Bis(diorganylamino)dihalodiboroxanes as Building Blocks for Boron Heterocycles†

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Bis(diorganylamino)dihalo-1,3-diboroxanes **1** result from the controlled hydrolysis of (diorganylamino)dihaloboranes substituted with bulky dialkyl- or alkylarylamino groups. Dehalogenation with sodium/potassium alloy gives 1,4-dioxa-2,3,5,6-tetraborinanes **3** and, in the case of the di(*s*-butyl)amino groups, the corresponding oxadiborirane **4**. If the dehalogenation is carried out in the presence of bi- or tricyclic aromatic compounds, addition of a $B(NR_2)OB(NR_2)$ moiety is observed, and the corresponding 1,3-(1,2-dihydronaphthaline-1,2-diyl)diboroxane (**5**), 1,3-(9,10-dihydroanthracene-9,10-diyl)diboroxane (**6**), and 1,3-(9,-10-dihydrophenanthrene-9,10-diyl)diboroxane (**7**) species are obtained. The compounds were characterized by NMR spectroscopy (^1H, ^{11}B, ^{13}C), MS (EI and FI), and elemental analyses. X-ray crystal structure determinations are presented for **1a**, **3a**, **5a**, and **6b**.

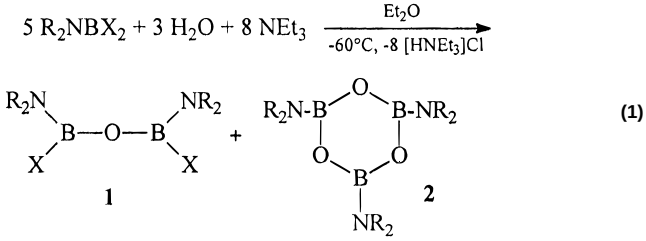
Introduction

Kinetic stabilization by steric factors is responsible for many unusual molecular structures and for reduced activity of chemical moieties. In the case of boron−nitrogen compounds, remarkable progress has been achieved especially in the isolation of monomeric iminoboranes[1] and aminoiminoboranes[2] from which a rich chemistry of reactions has developed. In contrast to this, only a few attempts have been made to extend this concept to boron−oxygen species. The extremely sterically demanding tris(trimethylsilyl)methyl group was used in the attempted stabilization of a B≡O triple bond; however, the intermediate could only be isolated as the corresponding trimeric boroxine.[3] The first three-membered oxadiborirane ring[4] resulted from the dehalogenation of 1,3-dichloro-1,3-bis[tris(trimethylsilyl)-methyl]-1,3-diboroxane,[4] the only halogen-containing diboryl oxide described so far. Replacement of bulky organyl groups by sterically demanding diorganylamino substituents bonded to boron leads to additional electronic stabilization of such compounds. The π-bonding from the nitrogen to the boron atom diminishes the electron deficiency of the latter, thus giving more thermodynamic stability to classical structures. 1,3-Diamino-1,3-dihalodiboroxanes have not been prepared previously, and it is to be expected that bulky substituents on the nitrogen atoms will influence their formation and chemistry.

Results and Discussion

Upon cautious hydrolysis of (dialkylamino)dihaloboranes in wet diethyl ether containing triethylamine, using a slight excess of the (dialkylamino)dihaloborane, the formation of products indeed is controlled by steric factors.

In contrast to the stoichiometry defined by eq 1, the molar equivalents used in the reaction are R_2NBX_2:H_2O:NEt_3 = 2:1:2. Upon distillation of the reaction mixture,



(1)

excess (dialkylamino)dihaloborane is recovered unchanged as the fraction with the lowest boiling point. Table 1 presents products and their yields obtained by the hydrolysis of the (dialkylamino)dihaloboranes as described before. Yield percentages are rounded figures; for details, see Table 3. The yields do not add up to 100% due to distillation/sublimation losses.

