that ensues at mercury electrodes, and provides a more facile path to reduction via eq 12.

$$Cd(RR'dtc)_2 + Hg \rightleftharpoons Hg(RR'dtc)_2 + Cd(Hg) \quad (12)$$

That is, the differences in reduction behavior for the two metal systems at the two electrode surfaces also may be partly accounted for by considering the standard reduction potentials for these metals[11] at metal and amalgamated electrode surfaces.

$$Cd^{2+} + 2e^- \rightleftharpoons Cd \quad E^\circ = -0.403 \text{ V vs SHE} \quad (13)$$

$$Cd^{2+} + 2e^- \rightleftharpoons Cd(Hg) \quad E^\circ = -0.352 \text{ V vs SHE} \quad (14)$$

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\circ = -0.763 \text{ V vs SHE} \quad (15)$$

$$Zn^{2+} + 2e^- \rightleftharpoons Zn(Hg) \quad E^\circ = -0.763 \text{ V vs SHE} \quad (16)$$

These values are for measurements in aqueous solution, relative to the potential of the standard hydrogen electrode. Values in dichloromethane are unknown but can be presumed to be parallel. If this is the case, then the formation of zinc amalgam from zinc(II) is more difficult than formation of cadmium amalgam from cadmium, as is the case in other solvents. However, interestingly the reduction of metal(II) to the amalgam state is favored over production of the elemental state for cadmium, but this is not the case for zinc. Thus, thermodynamic as well as kinetic data offer some explanation as to (a) the insensitivity of the $Zn(RR'dtc)_2$ reduction potential to electrode material and (b) the relative ease of reduction of $Cd(RR'dtc)_2$ at mercury relative to platinum electrodes. Therefore, it seems that both kinetic and thermodynamic factors may account for the unexpected difficulty in reduction of the cadmium complexes at platinum electrodes.

Conclusion

The electrochemistry of $Zn(RR'dtc)_2$ complexes is similar in many respects to that of the cadmium analogues. This is particularly true under oxidative conditions. Polarographic oxidation processes observed at mercury electrodes in the presence of $Zn(RR'dtc)_2$ occur at almost the same potential as for the cadmium complexes and in a similarly narrow potential range. The results show that a bimetallic dithiocarbamate cation of the kind $[MHg(RR'dtc)_2]^{2+}$ is produced as an intermediate in the oxidation process observed at mercury electrodes. In both cases, the formation of the stable $Hg(RR'dtc)_2$ complexes and the metal perchlorate salt was noted on the longer time scale of controlled-potential electrolysis experiments. At platinum electrodes, $Zn(RR'dtc)_2$ compounds are more difficult to oxidize than $Cd(RR'dtc)_2$. Both species are assumed to be initially oxidized to $[M(R_2R'_2tds)]^{2+}$ complexes. For $Zn(RR'dtc)_2$, the ultimate oxidation product is a more highly ligand oxidized species that may possibly be connected with the solvent oxidation processes that overlap with the zinc oxidation process.

Reduction processes for $Zn(RR'dtc)_2$ are similar at both platinum and mercury electrodes. This is in sharp contrast to the case for $Cd(RR'dtc)_2$, for which a reduction process at a platinum surface was not even observed. At mercury electrodes, reduction processes for the cadmium complexes were seen to be significantly dependent on the presence of an exchange reaction to form the mercury dithiocarbamate complexes and metal amalgam.[3] While such behavior was also observed for $Zn(RR'dtc)_2$ complexes, its contribution to the reduction process was relatively small on the polarographic time scale, and the major irreversible two-electron-reduction response at very negative potentials was almost identical with that found at platinum electrodes.

Registry No. $Zn(Me_2dtc)_2$, 137-30-4; $Zn(Et_2dtc)_2$, 14324-55-1; $Zn((n\text{-}Pr)_2dtc)_2$, 15694-56-1; $Zn((i\text{-}Pr)_2dtc)_2$, 14434-68-1; $Zn((n\text{-}Bu)_2dtc)_2$, 136-23-2; $Zn((i\text{-}Bu)_2dtc)_2$, 36190-62-2; $Zn((c\text{-}Hx)_2dtc)_2$, 35091-69-1; $Zn((pip)dtc)_2$, 13878-54-1; $Zn((pyrr)dtc)_2$, 40211-68-5; $Hg(Me_2dtc)_2$, 15415-64-2; $Hg(Et_2dtc)_2$, 14239-51-1; $Hg((n\text{-}Pr)_2dtc)_2$, 21439-57-6; $Hg((i\text{-}Pr)_2dtc)_2$, 21439-56-5; $Hg((n\text{-}Bu)_2dtc)_2$, 21439-58-7; $Hg((i\text{-}Bu)_2dtc)_2$, 79001-48-2; $Hg((c\text{-}Hx)_2dtc)_2$, 21439-59-8; $Hg((pip)dtc)_2$, 21439-62-3; $Hg((pyrr)dtc)_2$, 41060-60-0; $Cd((n\text{-}Pr)_2dtc)_2$, 55519-99-8; $Cd(Et_2dtc)_2$, 14239-68-0; Hg, 7439-97-6; Pt, 7440-06-4; $[ZnMe_4tds]^{2+}$, 124381-29-9; $[ZnEt_4tds]^{2+}$, 124381-30-2; $[Zn(n\text{-}Pr)_4tds]^{2+}$, 124381-31-3; $[Zn(i\text{-}Pr)_4tds]^{2+}$, 124381-32-4; $[Zn(n\text{-}Bu)_4tds]^{2+}$, 124381-33-5; $[Zn(i\text{-}Bu)_4tds]^{2+}$, 124381-34-6; $[Zn(c\text{-}Hx)_4tds]^{2+}$, 124381-35-7; $[Zn(pip)_2tds]^{2+}$, 124381-36-8; $[Zn(pyrr)_2tds]^{2+}$, 124381-37-9; Zn, 7440-66-6; zinc amalgam, 11146-96-6.

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Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Preparation and Reactions of Bis(aminoboryl) Oxides[1]

M. Komorowska, K. Niedenzu,* and W. Weber

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Bis(aminoboryl) oxides (=1,3,2-diboroxanes) of the general type $[(CH_3)_2N]RBOBR[N(CH_3)_2]$ (**1a**, R = $N(CH_3)_2$; **1b**, R = C_2H_5, **1c**, R = C_6H_5) have been prepared by the controlled hydrolysis of (dimethylamino)chloroboranes, $(CH_3)_2NBClR$. The compounds rearrange at elevated temperatures in an equilibrium reaction with the formation of boroxins, $(RBO)_3$, and bis(dimethylamino)boranes, $[(CH_3)_2N]_2BR$, a reaction that can also be used for the preparation of compounds of type **1**. However, irreversible decomposition of **1** by organyl group migration to yield (dimethylamino)diorganylboranes, $(CH_3)_2NBR_2$, and *B,B',B''*-tris(dimethylamino)boroxin, $[(CH_3)_2NBO]_3$, has also been observed at elevated temperatures. Transamination reactions of **1** have been utilized for the preparation of additional bis(aminoboryl) oxides, e.g., $(C_4H_8N)(C_6H_5)BOB(C_6H_5)(NC_4H_8)$ (**2**, C_4H_8NH = pyrrolidine), as well as for the synthesis of heterocyclic systems containing an annular BOB group, e.g., $O(\mu\text{-}RBNR')_2CX$ (**4**, X = O, S) from the reaction of **1** with (thio)ureas, $(R'HN)_2CX$. The heterocycle $O(\mu\text{-}C_2H_5BNCH_3)_2BC_2H_5$ (**3**) was obtained from the reaction of **1b** with $C_2H_5B(NHCH_3)_2$. Transamination of **1** with amides or aminoboronation reactions with isocyanates gave bicyclic systems (by intramolecular coordination) of the amidoborane, $(R'CONR'')RBOBR(NR''COR')$ (**8**), or ureidoborane, $[(CH_3)_2NCONR']RBOBR[NR'CON(CH_3)_2]$ (**6**), type, respectively. A triply bridged species containing both three- and four-coordinate boron, $RB(\mu\text{-}NHCH_3)(\mu\text{-}OBRO)(\mu\text{-}NCH_3CHNCH_3)BR$ (**10**), was obtained from the reaction of **1c** with *N*-methylformamide.

