CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENNSYLVANIA

Preparation and Properties of the Mono- and Bisborane Adducts of N,N′-Dimethylpiperazine and Triethylenediamine

BY A. R. GATTI AND THOMAS WARTIK

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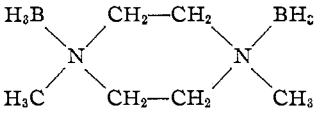
Recently, the preparation and characterization of the monoborane adduct of N,N,N′,N′-tetramethylethylenediamine (TMED) was reported.[1] This was one of very few reported preparations of a monoadduct of a simple difunctional Lewis base.

We now wish to report the preparation of two additional members of this class, the monoborane adducts of N,N′-dimethylpiperazine (hereafter referred to as DMP) and triethylenediamine (referred to as TEDA). One of these, TEDA·BH_3, represents the first example of a compound of this type which is stable at room temperature and above.

The bisborane adduct of DMP, previously unreported, was prepared by addition of gaseous diborane to an ether solution containing excess DMP, and the white, air-stable precipitate was purified by vacuum sublimation at 110°. This purified product melted at 177–178° dec. Gas evolution and partial resolidification were noted when the sample was held above its melting point for a short time. Analysis gave a C:B ratio of 3.04, in good agreement with the expected value.

The H^1 and B^{11} nmr spectra indicate a symmetrical molecule with the structure[2]



The proton spectrum appears as a typical AB system in which the splitting pattern in ppm (with observed relative intensities in parentheses) is: 3.49 (1.00), 3.40 (1.20), 2.87 (1.22), 2.79 (1.03). The theoretical relative intensities (calculated using the coupling constant J = 8.5 cps and the difference in chemical shifts ($\delta_B - \delta_A$) = 60.9 cps) are 1.00:1.32:1.32:1.00. Protons bonded to boron were not observable with the available instrumentation. The remainder of the nmr and the infrared data are presented in Tables I–III.

TABLE I

B¹¹ NUCLEAR MAGNETIC RESONANCE SPECTRA

	Character	Rel intens	δ, ppm[a]	J, cps
DMP·$2BH_3$[b]	Quartet	1.0:2.9:3.0:1.1	+30.4	99
DMP·BH_3[c]	Quartet	1.0:3.1:2.8:0.9	+27.7	96
TEDA·$2BH_3$[b]	Quartet	1.0:3.3:3.2:1.0	+29.2	97

[a] *Vs.* trimethoxyborane as an external reference. [b] In acetonitrile. [c] In DMP.

TABLE II

ASSIGNMENT OF PROTON SHIFTS[a] IN DMP·$2BH_3$ AND TEDA·$2BH_3$[b]

	Methyl	Methylene
DMP·$2BH_3$[c,d]	2.72 (1.66)	2.83 (1.02), 3.44 (1.00)
TEDA·$2BH_3$[e]		3.06

[a] Relative to tetramethylsilane as an internal reference. [b] Observed relative areas indicated in parentheses. [c] Obtained on 100-Mc instrument. [d] In chloroform. [e] In acetonitrile.

TABLE III

INFRARED ABSORPTIONS (CM⁻¹) OF DMP·$2BH_3$

3003 w	1383 vw	1135 s
2958 m	1368 vw	1106 m
2392 vs	1328 m	1038 m
2347 s	1300 s	997 s
2278 s	1196 s	960 m
2096 w	1160 s	912 w
1453 s	1147 s	866 s

DMP·$2BH_3$ was quite soluble in excess DMP although the rate of solution at room temperature was extremely slow. When a portion of this solution was cooled to 0° and subjected to pumping, a white, crystalline solid was obtained which melted to a clear, colorless liquid at 14–16°. The clear melt slowly became turbid and, after standing at room temperature for 18 hr, the sample decomposed to a new white solid (shown by its infrared spectrum to be DMP·$2BH_3$) and a clear liquid (identified as DMP by its infrared spectrum). The ratio of amine released to diadduct formed was 0.98, which agrees well with the value expected for the reaction

$$2\text{DMP}\cdot BH_3 \rightleftharpoons \text{DMP}\cdot 2BH_3 + \text{DMP}$$

Proton magnetic resonance spectra of the DMP solution showed a very complex splitting pattern which was not readily interpreted owing to the proximity of many of the bands to those of the solvent. The B^{11} nmr spectrum appeared as a quartet of approximate relative areas 1:3:3:1 centered at +27.7 ppm *vs.* trimethoxyborane as an external reference. The coupling constant was 96 cps.

The bisborane adduct of TEDA was also prepared by precipitation from ether solution and was purified by crystallization from acetonitrile. This white, crystalline, air-stable compound was nonvolatile and did not melt at temperatures up to 350°, but darkened slightly above 300°. Analysis gave a C:B ratio of 2.98, in good agreement with the theoretical value of 3.00.

The H^1 and B^{11} nmr spectral data as well as the infrared absorptions are presented in Tables I, II, and IV.

Since TEDA is a solid melting above 100°, it is not suited for use as solvent in the preparation of the monoborane adduct. Instead, TEDA·$2BH_3$ was dissolved in TMED at 70°.

$$\text{TEDA}\cdot 2BH_3 + \text{TMED} \rightleftharpoons \text{TEDA}\cdot BH_3 + \text{TMED}\cdot BH_3$$

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[1] A. R. Gatti and T. Wartik, *Inorg. Chem.*, **5**, 329 (1966).

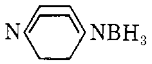
[2] The possibility of geometrical isomerism exists since the BH_3 groups may be axial–axial or axial–equatorial.