The yields of the diboroxanes **1** are better (as to be expected) for **1a**−**c** compared to **1d**−**f**. An X-ray structure analysis was performed for **1a** (Figure 1). With increasing steric hindrance by the alkyl groups, the yield of the corresponding diboroxane **1** increases compared to that of the boroxine **2**. With R_2 = Pr_2 or Me + cyclo-C_6H_{11}, **1g** was obtained in a small yield compared to the main products **2g**.[5] Traces of **1i** in relation to **2i** were identified by MS (*m*/*e* 320 [M^+]) in addition to $PhN(Me)BCl_2$ (*m*/*e* 187) in a fraction subliming at 100 °C (0.0013 Torr). The yields are estimated in this case. Cautious hydrolysis of Me_2NBCl_2 and Et_2NBCl_2 yielded only the corresponding boroxines.[6,7]

The reaction of the 1,3-(dialkylamino)-1,3-dichlorodiboroxanes **1a**−**c** with sodium/potassium alloy in hexane or octane gives rise to the 1,4-dioxa-2,3,5,6-tetrabori-

† This paper is dedicated to Professor W. Siebert on the occasion of his 60th birthday.

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Table 1. Products of the Hydrolysis of Dialkylaminodihaloboranes

1,3-bis(dialkylamino)-1,3-dihalodiboroxanes **1**			yield %	tris(dialkylamino)boroxines			yield %
1a:	R = ^{i}Pr	X = Cl	76	**2a:**	R = ^{i}Pr	X = Cl	17
1b:	R = ^{i}Bu	X = Cl	73	**2b:**	R = ^{i}Bu	X = Cl	21
1c:	R = ^{s}Bu	X = Cl	71	**2c:**	R = ^{s}Bu	X = Cl	17
1d:	R = ^{i}Pr	X = Br	24	**2a:**	R = ^{i}Pr	X = Br	44
1e:	R = ^{i}Bu	X = Br	46	**2b:**	R = ^{i}Bu	X = Br	23
1f:	R = ^{s}Bu	X = Br	31	**2c:**	R = ^{s}Bu	X = Br	29
1g:	R = ^{n}Pr	X = Cl	5	**2g:**	R = ^{n}Pr	X = Cl	85
1h:	R=cyclo-C_6H_{11}	X = Cl	38	**2h:**	R=cyclo-C_6H_{11}	X = Cl	40
1i:	R_2 = Me + C_6H_5	X = Cl	~ 1	**2i:**	R_2 = Me + C_6H_5	X = Cl	>70

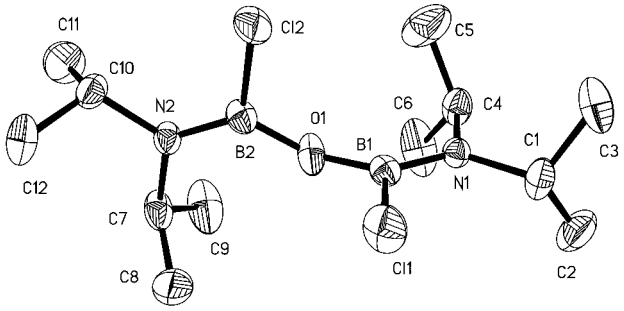
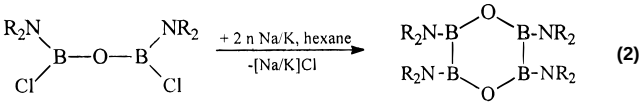


Figure 1. Crystal structure of **1a** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

nane ring system (eq 2). This B_4O_2 ring so far has only



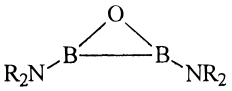
(2)

1a - 1c **3a - 3c**

3a: R = iPr
3b: R = iBu
3c: R = sBu

been reported in the dimeric condensate of 3,7-dihydroxy-1,8-dimethyl-*closo*-dicarbaundecaborane(11). No X-ray structure analysis was reported.[8]

In the course of these reactions, the corresponding 2,3-bis(dialkylamino)oxadiboriranes **4a**−**c** are also formed.