Introduction

Although a variety of diboryl oxides (=1,3,2-diboroxanes) of the general type RR'BOBRR' are known,[2] the preparation of only one species has been described where one of the boron substituents is a simple amino group, i.e., $[(CH_3)_2N](C_6H_5)BOB(C_6H_5)[N(CH_3)_2]$.[3,4] Furthermore, $[(CH_3)_2N]HBOBH[N(CH_3)_2]$ has

(1) Boron–Nitrogen Compounds. 123 (K.N.). Part 122: Komorowski, L.; Niedenzu, K. *Z. Naturforsch.*, in press. Parts of the experimental work were extracted from ref 3.

(2) *Gmelin Handbook of Inorganic Chemistry*; Springer Verlag: Berlin, 1977; New Supplement Series, Vol. 48, Boron Compounds 16, pp 73–100.

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been observed among the products of the reaction of carbon atoms with (dimethylamino)borane, $(CH_3)_2NBH_2$, and was characterized by spectroscopic data.[5] Attempts to prepare $[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ by the reaction of $[(CH_3)_2N]_2BCl$ with HgO have failed,[6,7] but the formation of the former by the interaction of $[(CH_3)_2N]_3B$ with $[(CH_3)_2NBO]_3$ in a 3:1 molar ratio (see eq 2, below) had been indicated, although the compound was not isolated.[3] All of the other relatively scarce 1,3,2-diboroxanes containing a B-N bond always contain the nitrogen (and most often also the boron) incorporated into a heterocyclic system. On the other hand, species of the type RR'BOBRR', where R and/or R' are terminal amino groups derived from a volatile amine, should be valuable starting materials for the preparation of a variety of diboron derivatives containing the BOB moiety, including heterocyclic species. One relevant example employing $[(CH_3)_2N](C_6H_5)BOB(C_6H_5)[N(CH_3)_2]$ (**1c**) has already been described.[4]

The present study reports the preparation, characterization, and representative reactions of some bis((dimethylamino)boryl) oxides, $[(CH_3)_2N]RBOBR[N(CH_3)_2]$ (**1**), i.e., 1,3,2-diboroxanes containing terminal boron-bonded $N(CH_3)_2$ groups.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined in sealed capillaries on a Mel-Temp block. Reactions and transfers were carried out in an inert atmosphere. Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL-200 or VXR-400 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating shifts downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR; external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet. An asterisk denotes a broad signal. Coupling constants J are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F instrument; data are normally listed to m/z 50 for 5% or greater relative abundances (in parentheses) only.

$[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ (1a). A solution of 0.6 g (33 mmol) of water in 75 mL of ether was added dropwise and with stirring to a solution of 9.0 g (67 mmol) of bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$,[8] and 7.3 g (72 mmol) of triethylamine in 300 mL of pentane. A colorless precipitate formed immediately. The mixture was refluxed for 30 min and then stirred at room temperature for 24 h, a small amount of precipitate was filtered off, and the clear liquid was distilled under reduced pressure to give 5.2 g (70%) of **1a**, bp 30 °C (7 Torr). Anal. Calcd for $C_8H_{24}B_2N_4O$ (M_r = 219.92): C, 44.92; H, 11.31; B, 10.11; N, 26.19; O, 7.48. Found: C, 44.37; H, 11.34; B, 10.03; N, 26.09.

NMR data: $\delta(^1H)$ 2.72 (1 H, s), 2.52 (1 H, s) (coalescence of signals at 48 °C); $\delta(^{11}B)$ 27.5 (s, $h_{1/2}$ = 100 Hz); $\delta(^{13}C)$ 39.7, 39.1. Mass spectrum (13 eV): m/z 143 (38), 142 (10), 136 (8), 135 (8), 134 (30), 133 (20), 121 (6), 119 (16), 100 (5), 99 (100), 98 (29), 90 (28). A small ion cluster was observed at m/z 211.

Alternate Procedure. A stirred mixture of 31.3 g (0.1 mol) of $[(CH_3)_2NBO]_3$ (see below) and 42.9 g (0.3 mol) of $[(CH_3)_2N]_3B$[9] was heated to 100 °C for 90 min and slowly cooled to room temperature. Distillation of the product under vacuum gave 47.5 g (74%) of pure **1a**, bp 30 °C (7 Torr), identical (NMR data) with the preceding material.

$[(CH_3)_2NBO]_3$. A stirred mixture of 17.4 g (0.25 mol) of finely ground dried (2 h at 200 °C under vacuum) B_2O_3 and 38.6 g (0.27 mol) of $[(CH_3)_2N]_3B$[9] was heated in an oil bath at 180 °C. After 5 h, the refluxing subsided considerably; heating was continued for 8 h, and then the temperature of the bath was slowly increased to 210 °C. When the mixture was kept at that temperature for 2 h more, most of the B_2O_3 had dissolved and heating was continued for an additional 4 h. At that time a very minor amount of insoluble material remained and began to turn brown. The oil bath was removed and the material solidified on cooling to room temperature, mp 64 °C (lit.[10] mp 64 °C). The product, $\delta(^1H)$ 2.65 (s), can be further purified by distillation; bp 90 °C (9 Torr).

$[(CH_3)_2N](C_2H_5)BOB(C_2H_5)[N(CH_3)_2]$ (1b) was prepared in a fashion analogous to that for **1a** by reaction of 11.5 g (96 mmol) of (dimethylamino)chloroethylborane, $(CH_3)_2NBCl(C_2H_5)$,[11] and 9.8 g (97 mmol) of triethylamine in 600 mL of pentane with 0.9 g (50 mmol) of water in 100 mL of ether. Distillation of the product over a 30-cm silver-mantle column gave 7.8 g (44%) of **1b**, bp 35 °C (1 Torr). Anal. Calcd for $C_8H_{22}B_2N_2O$ (M_r = 183.90): C, 52.25; H, 12.06; B, 11.76; N, 15.23; O, 8.70. Found: C, 52.63; H, 12.55; B, 11.72; N, 15.29.

NMR data: $\delta(^1H)$ 2.63 (3 H, s), 2.57 (3 H, s), 0.9–0.7 (5 H, unresolved m) (coalescence of the two methyl signals occurred at 85 °C); $\delta(^{11}B)$ 31.4 (s, $h_{1/2}$ = 175 Hz); $\delta(^{13}C)$ 37.2, 35.6, 8.3, 7*. Mass spectrum (14 eV): m/z 155 (100), 154 (20), 99 (39).