TABLE IV

INFRARED ABSORPTIONS (CM^{-1}) OF TEDA·2BH$_3$

2985 m	1460 s	996 m
2915 w	1328 s	873 m
2370 vs	1159 vs	851 s
2309 s	1071 s	841 sh
2273 s	1059 s	

Cooling this solution to room temperature produced a white, air-stable precipitate which could be purified by sublimation *in vacuo* at 100°. The sublimed material melted at 167–170° with decomposition as evidenced by rapid resolidification above the melting point. TEDA·BH$_3$, it may be noted, is the first monoborane adduct of a difunctional base to exhibit thermal stability at and above room temperature. Analysis gave a C:B ratio of 6.01 in good agreement with the value expected for the structure



A sample heated to 180° for several hours and then fractionally sublimed led to recovery of TEDA, TEDA·2BH$_3$, and the starting material, each identified by its infrared spectrum (the infrared absorptions are presented in Table V). The ratio of TEDA to TEDA·2BH$_3$ recovered was 0.95, which agrees with the value expected for the reaction

TABLE V

INFRARED ABSORPTIONS (CM^{-1}) OF TEDA·BH$_3$

2967 s	1477 m	1040 m
2898 m	1460 s	989 m
2358 s	1372 w	962 m
2315 s	1324 s	872 s
2273 s	1287 m	838 s
2203 m	1174 vs	804 m
2128 w	1063 s	790 m
2045 w	1048 s	669 m

$$2\text{TEDA}\cdot\text{BH}_3 \rightleftharpoons \text{TEDA} + \text{TEDA}\cdot2\text{BH}_3$$

The proton nmr spectrum of a benzene solution of the monoborane adduct of TEDA revealed a single resonance which was identical in chemical shift with that of authentic TEDA. While the measurement was being made, a white precipitate assumed to be TEDA·2BH$_3$ appeared. Since, over a period of several months, the crystalline monoadduct has shown no evidence of such deterioration, we infer that the monoadduct is stable in the solid phase but unstable (with respect to disproportionation) in solution.

Experimental Section

All preparations and sublimations with the exception of those involving the monoborane adduct of TEDA were carried out in conventional Stock-type vacuum apparatus. The diadducts were made by vigorously stirring a cold ether solution of excess amine under a diborane atmosphere until no further pressure change occurred. DMP·2BH$_3$ was isolated by filtration under a nitrogen atmosphere and was returned to the vacuum apparatus for sublimation. TEDA·2BH$_3$ was crystallized by concentration of an acetonitrile solution in a nitrogen stream.

TEDA·BH$_3$ was prepared in air by heating TEDA·2BH$_3$ with excess TMED in a water bath at 70°, crystallized by cooling to room temperature, and isolated by suction filtration. The product was washed several times with hexane and purified by vacuum sublimation.

Proton nmr spectra were determined with a Varian A60 and a Varian HA100 spectrometer while B^{11} nmr spectra were obtained with a Varian 4300-2 12-Mc spectrometer.

Infrared spectra were run on mineral oil and perchlorobutadiene mulls using a Beckman IR 5A spectrophotometer.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Boroxine: A Simplified Preparation[1]

BY L. BARTON, F. A. GRIMM, AND RICHARD F. PORTER

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Methods presently available for the preparation of boroxine ($H_3B_3O_3$) are a high-temperature reaction of H_2O with elemental boron[2] and an explosive reaction of B_5H_9 and oxygen.[3] Gaseous $H_3B_3O_3$ is thermodynamically unstable with respect to B_2O_3(s) and B_2H_6(g) at ordinary temperatures.[4] However, under certain conditions, the decomposition reaction is not rapid and it is possible to isolate small quantities of this compound for chemical studies.[5,6] An alternative preparative procedure, starting with diborane and oxygen, offers certain advantages that are described in this paper.

Experimental Section

Diborane was obtained from the reaction of stannous chloride with potassium borohydride *in vacuo* at 250°.[7] Oxygen, research grade, was obtained from the Matheson Co. and used without further purification. The reaction was carried out in a 350-ml Pyrex vessel illustrated in Figure 1. Reaction mixtures were prepared by first adding B_2H_6 and then slowly adding O_2 from a reservoir at pressures high enough to prevent backflow of B_2H_6. The reaction was initiated by applying an electrical discharge from a Tesla coil to a piece of Kovar wire sealed through the neck of the reaction vessel. For these experiments it is imperative that the reaction vessels be taped and placed behind a safety shield. The total pressure of the reaction mixtures never exceeded 40 mm. Under these conditions, initiation of the reaction was noted by a flash of light. It should be cautioned, however, that at higher pressures the explosive reaction may be intense enough to fragment the reaction vessel. Mass spectrometric analyses indicated that the gaseous products were mainly H_2(g) and $B_3O_3H_3$(g). Deuterated boroxine was obtained by substituting B_2D_6 for normal diborane in the reaction. Infrared spectra of $H_3B_3O_3$(g) and $D_3B_3O_3$(g) are shown in Figure

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(1) Work supported by the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency.

(2) W. P. Sholette and R. F. Porter, *J. Phys. Chem.*, **67**, 177 (1963).

(3) G. H. Lee, S. H. Bauer, and S. E. Wiberley, *ibid.*, **67**, 1742 (1963).

(4) R. F. Porter and S. K. Gupta, *ibid.*, **68**, 208 (1964).

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(6) G. H. Lee and R. F. Porter, *Inorg. Chem.*, **5**, 1329 (1966).

(7) W. Jeffers, *Chem. Ind.* (London), 431 (1961).