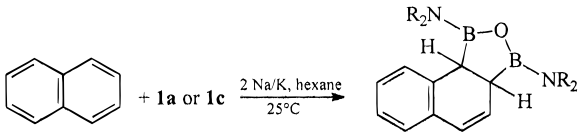


4a: R = ^{i}Pr
4b: R = ^{i}Bu
4c: R = ^{s}Bu

While **4a** and **4b** can only be detected by field ionization mass spectrometry (FI-MS) in the low-boiling forerun of the distillation, **4c** (where R is most bulky) can be separated in a pure state. **4c** is only the second oxadiborirane described[4] and the first one carrying B−amino groups. Its unequivocal identification rests upon its boiling point (compared to **3c**) and the FI-MS isotopic pattern. The radicals and/or biradicals formed upon dehalogenation of the 1,3-bis(dialkylamino)-1,3-dihaloboranes **1** apparently are highly reactive species. Besides combining to give the corresponding 1,4-dioxa-2,3,5,6-tetraborinanes **3** or diboriranes **4**, respectively, they can attack other radical species in the solution or the solvent. This leads to numerous byproducts of the reactions (eq 2) which were detected by FI-MS: tris(dialkylamino)boroxines $[R_2NBO]_3$ (**2**), bis(dialkylamino)boranes $[R_2N]_2BH$, bis(dialkylamino)chloroboranes $[R_2N]_2BCl$, bis(dialkylamino)-1,3-diboroxanes $R_2NB(H)OB(H)NR_2$, and bis(dialkylamino)-1-chloro-1,3-diboroxanes $R_2NB(H)OB(Cl)NR_2$.

If the dehalogenation of **1a** or **1c** with sodium/potassium alloy (in hexane:dimethoxyethane = 3:1) is carried out in the presence of naphthalene, the 1,2-diborylated 1,2-dihydronaphthalene derivatives **5** are formed.

An X-ray crystal structure analysis was carried out for **5a**. **5a** and **5c** are the first 1,2-diborylated species obtained from naphthalene. The 1,2-addition across the



(3)

5a: R = ^{i}Pr
5c: R = ^{s}Bu

double bond of one ring of the naphthalene system leaves the aromaticity of the second ring undisturbed. Probably the formation of the five-membered ring in this case favors the 1,2-addition. It should be noted that 1,4-additions of boron species to naphthalene[9,10] by one or two boron atoms are well documented. Likewise, naphthalene species that are diborylated in the 1,8-positions are obtained from the 1,8-dilithiated[11−13] or the 1,8-dimercurated[14,15] precursors.

Reaction of the dehalogenation intermediates of **1a**−**c** with anthracene (eq 4) and analogously of **1b** with phenanthrene (eq 5) gives the corresponding addition products **6** and **7** to the 9- and 10-position of the aromatics. An X-ray crystal structure is provided for **6b**. Hydrolysis of **5a**, **6a**, and **7** with aqueous KOH yielded 1,2-dihydronaphthalene, 9,10-dihydroanthracene, and 9,10-dihydrophenanthrene, respectively.

It should be noted that 9,10-dihydroanthracene derivatives bridged in the 9,10-position by groups containing one, two, or three boron atoms as well as a B−N−B sequence are described in a thesis[16] but are not published yet.

NMR Data. The ^{11}B NMR chemical shifts of all compounds described are in the expected range.[17]

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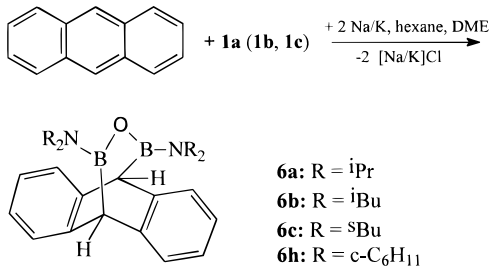
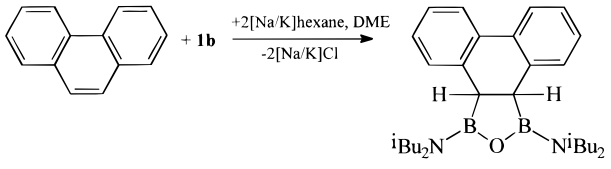


(4)

6a: R = ^{i}Pr
6b: R = ^{i}Bu
6c: R = ^{s}Bu
6h: R = c-C_6H_{11}



(5)

7

The compounds **1c**, **1f**, **3c**, **4c**, **5c**, and **6c** carrying di-*s*-butylamino groups contain chiral C atoms. Therefore splitting of the signals for the NCHCH_3 group is expected in the ^{1}H and ^{13}C NMR spectra. However, the observed splitting (four signals in the ^{13}C NMR and doublets or unresolved multiplets in the ^{1}H NMR spectra) could also be caused by sterically hindered rotation about the (BN) bonds.

Crystal Structures. Selected bond lengths and angles are compiled in Table 2.