Alternate Procedure. A stirred mixture of 5.0 g (29.8 mmol) of *B,B',B''*-triethylboroxin, $(C_2H_5BO)_3$,[12] and 11.5 g (89.5 mmol) of bis(dimethylamino)ethylborane, $[(CH_3)_2N]_2BC_2H_5$,[13] was heated for 1.5 h in an oil bath at 125 °C. The mixture was slowly cooled to room temperature and then distilled under vacuum over a 10-cm silver-mantle column to give 15.1 g (91.5%) of **1b**, bp 35 °C (1 Torr).

$[(CH_3)_2N](C_6H_5)BOB(C_6H_5)[N(CH_3)_2]$ (1c) was prepared according to eq 1 in a fashion analogous to that of the preceding compounds by using (dimethylamino)chlorophenylborane, $(CH_3)_2NBCl(C_6H_5)$,[14-16] as the starting material. However, distillation under vacuum gave only a product of bp 125 °C (1 Torr), which was contaminated by ca. 10–15% of bis(dimethylamino)phenylborane[17] (NMR). Purification of the crude material by recrystallization as outlined previously was also not efficient, since it was difficult to remove traces of residual $(C_2H_5)_3N{\cdot}HCl$. Therefore, the previously described[4] ligand exchange reaction according to eq 2 is the preferable method for the preparation of **1c**. As noted before,[4] the product does not even have to isolated if it is to be used for subsequent transformations (see the following experiment).

$(C_4H_8N)(C_6H_5)BOB(C_6H_5)(NC_4H_8)$ (2). A mixture of 10.4 g (33 mmol of *B,B',B''*-triphenylboroxin, $(C_6H_5BO)_3$, and 17.6 g (100 mmol) of bis(dimethylamino)phenylborane, $[(CH_3)_2N]_2BC_6H_5$,[17] was heated for 90 min to 125 °C to generate **1c** in situ. After the product was cooled to room temperature, 25.0 g (350 mmol) of freshly distilled (over metallic sodium) pyrrolidine was added. The stirred mixture was then slowly warmed until it started boiling; it was kept at that temperature for 30 min. After the mixture was cooled to room temperature, the desired product precipitated. It was collected, washed with 10 mL of pyrrolidine, and dried under vacuum (3 days, oil pump) to give 31.2 g (64%) of **2**, mp 91–93 °C. Anal. Calcd for $C_{20}H_{26}B_2N_2O$ (M_r = 332.06): C, 72.34; H, 7.89; B, 6.51; N, 8.44; O, 4.82. Found: C, 70.50; H, 8.19; N, 8.35.

NMR data: $\delta(^1H)$ 7.5 (2 H, m), 7.3 (3 H, m), 3.3 (4 H, ill-resolved t), 1.7 (4 H, m); $\delta(^{11}B)$ 28.5 (s, $h_{1/2}$ = 360 Hz); $\delta(^{13}C)$ 138.6*, 133.0, 128.1, 127.2, 47.8, 46.4, 26.8, 25.5. Mass spectrum: m/z 333 (14), 332 (72), 331 (58), 330 (17), 304 (7), 303 (8), 262 (23), 261 (16), 260 (14), 259 (8), 255 (32), 254 (29), 253 (70), 252 (33), 234 (12), 233 (6), 237 (18), 226 (10), 225 (6), 185 (7), 184 (6), 165.5 (17), 158 (100), 156 (21), 155 (7), 151 (10), 130 (9), 129 (10), 127 (7), 116 (27), 115 (8), 106 (8), 105 (7), 104 (7), 91 (28), 89 (43), 82 (8), 78 (9), 72 (78), 71 (24), 70 (51), 69 (8).

$O(\mu\text{-}C_2H_5BNCH_3)_2BC_2H_5$ (3). A stirred mixture of 3.0 g (16.3 mmol) of **1b** and 3.2 g (31.3 mmol) of bis(methylamino)ethylborane, $C_2H_5B(NHCH_3)_2$,[18] was slowly heated to 100 °C. Dimethylamine evolved, and the mixture was kept at the cited temperature for 6 h. The excess $C_2H_5B(NHCH_3)_2$ was distilled off under atmospheric pressure, and the residue was distilled under vacuum over a 15-cm silver-mantle column to give 2.5 g (78%) of the desired product, bp 67–69 °C (1 Torr). Anal. Calcd for $C_8H_{21}B_3N_2O$ (M_r = 193.77): C, 49.59; H, 10.92; B, 16.74; N, 14.46; O, 8.26. Found: C, 49.69; H, 11.02; B, 16.74; N, 14.34.

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NMR data: $\delta(^1H)$ 2.81 (6 H, s), 1.00–0.96 (15 H, m); $\delta(^{11}B)$ 37.7 (1 B, s, $h_{1/2}$ = 220 Hz), 35.5 (2 B, s, $h_{1/2}$ = 240 Hz); $\delta(^{13}C)$ 31.6, 8.2*, 7.8, 7.4, 6.0*. Mass spectrum: m/z 195 (5), 194 (57), 193 (38), 192 (12), 166 (6), 165 (100), 164 (69), 163 (27), 137 (63), 136 (53), 135 (26), 109 (60), 108 (57), 107 (15), 93 (14), 92 (7), 82 (24), 81 (24), 80 (26), 68 (22), 67 (15), 65 (9), 54 (15), 52 (16), 51 (8), 44 (7), 40 (28), 39 (7), 38 (7), 36 (12), 32 (9).

O[μ-$(CH_3)_2NBNCH_3]_2$CO (4a). A mixture of 4.4 g (20 mmol) of **1a** and 1.8 g (20 mmol) of *N,N'*-dimethylurea was stirred at room temperature for 6 days. The mixture thickened increasingly, and after the given period of time it had become a thick paste. This was heated with stirring in an oil bath of 150 °C for 12 h, during which time the calculated amount of dimethylamine was given off. The product was distilled under high vacuum and then sublimed to give 3.2 g (77%) of **4a**, mp 78–80 °C. Anal. Calcd for $C_7H_{18}B_2N_4O_2$ (M_r = 211.87): C, 39.68; H, 8.56; B, 10.20; N, 26.44; O, 15.10. Found: C, 37.55; H, 8.64, B, 10.69; N, 24.36.

NMR data: $\delta(^1H)$ 3.00 (1 H, s), 2.73 (2 H, s); $\delta(^{11}B)$ 23.2 (s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 162.1, 37.3, 31.8. Mass spectrum: m/z 213 (10), 212 (100), 211 (61), 210 (12), 197 (96), 184 (8), 183 (6), 176 (8), 175 (6), 156 (16), 155 (12), 154 (56), 153 (26), 152 (5), 143 (7), 140 (43), 139 (21), 138 (5), 132 (8), 127 (18), 126 (11), 113 (48), 112 (27), 111 (20), 110 (9), 105 (6), 99 (83), 98 (23), 97 (11), 91 (11), 85 (31), 84 (14), 83 (59), 82 (16), 76.5 (23), 76 (10), 70 (10), 69.5 (5), 69 (13), 68 (8), 63 (9), 58 (7), 56 (63), 55 (15), 54 (9).

