reaction had occurred quite rapidly. The reaction vessel was then immersed in a liquid nitrogen trap, and the unreacted CO(g) was removed by pumping. Immediately after removing the excess CO(g), the infrared spectrum of the gaseous mixture containing $B_2H_6(g)$ and $BH_3CO(g)$ at a known pressure was recorded; the partial pressure of $B_2H_6(g)$ was determined from absorption intensity measurements and a calibration curve obtained from a series of measurements with pure $B_2H_6(g)$. The partial pressures of BH_3CO were obtained by difference. The pressure of unreacted CO was calculated from the material balance relation: $P_{CO}\text{ (initial)} = P_{CO}\text{ (final)} + P_{BH_3CO}$. The mixture of $B_2H_6(g)$ and $BH_3CO(g)$ can be separated by vacuum distillation in a liquid nitrogen–isopentane slush bath[7] at −160°. A summary of the data showing the yield of $BH_3CO(g)$ obtained under different experimental conditions is given in Table I. Samples of BD_3CO

TABLE I

DATA ILLUSTRATING THE YIELD OF $BH_3CO(g)$ OBTAINED IN THE REACTION OF BOROXINE WITH CO

Initial Temp., °C.	Sample history	Initial P_{CO}, mm.	Final P_{CO}, mm.	Final $P_{B_2H_6}$, mm.	Final P_{BH_3CO}, mm.	P_{BH_3CO} (calcd.),[a] mm.
−29	Sample warmed to 23°; immediate analysis	134.0	102.4	68.4	31.6	20.4
+23	Sample warmed to 85°; immediate analysis at 23°	88.5	65.5	25.8	23.0	8.0
−28	Sample warmed to 80°; immediate analysis at 23°	76.0	47.5	104.0	28.5	11.7
+23	Sample warmed to 85°; immediate analysis at 23°	45.0	33.0	18.0	12.0	3.4
−32	Sample warmed to 23°; immediate analysis	88.0	60.0	56.0	28.0	10.8
−28	Sample warmed to 23°; immediate analysis	211.0	145.0	64.0	66.0	28.1
+23	Sample warmed to 60°; immediate analysis at 23°	118.0	91.5	11.0	26.5	7.3
−34	Sample maintained at 23° for 60 hr.	219.0	177.8	117.8	41.2	46.3

[a] Calculated from equilibrium data for the reaction of B_2H_6 and CO (ref. 3) and highest reaction temperature.

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