In the structure of **1a**, the boron atoms are surrounded in an almost planar, distorted trigonal environment by the oxygen, nitrogen, and chlorine atoms. The molecule, however, is twisted by 79.1° about the oxygen atom. Bond lengths of the B−O bonds (1.367(3) Å) correspond to those observed in Me_2BOMe by electron diffraction[18] (1.363(2) Å, mean value) while in tetrakis(amino)diboroxane {[$(Me_3Si)_2$N][Me_3SiNH]B}$_2$O they are slightly longer (1.385(3) Å) by X-ray diffraction.[19] The B−N distances (1.383(3) Å, mean value) are shortened compared to 2,4,6-trichloroborazine (1.413(10) Å),[20] thus indicating that π-bonding is mainly concentrated in this bond. On the other hand, the B−Cl bonds appear rather long (1.809(3) Å, mean value). Typical B−Cl distances are 1.760(15) Å (in 2,4,6-trichloroborazine, X-ray diffraction data,[20] and 1.750(5) Å in $MeBCl_2$, from the microwave spectrum.[21] The B−Cl distance in **1a** corresponds to a species carrying chlorine atoms bonded to tetracoordinated boron as in 1,5-dichloro-3,7-bis(trifluoromethyl)-4,8-bis(2′,6′-dimethylphenyl)-2,6,9-trioxa-1,5-diborabicyclo[3.3.1]nonadiene with a B−Cl distance of 1.817(3) Å (mean value).[22]

In **3a**, the two oxygen atoms are positioned on a 2-fold axis. The conformation is twisted in relation to the boron atoms, which show deviations of 0.3−0.4 Å from the least-squares plane. The BOB bond angles are widened (117.3(3)°, mean value) compared to the OBB angles (112.2(2)°). The B−O distances (1.408(3) Å, mean value) are ∼0.02 Å longer than in 2,4,6-trimethylboroxine[23] (1.39(2) Å from electron diffraction) and correspond to those in $K_3(BO_2)_3$ (1.398(3) Å, by X-ray diffraction).[24,25] The B−B bond lengths (1.729(4) Å) exceed those of a B−B bonded bis(dioxaborolanyl) (1.711(6) Å)[26] by 0.018 Å, probably due to the better π-donation from the N-substituent in **3a**. Also the B−B distances in 1,2,4,5-tetrakis(dimethylamino)-1,2,4,5-tetraborinane (1.711(2) Å)[27] and in 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (1.714(4) Å)[28] are shorter compared to the B−B bond in **3a** where the boron atoms carry N- and O-substituents. The B−N distances (1.400(3) Å, mean value) are in the normal range generally found in aminoboranes,[28] borazines,[20] or the just-mentioned diborane(4) derivative.[27]

In **5a**, bond lengths of the B_2O skeleton correspond to those in **3a**; however, the BOB angle (111.2(2)°) is rather small, due to the incorporation of the diboroxane system into the five-membered ring. The B−C distances (1.602(3) and 1.626(5) Å) are comparable to those in other five-membered ring systems containing a boron atom and a conjugated double bond.[29] The five-membered and six-membered (nonaromatic) rings form an envelope conformation with C3 (0.46 Å) and C9b (0.55 Å) folded above the plane formed by the other atoms in the rings.

6b shows an almost planar arrangement of the C_2B_2O bridge (the deviation is only 5.3°). Bond lengths are in the usual range. The BOB angle is widened to 131.4(1)° and also the OBC angles are 118.9(1)°, mean value) due to the bridging function between C9 and C10 of the dihydroanthrancene.

Experimental Section

All reactions were performed in an inert atmosphere of dry nitrogen in dry solvents saturated with nitrogen. Most high-vacuum distillations or sublimations were performed using a rotating three-bulb system. Bulb volumes (100, 250, 500 mL) were adapted to the amount of the reaction products. The system was rotated by a motor adapted from a Büchi Rotavapor. In these cases, boiling point (bp) and sublimation point (sublp) temperatures are those of the air bath. Melting points were determined in sealed capillaries. In the case of melting point (mp) (dec) the temperature given is when decomposition starts. Elemental analyses were performed by the analytical laboratory of the institute of inorganic chemistry and by Mikroanalytisches Labor Beller, Göttingen, Germany. NMR spectra were recorded on Bruker AM-250 or MSL-400 instruments. Heteroelement spectra were recorded in the proton-decoupled mode. Solvents and standards used were as follows: ^{1}H, ^{13}C, $CDCl_3$/TMS internal; ^{11}B, $CDCl_3/F_3B{\cdot}OEt_2$ external. Assignments of ^{13}C signals were made by distortionless enhancement of polarization transfer (DEPT, 100.60 MHz). Mass spectra were obtained in a Varian CH5 instrument (electron impact (EI) 70 eV and field ionization (FI)) and a Finnigan MAT 8230 (EI, 70 eV) spectrometer.