The same compound (**4a**) has previously been obtained in 75% yield from the interaction of tris(dimethylamino)borane with *N,N'*-dimethylurea; the following NMR data (solution in CH_2Cl_2) were reported for a species of mp 105–109 °C and bp 125 °C (2 × 10^{-3} Torr): $\delta(^1H)$ 2.97 (1 H, s), 2.73 (2 H, s); $\delta(^{11}B)$ 23.4.[19]

O(μ-$C_2H_5BNCH_3)_2$CO (4b). A stirred mixture of 4.05 g (22 mmol) of **1b** 1.94 g (22 mmol) of *N,N'*-dimethylurea, and 50 mL of toluene was heated for 4 h to 50–60 °C and was then refluxed for 1 h. The solvent was distilled off to leave 3.75 g (94%) of a colorless crystalline material, mp 48–52 °C. It was purified by sublimation under vacuum to give **4b**, mp 51–53 °C. Anal. Calcd for $C_7H_{16}B_2N_2O_2$ (M_r = 181.84): C, 46.24; H, 8.87; B, 11.89; N, 15.41; O, 17.60. Found: C, 46.31; H, 8.78; N, 15.29.

NMR data: $\delta(^1H)$ 2.98 (3 H, s), 1.04 (5 H, s); $\delta(^{11}B)$ 35.9 (s, $h_{1/2}$ = 260 Hz); $\delta(^{13}C)$ 159.0, 30.5, 8*, 7.4. Mass spectrum: m/z 183 (5), 182 (51), 181 (100), 180 (42), 179 (5), 168 (5), 155 (6), 154 (6), 153 (6), 139 (8), 138 (7), 125 (7), 124 (8), 96 (6), 88 (53), 69 (7), 68 (15), 58 (44), 55 (5).

O(μ-$C_2H_5BNCH_3)_2$CS (4e). A stirred mixture of 2.85 g (15.5 mmol) of **1b**, 1.61 g (15.5 mmol) of *N,N'*-dimethylthiourea, and 50 mL of toluene was heated in an oil bath of 50–60 °C for 6 h and then refluxed for 16 h. Toluene was distilled off, and the liquid residue was distilled under vacuum to give 3.0 g (97%) of **4e**, bp 94 °C (1 Torr). Anal. Calcd for $C_7H_{16}B_2N_2OS$ (M_r = 197.90): C, 42.98; H, 8.15; B, 10.92; N, 14.15; O, 8.08; S, 16.02. Found: C, 42.49; H, 8.15; B, 10.92; N, 14.31; S, 16.02.

NMR data: $\delta(^1H)$ 3.34 (3 H, s), 1.07 (5 H, m); $\delta(^{11}B)$ 34.1 (s, $h_{1/2}$ = 300 Hz); $\delta(^{13}C)$ 191.6, 37.9, 9.3*, 7.5. Mass spectrum: m/z 199 (14), 198 (100), 197 (97), 196 (38), 181 (11), 171 (9), 170 (17), 169 (43), 168 (32), 167 (11), 165 (5), 164 (6), 153 (7), 143 (7), 142 (6), 141 (10), 140 (6), 139 (22), 138 (24), 137 (7), 125 (21), 124 (22), 123 (13), 114 (7), 113 (6), 101 (5), 100 (6), 97 (12), 95 (10), 72 (12), 69 (18), 68 (45), 67 (20), 66 (10), 57 (9), 56 (5), 55 (14), 54 (6).

O(μ-$C_6H_5BNH)_2$CO (4c). A stirred mixture of a solution of 5.6 g (20 mmol) of **1c** in 30 mL of toluene and 1.2 g (20 mmol) of urea was heated to reflux for 12 h. The solid material was collected and heated under high vacuum (10^{-3} Torr) until the remaining dimethylamine had been given off, and then was sublimed at a bath temperature of 130–150 °C to give 4.1 g (82%) of **4c**, mp 261–264 °C dec. Anal. Calcd for $C_{13}H_{12}B_2N_2O_2$ (M_r = 249.87): C, 62.49; H, 4.84; B, 8.65; N, 11.21; O, 12.81. Found: C, 61.40; H, 5.01; B, 8.68; N, 11.92.

NMR data (solution in $(CD_3)_2SO$): $\delta(^1H)$ 9.33* (1 H, s), 8.2 (2 H, m), 7.7 (3 H, m); $\delta(^{11}B)$ (at 140 °C for increased solubility) 31.5 (s, $h_{1/2}$ = 700 Hz). Mass spectrum: m/z 251 (19), 250 (100), 249 (62), 248 (7), 208 (8), 207 (20), 206 (13), 205 (6), 180 (8), 179 (5), 173 (8), 172 (5), 165 (12), 164 (35), 163 (18), 131 (5), 130 (13), 129 (7), 105 (13), 104 (36), 103 (82), 102 (24), 87 (5), 78 (10), 77 (20), 76 (14), 52 (13), 51 (7).

O(μ-$C_6H_5BNCH_3)_2$CO·$(CH_3)_2$NH (5a). A mixture of 5.6 g (20 mmol) of **1c**, 1.8 g (20 mmol) of *N,N'*-dimethylurea, and 20 mL of toluene was stirred at 60–70 °C. Dimethylamine evolved and a colorless precipitate formed. It was collected, washed with toluene, and dried under vacuum to give 3.5 g (64%) of **5a**, mp 173–174 °C dec. Anal. Calcd for $C_{17}H_{23}B_2N_3O_2$ (M_r = 323.01): C, 63.21; H, 7.18; B, 6.69; N, 13.01; O, 9.91. Found: C, 61.55; H, 7.52; N, 12.74.

NMR data (solution in CD_2Cl_2): $\delta(^1H)$ 7.7 (4 H, m), 7.4 (6 H, m), 6.65* (1 H, s), 2.95 (6 H, s), 2.42 (6 H, s); $\delta(^{11}B)$ 20.6 (s, $h_{1/2}$ = 800 Hz). The EI mass spectrum of the material was essentially identical with that of the following compound (**4d**), except that additional strong peaks were observed for dimethylamine.

O(μ-$C_6H_5BNCH_3)_2$CO (4d). A mixture of 8.3 g (26.5 mmol) of $(C_6H_5BO)_3$ and 14.0 g (79.5 mmol) of $[(CH_3)_2N]_2BC_6H_5$[17] was heated for 90 min to 125 °C in order to generate **1c** in situ. After the mixture had cooled to room temperature, 150 mL of toluene and 7.0 g (79.5 mmol) of *N,N'*-dimethylurea were added and the stirred mixture was heated to reflux for 4 days. Toluene was distilled off, and the residue was distilled under vacuum to give 20.0 g (98%) of product. It was further purified by sublimation. The glassy sublimate slowly crystallized on standing to give **4d**, mp 98–102 °C. Anal. Calcd for $C_{15}H_{16}B_2N_2O_2$ (M_r = 277.93): C, 64.82; H, 5.80; B, 7.78; N, 10.08; O, 11.51. Found: C, 63.05; H, 6.07; B, 7.80; N, 9.97.

NMR data: $\delta(^1H)$ 7.9 (2 H, m), 7.5 (3 H, m), 3.30 (3 H, s); $\delta(^{11}B)$ 33.5 (s, $h_{1/2}$ = 500 Hz); $\delta(^{13}C)$ 159.2, 133.8, 130.4, 127.6, 32.3. Mass spectrum: m/z 279 (11), 278 (59), 277 (100), 276 (49), 275 (11), 220 (5), 165 (6), 118 (5), 117 (17), 116 (48), 115 (12), 105 (9), 104 (6), 91 (10), 90 (5), 89 (42), 88 (29), 87 (8), 58 (16).

