fluoride reacts with dinitrogen tetroxide to form nitrosyl tetrafluoroborate, nitryl tetrafluoroborate, and boric oxide as shown in eq. 4.

$$3N_2O_4 + 8BF_3 = 3NO_2BF_4 + 3NOBF_4 + B_2O_3 \qquad (4)$$

As in the case of the reaction of sodium nitrate, there was no evidence for the presence of nitryl tetrafluoroborate among the products. Evans reports that the ratio of nitrosyl to nitryl tetrafluoroborate in the product was a function of the reaction conditions. In view of the identification of NO, $NOBF_4$, and $NaBF_4$ among the ultimate products of the reaction of sodium nitrite with boron trifluoride eq. 5 is implied. However, we did not detect $NO_2BF_4$ among the products, and one possible explanation is that in addition to eq. 5 some reaction took place *via* eq. 6 which would reduce the quantity of $NO_2BF_4$ produced and render its detection difficult. In any case, reaction 2 proposed by Sprague, *et al.*, for the interaction of $NaNO_2$ with $BF_3$, appears incorrect since it does not account for NO and $NOBF_4$ production. Furthermore, the instability of $NaNO_2$ in the presence of $BF_3$ at low temperature indicates that their product, formulated as $[NO^+][NO_2\cdot 2BF_3^-]$, is unlikely.

$$18NaNO_2 + 40BF_3 = 6NO + 18NaBF_4 + 5B_2O_3 + 9NOBF_4 + 3NO_2BF_4 \qquad (5)$$

$$3NaNO_2 + 8BF_3 = 3NaBF_4 + B_2O_3 + 3NOBF_4 \qquad (6)$$

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## Mode of Attachment of Amides in $B_{10}H_{12}\cdot$2amide Complexes

BY W. R. HERTLER AND E. L. MUETTERTIES

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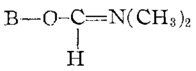
Earlier work in two laboratories[1,2] described the reaction of decaborane(14) with dimethylformamide (DMF) to give $B_{10}H_{12}\cdot 2DMF$. Pace, *et al.*, proposed that the amide in $B_{10}H_{12}\cdot 2DMF$ was bonded to boron through oxygen on the basis of infrared spectral data.[2] In subsequent work, it was found[3] that $B_{10}H_{10}^{2-}$ reacted with dimethylformamide in the presence of strong acid to give $2\text{-}B_{10}H_9\cdot DMF^-$. The structure $2\text{-}B_{10}H_9\text{-}OCH{=}N(CH_3)_2^-$ was proposed for this product because the proton magnetic resonance spectrum showed the presence of two nonequivalent methyl groups at $\tau$ 6.9 (doublet, $J$ = 0.8 c.p.s.) and 7.1 (doublet, $J$ = 1.2 c.p.s.), corresponding, respectively, to the methyl groups *cis* and *trans* to the "formyl" hydrogen atom. Absorption in the infrared spectrum of the product at 1680 cm.$^{-1}$ was noted. Similarly, the presence of two methyl resonances (doublets, $J$ = 0.8 and 1.3 c.p.s.) in the n.m.r. spectrum of $BCl_3\cdot DMF$ led to the assignment of B–O rather than B–N bonding.[4]

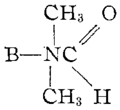
Recently Fein, *et al.*,[5] reinvestigated the reaction of decaborane(14) with dimethylformamide and other amides. They assigned an infrared absorption at 1675 cm.$^{-1}$ to C=O stretching and proposed that $B_{10}H_{12}\cdot 2DMF$ has the structure $B_{10}H_{12}[N(CH_3)_2CHO]_2$.

In order to resolve the conflicting structural assignments (*i.e.*, to determine whether the bonding is of type A or B), an n.m.r. study was undertaken and is the subject of this note.



$$B{-}O{-}\underset{\underset{H}{|}}{C}{=}N(CH_3)_2$$

A



B

The 60-Mc. proton n.m.r. spectrum of $B_{10}H_{12}\cdot 2DMF^5$ in DMF-$d_7$ at 29° shows a multiplet of intensity 1 centered at $\tau$ 2.0, a doublet at $\tau$ 6.95 ($J$ = 0.6 c.p.s.) of intensity 3, and a doublet at $\tau$ 7.25 ($J$ = 1 c.p.s.) of intensity 3. If bonding is of type A, then the doublets at $\tau$ 6.95 and 7.25 can be assigned, respectively, to methyl groups *cis* and *trans* to the "formyl" hydrogen atom ($\tau$ 2.0). These results and their interpretation are similar to those reported earlier[3] for $2\text{-}B_{10}H_9OCH{=}N(CH_3)_2^-$. In order to rationalize the spectral data in terms of a type-B structure, it is necessary to invoke a barrier to rotation about the C–N$(CH_3)_2$ bond so that the two methyl groups are nonequivalent and unequally coupled to the formyl hydrogen atom. The barrier to rotation about the C–N bond in DMF has been attributed to C=N character resulting from overlap of the p orbitals of nitrogen and carbonyl carbon.[6] In the case of structure B, there is no possibility for such delocalization, and any barrier to rotation would have to be due to steric hindrance. Such a barrier should be small, and the two methyl groups should become equivalent at elevated temperatures. At 50°, the two methyl resonances of $B_{10}H_{12}\cdot 2DMF$ are unchanged in position, but the intensity of the peaks gradually diminishes as new peaks appear at the same positions as the peaks of free DMF, namely $\tau$ 2.28, 7.36 (doublet, $J$ = 0.7 c.p.s.), and 7.51 (doublet, $J$ = 1.3 c.p.s.). Apparently at 50°, ligand exchange occurs as

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

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]

BY SATISH K. WASON AND RICHARD F. PORTER

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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: $P_{CO}$ (initial) = $P_{CO}$ (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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(1) Work supported by the Army Research Office (Durham) and the Advanced Research Projects Agency.

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