Starting materials were prepared according to the following

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a, 3a, 5a, and 6b

Compound **1a**

O(1)−B(1)	1.367(3)	O(1)−B(2)	1.367(3)	B(1)−N(1)	1.382(3)	B(1)−Cl(1)	1.808(3)
N(1)−C(4)	1.479(3)	N(1)−C(1)	1.490(3)	B(2)−N(2)	1.384(3)	B(2)−Cl(2)	1.810(3)
N(2)−C(10)	1.481(3)	N(2)−C(7)	1.498(3)				
B(1)−O(1)−B(2)	134.2(2)	O(1)−B(1)−N(1)	123.5(2)	O(1)−B(1)−Cl(1)	115.6(2)	N(1)−B(1)−Cl(1)	120.7(2)
B(1)−N(1)−C(4)	123.1(2)	B(1)−N(1)−C(1)	123.1(2)	O(1)−B(2)−N(2)	123.7(2)	O(1)−B(2)−Cl(2)	115.7(2)
N(2)−B(2)−Cl(2)	120.6(2)	B(2)−N(2)−C(10)	123.6(2)	B(2)−N(2)−C(7)	121.5(2)		

Compound **3a**

O(1)−B(1)	1.406(3)	B(1)−N(1)	1.397(3)	B(1)−B(2)	1.729(4)	N(1)−C(14)	1.471(3)
N(1)−C(11)	1.480(3)	O(2)−B(2)	1.411(3)	B(2)−N(2)	1.402(3)		
B(1)−O1)−B(1)#1	116.9(3)	N(1)−B(1)−O(1)	119.2(2)	N(1)−B(1)−B(2)	127.5(2)	O(1)−B(1)−B(2)	112.7(2)
B(1)−N(1)−C(14)	119.8(2)	B(1)−N(1)−C(11)	123.9(2)	B(2)#1−O(2)−B(2)	117.7(3)	N(2)−B(2)−O(2)	118.4(2)
N(2)−B(2)−B(1)	129.6(2)	O(2)−B(2)−B(1)	111.8(2)				

Compound **5a**

O(1)−B(2)	1.393(4)	O(1)−B(10)	1.402(4)	B(2)−N(2)	1.403(4)	B(2)−C(3)	1.602(4)
C(3)−C(4)	1.505(4)	C(3)−C(9B)	1.558(4)	C(4)−C(5)	1.333(4)	C(5)−C(5A)	1.469(5)
C(5A)−C(9A)	1.401(4)	C(9A)−C(9B)	1.515(4)	C(9B)−B(10)	1.626(5)	B(19)−N(1)	1.395(4)
N(1)−C(11)	1.483(4)	N(1)−C(14)	1.487(4)				
B(2)−O(1)−B(10)	111.2(2)	O(1)−B(2)−N(2)	123.1(3)	O(1)−B(2)−C(3)	109.1(3)	N(2)−B(2)−C(3)	127.7(3)
C(4)−C(3)−C(9B)	110.3(2)	C(4)−C(3)−B(2)	105.9(2)	C(9B)−C(3)−B(2)	101.9(2)	C(5)−C(4)−C(3)	123.3(3)
C(4)−C(5)−C(5A)	121.2(3)	C(9A)−C(5A)−C(5)	118.8(3)	N(1)−B(10)−O(1)	120.0(3)	N(1)−B(10)−C(9B)	131.0(3)
O(1)−B(10)−C(9B)	109.0(3)	B(10)−N(1)−C(11)	122.3(2)	B(10)−N(1)−C(14)	122.8(2)	B(2)−N(2)−C(24)	121.6(2)
B(2)−N(2)−C(21)	122.8(2)						