The same material (**4d**) was obtained on heating of **5a** above its melting point until the evolution of dimethylamine ceased (purification by distillation and sublimation as above).

A material of mp 105–109 °C, bp 125 °C (2 × 10^{-3} Torr) has previously been obtained in 75% yield by treatment of *N,N'*-dimethylurea with 2 molar equiv of *n*-butyllithium and subsequent reaction with dichlorophenylborane. NMR data (solution in CD_2Cl_2): $\delta(^1H)$ 7.65–7.01 (5 H, m), 2.95 (3 H, s); $\delta(^{11}B)$ 35.2.[19]

O(μ-$C_6H_5BNCH_3)_2$CS·$(CH_3)_2$NH (5b). A stirred mixture of 5.6 g (20 mmol) of **1c**, 2.1 g (20 mmol) of *N,N'*-dimethylthiourea, and 25 mL of toluene was refluxed for 24 h. After it was cooled to room temperature, it separated in two phases, one of which crystallized on standing overnight. The precipitate was collected, washed with toluene, and dried under vacuum to give 6.1 g (90%) of **5b**, mp 174–176 °C dec. The elemental analysis gave reasonable but varying data and nitrogen was consistently found to be high. However, the NMR and mass spectral data clearly substantiate the existence of the compound (though impure).

NMR data (solution in CD_2Cl_2): $\delta(^1H)$ 7.6 (2 H, m), 7.3 (3 H, m), 3.28 (3 H, s), 2.33 (3 H, s); additional small signals were observed at $\delta(^1H)$ 7.17, 2.92, and 2.83. The mass spectrum was essentially identical with that of the following compound (**4f**), except for the observation of additional peaks for dimethylamine at m/z 45 and 44.

O(μ-$C_6H_5BNCH_3)_2$CS (4f). The product of the preceding reaction was heated to 120 °C at 10^{-3} Torr in a sublimator. Dimethylamine was given off and the material slowly sublimed to give colorless **4f**, mp 138–139 °C. Anal. Calcd for $C_{15}H_{16}B_2N_2OS$ (M_r = 293.99): C, 61.28; H, 5.49; B, 7.35; N, 9.53; O, 5.44; S, 10.91. Found: C, 61.07; H, 5.58; B, 7.37; N, 9.36.

NMR data: $\delta(^1H)$ 7.75 (2 H, m), 7.4 (3 H, m), 3.63 (3 H, s); $\delta(^{11}B)$ 32.0 (s, $h_{1/2}$ = 450 Hz, recorded on a solution in CD_2Cl_2). Mass spectrum: m/z 295 (18), 294 (75), 293 (100), 292 (47), 291 (6), 234 (10), 233 (5), 208 (5), 165 (9), 164 (8), 163 (5), 147 (5), 117 (7), 116 (21), 115 (6), 105 (5), 104 (9), 91 (10), 89 (22), 88 (8), 87 (7), 77 (6).

[$(CH_3)_2NCONCH_3$](C_2H_5)BOB(C_2H_5)[$NCH_3CON(CH_3)_2$] (6a). A solution of 4.10 g (22.3 mmol) of **1b** and 2.54 g (44.6 mmol) of methyl isocyanate in 20 mL of toluene was slowly heated so that the mixture began to reflux after about 1 h. The mixture was then refluxed for 3 h and cooled to room temperature. A colorless precipitate formed and was collected, washed with toluene, and dried under vacuum to give 3.55 g of colorless crude product, mp 124–148 °C. Concentration of the toluene solutions gave 2.55 g of additional, slightly yellow material for a total yield of 92%. Recrystallization from toluene gave **6a**, mp 147–149 °C. Anal. Calcd for $C_{12}H_{28}B_2N_4O_3$ (M_r = 298.00): C, 48.37; H, 9.47; B, 7.25; N, 18.80; O, 16.11. Found: C, 48.56; H, 9.31; B, 7.11; N, 18.97.

NMR data: $\delta(^1H)$ 2.82 (6 H, s), 2.74 (3 H, s), 0.83 (3 H, t, J = 7), 0.4* (2 H, unresolved q); $\delta(^{11}B)$ 5.1 (s, $h_{1/2}$ = 200 Hz); $\delta(^{13}C)$ 164.9, 39.1, 34.4, 10.5*, 9.0. Mass spectrum (14 eV): m/z 269 (26), 268 (11), 213 (10), 212 (100), 211 (54), 210 (7), 198 (5), 197 (51), 196 (26), 156 (11), 102 (9), 57 (6).

[$(CH_3)_2NCONCH_3$](C_6H_5)BOB(C_6H_5)[$NCH_3CON(CH_3)_2$] (6b). A stirred solution of 14 g (50 mmol) of **1c** and 5.7 g (100 mmol) of methyl isocyanate in 25 mL of toluene was slowly heated so that the mixture began to reflux after about 45 min. During this period a precipitate began to form and the mixture was refluxed for 3 h. The precipitate was collected, washed with toluene, and dried under vacuum to give 13.2 g (67%) of **6b**, mp 198–205 °C dec. Anal. Calcd for $C_{20}H_{28}B_2N_4O_3$ (M_r

(19) Maringgele, W. *Chem. Ber.* **1982**, *115*, 3271–3289.

= 394.09): C, 60.95; H, 7.16; B, 5.49; N, 14.22; O, 12.18. Found: C, 59.75; H, 7.63; N, 14.11.

NMR data: $\delta(^1H)$ 7.55 (2 H, m), 7.15 (3 H, m), 2.92 (6 H, s), 2.60 (3 H, s); $\delta(^{11}B)$ 3.1 (s, $h_{1/2}$ = 220 Hz); $\delta(^{13}C)$ 164.2, 132.1, 126.8, 126.0, 38.9, 35.1. Mass spectrum: *m/z* 394 (8), 294 (15), 293 (100), 292 (63), 291 (9), 189 (12), 132 (16), 118 (7), 103 (5), 102 (16), 91 (10), 85 (19), 79 (7), 72 (30), 59 (13), 58 (5).

$[(CH_3)_2NCONC_6H_5](C_6H_5)BOB(C_6H_5)[NC_6H_5CON(CH_3)_2]$ (6c). A stirred solution of 11.2 g (40 mmol) of **1c** and 9.5 g (80 mmol) of phenyl isocyanate in 25 mL of toluene was refluxed for 90 min. The precipitate was collected, stirred with 25 mL of hot toluene for 10 min, filtered, and dried under vacuum to yield 13.2 g (64%) of **6c**, mp 211 °C dec. Anal. Calcd for $C_{30}H_{32}B_2N_4O_3$ (M_r = 518.23): C, 69.53; H, 6.22; B, 4.17; N, 10.81; O, 9.26. Found: C, 69.46; H, 6.19; B, 4.16; N, 10.79.

NMR data (solution in CD_2Cl_2): $\delta(^1H)$ 7.5* (m) + 7.1 (m) + 6.6 (m) (5 H total), 2.53 (3 H, s). Mass spectrum: *m/z* 518 (5), 356 (27), 355 (100), 354 (49), 251 (11), 179 (6), 147 (26), 132 (40), 131 (8), 119 (6), 91 (16), 77 (5), 72 (24).

$(OHCNCH_3)(C_6H_5)BOB(C_6H_5)(NCH_3CHO)$ (7a). A mixture of 5.8 g (11 mmol) of **6c** and 20 mL of *N*-methylformamide was heated to boiling. A clear solution resulted, which was kept boiling for 10 min and then cooled to room temperature. Excess *N*-methylformamide was removed under vacuum, and the residue was treated with a small portion of CH_2Cl_2. The solution was filtered off (leaving behind undissolved *N,N'*-dimethyl-*N'*-phenylurea), and the clear filtrate was evaporated. Some *N,N*-dimethyl-*N'*-phenylurea was sublimed off the residue (100 °C bath temperature at 10^{-3} Torr), and the remaining solid was recrystallized from benzene to give 2.03 g (60%) of **8a**, mp 170–172 °C. Anal. Calcd for $C_{16}H_{18}B_2N_2O_3$ (M_r = 307.95): C, 62.40; H, 5.89; B, 7.02; N, 9.10; O, 15.59. Found: C, 63.10; H, 5.57; N, 8.55.

NMR data: $\delta(^1H)$ 7.90* (1 H, s), 7.55 (2 H, m), 7.25 (3 H, m), 2.67 (3 H, s). Mass spectrum: *m/z* 309 (9), 308 (74), 307 (38), 251 (17), 250 (100), 249 (47), 248 (9), 231 (41), 230 (19), 190 (90), 189 (41), 105 (19), 104 (12), 59 (7).

$(CH_3CONCH_3)(C_6H_5)BOB(C_6H_5)(NCH_3COCH_3)$ (8b). A stirred mixture of 11.2 g (40 mmol) of **1c**, 5.8 g (80 mmol) of *N*-methylacetamide, and 25 mL of toluene was heated to reflux for 5 days while a slow stream of dry nitrogen was passed through the reaction vessel. The resultant crystalline precipitate was collected, washed with toluene, and dried under vacuum. It was recrystallized from chlorobenzene to give 10.6 g (79%) of **8b**, mp 226 °C dec. Anal. Calcd for $C_{18}H_{22}B_2N_2O_3$ (M_r = 336.01): C, 64.34; H, 6.60; B, 6.44; N, 8.34; O, 14.28. Found: C, 64.36; H, 6.52; N, 8.36.

NMR data (solution in CD_2Cl_2): $\delta(^1H)$ 7.55 (2 H, m), 7.25 (3 H, m), 2.67 (3 H, s), 2.23 (3 H, s); $\delta(^{11}B)$ 3.0 (s, $h_{1/2}$ = 150 Hz). Mass spectrum: *m/z* 336 (19), 335 (9), 264 (51), 263 (22), 262 (6), 204 (23), 203 (12), 56 (100).

$C_6H_5B(\mu\text{-}NHCH_3)(\mu\text{-}OBC_6H_5O)(\mu\text{-}NCH_3CHNCH_3)BC_6H_5$ (10). A mixture of 11.2 g (40 mmol) of **1c**, 4.7 g (80 mmol) of *N*-methylformamide, and 25 mL of toluene was slowly heated. When a bath temperature of about 100 °C was reached, dimethylamine began to evolve. The mixture was refluxed for 3 days, and volatiles were removed under reduced pressure and slow heating to about 150 °C. A brownish glassy residue remained, most of which was soluble in cold methanol (and was not further characterized). The insoluble crystalline material was purified by recrystallization from methanol to give 1 g of **10**, mp 204 °C. Anal. Calcd for $C_{22}H_{26}B_3N_3O_2$ (M_r = 396.90): C, 66.57; H, 6.60; B, 8.17; N, 10.59; O, 8.06. Found: C, 67.04; H, 6.80; N, 10.84.

NMR data (solution in CD_2Cl_2/CD_3OD): $\delta(^1H)$ 8.15 (m) + 8.3* (m) + 7.4 (m) (15 H total), 7.56 (1 H, s), 2.72 (6 H, s), 1.63 (3 H, d, J = 6.5), 3.2* (1 H, s); $\delta(^{11}B)$ 27.1 (1 B, s, $h_{1/2}$ = 500 Hz), 1.5 (2 B, s, $h_{1/2}$ = 120 Hz). Mass spectrum: *m/z* 398 (6), 397 (28), 396 (33), 395 (17), 320 (18), 263 (19), 217 (9), 216 (100), 215 (51), 214 (7), 159 (5), 118 (37), 117 (11), 116 (6), 112 (6), 91 (18), 89 (6), 72 (32), 71 (13), 55 (13). IR spectrum: ν(NH) = 3300 cm^{-1}; $\nu(CH_{formamidinium})$ = 2805 cm^{-1}.

Results

The present study illustrates that bis((dimethylamino)boryl) oxides (=1,3,2-diboroxanes) of the type $[(CH_3)_2N]RBOBR[N(CH_3)_2]$ (**1**) can be obtained by careful hydrolysis of the corresponding (dimethylamino)chloroboranes in the presence of triethylamine as hydrogen chloride acceptor, as is shown in eq 1.

$$2[(CH_3)_2N]RBCl + H_2O \xrightarrow[-2(C_2H_5)_3N\cdot HCl]{+2(C_2H_5)_3N} [(CH_3)_2N]RBOBR[N(CH_3)_2] \quad (1)$$

1a: R = $N(CH_3)_2$
1b: R = C_2H_5
1c: R = C_6H_5

An alternative method as illustrated in the equilibrium in eq 2 has previously been employed for the preparation of the diboryl oxide with R = C_6H_5 (**1c**).[3,4]

$$(RBO)_3 + 3[(CH_3)_2N]_2BR \rightleftarrows 3[(CH_3)_2N]RBOBR[N(CH_3)_2] \quad (2)$$

The species $[(CH_3)_2N]_2BOB[N(CH_3)_2]_2$ (**1a**) was readily obtained from bis(dimethylamino)chloroborane according to eq 1. The compound was distilled under reduced pressure without any decomposition and was characterized by NMR data. A 3:1 molar mixture of $[(CH_3)_2N]_3B$ and $[(CH_3)_2NBO]_3$ could give a ^1H NMR spectrum essentially identical with that observed for **1a**. However, the ^{11}B NMR spectrum of the latter compound exhibits only a single and sharp signal at 27.5 ppm, whereas $\delta(^{11}B)$ for $[(CH_3)_2N]_3B$ is observed at 27.3, and that for $[(CH_3)_2NBO]_3$ at 21.3.[20] The mass spectrum of **1a** was essentially that of *B,B',B''*-tris(dimethylamino)boroxin superimposed on that of tris(dimethylamino)borane. This illustrates that under the operating conditions of the mass spectrometer the equilibrium according to eq 2 is shifted to the left.

The synthesis of **1a** has also been performed in accordance with eq 2. For this, a procedure was developed for the preparation of $[(CH_3)_2NBO]_3$ from B_2O_3 and $[(CH_3)_2N]_3B$ that avoids the previously described[10] use of a bomb tube. Subsequent reaction of the product with $[(CH_3)_2N]_3B$ proceeded smoothly to give good yields of **1a**. The synthesis of this latter compound in a one-pot procedure from the reaction of B_2O_3 with $[(CH_3)_2N]_3B$ was found to be much less efficient.

The compound $[(CH_3)_2N]RBOBR[N(CH_3)_2]$ with R = C_2H_5 (**1b**) was also obtained by the procedure as outlined in eq 1, but the procedure according to eq 2 is just as suitable for the preparation of the compound. The (14-eV) mass spectrum of **1b** showed an ion peak for the species $M^+ - C_2H_5$, suggesting that this compound is somewhat more stable toward thermal rearrangement than **1a**.

Finally, the previously described[3,4] species with R = C_6H_5 (**1c**) was also prepared according to eq 1. In this case, the isolation of a pure material was not easily accomplished. The material cannot be distilled (even under high vacuum) without incurring some decomposition according to the equilibrium in eq 2; hence, the distilled product **1c** was always contaminated with bis(dimethylamino)phenylborane. The previously[4] employed recrystallization was also not very efficient for the purification of a material prepared according to eq 1, since some $(C_2H_5)_3N\cdot HCl$ was always carried along. Thus, the preparation of **1c** according to eq 2 is the recommended process for this particular compound, especially since the material can be generated in situ and used for further reactions without isolation or purification.[4]

The mass spectrum of **1c** exhibited a peak for the molecular ion. Indeed, the compound was found to be thermally stable up to about 130 °C. At higher temperatures the equilibrium eq 2 gives rise to decomposition, which is probably augmented by the volatility of the resultant bis(dimethylamino)phenylborane. When **1c** was heated to 200 °C, under atmospheric pressure, not only partial BO and BN exchange occurred but also irreversible decomposition via phenyl group migration according to eq 3 took

$$3\,\mathbf{1c} \rightarrow 3(C_6H_5)_2BN(CH_3)_2 + [(CH_3)_2NBO]_3 \quad (3)$$

place and was essentially complete within 40 h. It is worth noting that the two products of reaction 3 (identified by their IR[21,22] and NMR[20] spectra) were also formed on heating of $(C_6H_5BO)_3$ and $[(CH_3)_2N]_3B$ in a 2:3 molar ratio (2 h at 125 °C and then 4 days at 200 °C).

All of the compounds of type **1** are extremely sensitive to moisture. Surprisingly, hydrolysis of **1a** initiated at the B–O bond

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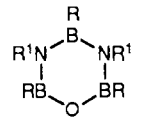
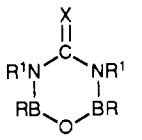
and bis(dimethylamino)hydroxyborane, $[(CH_3)_2N]_2BOH$, was observed as the initial product (NMR data) but could not be isolated in pure state.

A simple transamination was performed by employing (in situ generated) **1c** and pyrrolidine to give the diboryl oxide $(C_4H_4N)(C_6H_5)BOB(C_6H_5)(NC_4H_4)$ (**2**). Similarly, the reaction of **1b** with bis(methylamino)ethylborane gave the heterocycle **3** in



3: $R = C_2H_5$, $R^1 = CH_3$

good yield. This is the first example of an aimed synthesis of a boroxazine containing the B_3N_2O ring. Only one such species has previously been described: $O(\mu\text{-}CH_3BNSO_2CH_3)_2BCH_3$ was obtained in low yield from the reaction of 3,5-dimethyl-1,2,4-trithia-3,5-diborolane with CH_3SO_2NSO.[23] Additional transaminations of diboryl oxides of type **1** with ureas or thioureas gave compounds of type $O(\mu\text{-}BRNR')_2CX$ (**4**, X = O, S) with the release of dimethylamine.

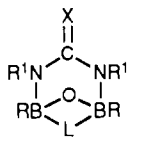


X = O X = S

4a: $R = N(CH_3)_2$, $R^1 = CH_3$
4b: $R = C_2H_5$, $R^1 = CH_3$
4c: C_6H_5, $R^1 = H$
4d: $R = C_6H_5$, $R^1 = CH_3$
4e: $R = C_2H_5$, $R^1 = CH_3$
4f: $R = C_6H_5$, $R^1 = CH_3$

The reaction of **1a** with 1 molar equiv of *N,N'*-dimethylurea proceeded cleanly to give the heterocycle **4a**. This latter compound has also been obtained by the reaction of $[(CH_3)_2N]_3B$ with *N,N'*-dimethylurea.[19] Although the present NMR data for **4a** agree well with those reported in the literature, there is a significant discrepancy in the melting point datum (here 78–80 °C; lit.[19] 105–109 °C). Similarly, **4d** has also been obtained by treatment of *N,N'*-dimethylurea with *n*-butyllithium and subsequent reaction with $C_6H_5BCl_2$.[19] Again, the NMR spectra of the reported[19] material and those of the present product were essentially identical, but there is a substaintial difference in the melting point of the products (here 98–102 °C; lit.[19] 144–148 °C). Indeed, the melting points of both **4a** and **4d** increased with time, unless the materials were stored and handled under strictly anhydrous conditions. However, concurrent with the increase in melting points was the emergence of additional signals of increasing intensity in the ^1H NMR spectra. These same contaminations were also observed when the products were recrystallized in the atmosphere. Thus, it is apparent that the reported higher melting points are due to partial hydrolysis of **4a** and **4d**, respectively. Repeated recrystallization of **4d** in the atmosphere finally gave a material that no longer exhibited the ^1H NMR spectrum of the original compound, but only those due to the contamination, which was then identified as a mixture of *B,B',B''*-triphenylboroxin and *N,N'*-dimethylurea. This illustrates the extreme hydrolytic sensitivity of compounds of type **4**, which parallels that of the 1,3,2-diboroxanes of type **1**.

It is of interest to note that intermediates of the type $O(\mu\text{-}RBNCH_3)_2CX\cdot(CH_3)_2NH$ (**5**; X = O, S) could be isolated and characterized from the reaction of equimolar amounts of **1** and *N,N'*-dimethyl(thio)urea. The room-temperature ^1H and ^{11}B NMR spectra of such adducts (**5**) illustrate the equivalence of the annular $(N)CH_3$ groups and the boron atoms. More significantly, $\delta(^{11}B)$ of these adducts (**5**) is at higher field than in species of type **4** but not quite in the range normally associated with isolated four-coordinate boron.[20] This observation leads to



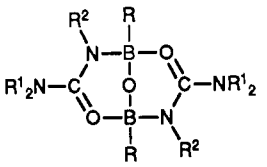
5a: X = O, R = C_6H_5, R^1 = CH_3, L = $(CH_3)_2NH$
5b: X = S, R = C_6H_5, R^1 = CH_3, L = $(CH_3)_2NH$

the assumption that at room temperature the species are fluxional in solution with the amine bonding to both boron atoms as indicated in **5**. This fluxionality is analogous to that observed for 1:1 molar adducts of *B,B',B''*-triorganylboroxins with amines,[24] hydrazines,[25] or ethylenediamines,[26] where such fluxionality has been demonstrated for solutions at room temperature but can be arrested (and evidenced by relevant ^{11}B NMR data) at low temperatures.[24,25] Also, the localization of the donor molecule at an individual boron atom of the boroxin ring in the solid state has been documented by single-crystal X-ray diffraction studies.[24] Indeed, the ^{11}B NMR spectrum of **5a** at room temperature exhibits only one signal at 20.6 ppm. The signal is very broad ($h_{1/2}$ = 1800 Hz) at −10 °C, and two new maxima begin to emerge. At −44 °C, these maxima can be clearly recognized at 31.8 and near 6 ppm, respectively. This observation suggests the arrest of the fluxionality at low temperatures, analogous to the previously observed cases of similar species as cited above.

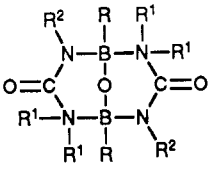
An aminoboronation by insertion of isocyanates into the B–N bonds of **1** proceeded readily to yield ureidoboranes according to eq 4. The ^{11}B NMR spectra showed the presence of four-co-

$$\mathbf{1} + 2R'NCO \rightarrow \underset{\mathbf{6}}{[(CH_3)_2NCONR']RBOBR[NR'CON(CH_3)_2]} \quad (4)$$

ordinate boron in the resultant products, for which the two structures **6** and **7** appear to be the most reasonable. Of these,



6a: $R = C_2H_5$, $R^1 = R_2 = CH_3$
6b: $R = C_6H_5$, $R^1 = R^2 = CH_3$
6c: $R = R^2 = C_6H_5$, $R^1 = CH_3$



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structure **6** with the carbonyl group (rather than the amino group) back-bonding to the second boron atom is the more likely one, as is suggested by a comparison with the product obtained from the reaction of **1c** with *N*-methylacetamide. Additional support for structure **6** as compared to **7** is provided by IR data. The CO absorption of species of type **4** is observed in the 1675–1700-cm^{-1} range; and it is found at 1636 cm^{-1} for tetramethylurea and at 1637 cm^{-1} for *N,N*-dimethyl-*N'*-phenylurea. However, the corresponding band is found as a strong absorption at 1586 cm^{-1} for **6b** and at 1553 cm^{-1} for **6c**. This significant shift to lower wavenumber is clearly in better consonance with the bicyclic structure of **6** than that of **7**. The reaction of **1c** with 2 molar equiv of *N*-methylacetamide proceeded to yield an aminoborane (**8**) according to eq 5. Again the ^{11}B NMR spectrum of the

$$\mathbf{1c} + 2CH_3CONHCH_3 \xrightarrow{-2(CH_3)_2NH} \underset{\mathbf{8}}{(CH_3CONCH_3)(C_6H_5)BOB(C_6H_5)(NCH_3COCH_3)} \quad (5)$$

resultant product evidenced the presence of four-coordinate boron, suggesting the bicyclic structure **8b** for the compound.

The ^{11}B chemical shift data for species of types **6** and **8** are essentially identical, being 3.0 and 3.1 ppm, respectively. This suggests the existence of analogous coordination about the boron

(23) Meller, A.; Habben, C. *Monatsh. Chem.* **1982**, *113*, 139–152.
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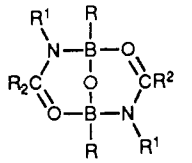
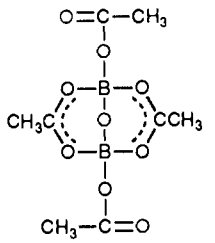


8a: R = C_6H_5, R^1 = CH_3, R^2 = H
8b: R = C_6H_5, R^1 = R_2 = CH_3



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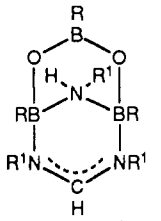
in the two species, thereby supporting the bicyclic structure **6** involving O–B coordination as the actual structure. In this context, it is also of interest to note that $(CH_3COO)_2BOB(OCOCH_3)_2$ (**9**) exhibits $\delta(^{11}B)$ 1.1,[21] and that a single crystal X-ray analysis has documented that **9** contains two types of acetyl groups as shown in the illustrated structure.[27] Hence, these data appear to give further credence to the structural assignment of the species of type **6**.

Another species of type **8**, i.e., **8a**, was obtained by the reaction of the ureidoborane **6a** with *N*-methylformamide, whereby a simple displacement of the urea moieties occurred with the formation of the amidoborane **8a**.

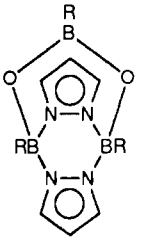
On reaction of **1c** with 2 molar equiv of *N*-methylformamide, only 1 molar equiv of dimethylamine was generated. On the basis of the analytical data and the NMR spectra of the product, structure **10** was assigned to the resultant material (which was,



10: R = C_6H_5, R^1 = CH_3

however, obtained only in ca. 20% maximal yield). The formation of **10** can be interpreted by the intermediate formation of a formamidinium species under the reaction conditions, as is known for the interaction of *N*-methylformamide with dimethyl sulfoxide.[28] However, the transfer of the $NHCH_3$ group from the amide to the boron has no ready explanation.

Compound **10** contains a bridging OBRO unit and thus is structurally related to the products obtained from the interaction of *B,B',B''*-triorganylboroxins with pyrazole, wherein the RBOBROBR unit of the boroxin is retained with the formation of a triply bridged species of type **11** containing both three- and four-coordinate boron.[29]



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To summarize, bis(aminoboryl) oxides (=1,3,2-diboroxanes) of the general type $[(CH_3)_2N]RBOBR[N(CH_3)_2]$ (**1**) have been prepared by two general methods. The compounds are extremely sensitive to moisture but are valuable precursors for the preparation of species containing a BOB group. For example, the dimethylamino groups have been replaced by transamination reactions to give linear or cyclic products containing three-coordinate boron (**2**–**4**). Aminoboronation of **1** with isocyanates yielded ureidoboranes, which exist in a bicyclic structure containing four-coordinate boron (**6**). Transamination of **1** with *N*-methylacetamide gave amidoboranes (**8**), which also contain four-coordinate boron. The latter type of compound was also obtained from the reaction of the ureidoboranes **6** with amides, whereas **1c** reacted with *N*-methylformamide to give a triply bridged species containing both three- and four-coordinate boron (**10**).

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Registry No. **1a**, 124357-22-8; **1b**, 124357-24-0; **1c**, 101834-81-5; **2**, 124399-60-6; **3**, 124357-23-9; **4a**, 84185-30-8; **4b**, 124379-85-7; **4c**, 124379-86-8; **4d**, 81233-30-9; **4e**, 124379-87-9; **4f**, 124379-88-0; **5a**, 124357-26-2; **5b**, 124357-27-3; **6a**, 124357-28-4; **6b**, 124357-29-5; **6c**, 124357-30-8; **8a**, 124357-31-9; **8b**, 124357-32-0; **10**, 124357-25-1; $[(CH_3)_2NBO]_3$, 17197-55-6; $[(CH_3)_2N]_2BCl$, 6562-41-0; $[(CH_3)_2N]_3B$, 4375-83-1; B_2O_3, 1303-86-2; $(CH_3)_2NBCl(C_2H_5)$, 1739-26-0; $(C_2H_5BO)_3$, 3043-60-5; $[(CH_3)_2N]_2BC_2H_5$, 7318-89-0; $(CH_3)_2NBCl(C_6H_5)$, 1196-44-7; $(C_6H_5BO)_3$, 3262-89-3; C_4H_8NH, 123-75-1; $C_2H_5B(NHCH_3)_2$, 7397-51-5; *N,N'*-dimethylurea, 96-31-1; *N,N'*-dimethylthiourea, 534-13-4; urea, 57-13-6; methyl isocyanate, 624-83-9; phenyl isocyanate, 103-71-9; *N*-methylformamide, 123-39-7; *N*-methylacetamide, 79-16-3.

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