Compound **6b**

O(1)−B(1)	1.389(2)	O(1)−B(2)	1.389(2)	B(1)−N(1)	1.408(2)	B(1)−C(9)	1.605(2)
B(2)−N(2)	1.406(2)	B(2)−C(10)	1.599(2)	C(8)−C(8A)	1.385(2)	C(8A)−C(9A)	1.403(2)
C(8A)−C(10)	1.525(2)	C(9)−C(9A)	1.519(2)	C(10)−C(10A)	1.519(2)		
B(1)−O(1)−B(2)	131.41(14)	O(1)−B(1)−N(1)	116.3(2)	O(1)−B(1)−C(9)	118.58(14)	N(1)−B(1)−C(9)	125.1(2)
O(1)−B(2)−N(2)	117.2(2)	O(1)−B(2)−C(10)	119.37(14)	N82)−B(2)−C(10)	123.4(2)	B(1)−N(1)−C(11)	125.25(14)
B(1)−N(1)−C(15)	120.93(13)	C(8)−C(8A)−C(9A)	119.7(2)	C(8)−C(8A)−C(10)	123.1(2)	C(9A)−C(8A)−C(10)	117.15(14)
C(9A)−C(9)−C(4A)	109.35(13)	C(9A)−C(9)−B(1)	106.44(13)	C(4A)−C(9)−B(1)	109.95(12)	C(10A)−C(10)−B(2)	105.69(13)
C(8A)−C(10)−B(2)	110.27(13)						

Table 3. Yields[a] of Compounds 1 and 2 in Relation to Steric Hindrance

		g % of			
		diboroxane **1**		boroxine **2**	
dihalogeno(diorganylamino)borane (0.5 mol)	amt (g)				
$(i\text{-Pr})_2NBCl_2$	90.5	59/76	**1a**	11/17	**2a**
$(i\text{-Bu})_2NBCl_2$	105	67/73	**1b**	15.5/20.8	**2b**
$(s\text{-Bu})_2NBCl_2$	105	65.5/71	**1c**	12.6/16.7	**2c**
$(i\text{-Pr})_2NBBr_2$	135.5	23.4/24	**1d**	42.6/44.2	**2a**
$(i\text{-Bu})_2NBBr_2$	145.5	52/45.8	**1e**	17.6/22.7	**2b**
$(s\text{-Bu})_2NBBr_2$	145.5	45/30.5	**1f**	22.5/29	**2c**
$(n\text{-Pr})_2NBCl_2$	90.5	4.5/5	**1g**	54/85	**2g**
$(\text{cyclo-}C_6H_{11})_2NBCl_2$	130.5	45/38	**1h**	41/39.8	**2h**

[a] The yields are based on the dihalogeno(diorganylamino)borane.

references: $(i\text{-Pr})_2NBCl_2$,[30] $(n\text{-Pr})_2NBCl_2$,[31] $(i\text{-Bu})_2NBCl_2$,[32] $(s\text{-Bu})_2NBCl_2$,[32] $c\text{-}C_6H_{11}N(CH_3)BCl_2$,[33,34] $(i\text{-Pr})_2NBBr_2$,[35] Me_2NBCl_2,[36] Et_2NBCl_2,[31] and $(c\text{-}C_6H_{11})_2NBCl_2$.[37] $(i\text{-Bu})_2NBBr_2$ (**A**) and $(s\text{-Bu})_2NBBr_2$ (**B**) were prepared by a general procedure for the preparation of aminodihalogenoboranes.[38]

Aminobromoboranes A and B. General Procedure. A mixture of 1 mol of triethylamine (101 g) and 1 mol (129 g) of the starting amine (diisobutylamine for **A** or di-*s*-butylamine for **B)** was added with stirring to 1.0 mol (250.5 g) of BBr_3 in 1 L CCl_4 at 0 °C within 2 h. After addition of the mixture of the amines, the slurry was refluxed for 4 h. Triethylammonium bromide was removed by filtration in a N_2 atmosphere. The solvent was then evaporated under reduced pressure and collected in a cold trap. The residue was distilled using a 10 cm Vigreux column and gave 256.5 g (85.8%) of **A** and 242.6 (81.1%) of **B**.

Dibromo(diisobutylamino)borane (A). Colorless liquid (bp 100 °C (7.5 Torr)). Anal. Calcd for $C_8H_{18}BBr_2N$ (298.86): C, 32.15; H, 6.08. Found: C, 32.61; H, 6.41. ^{1}H NMR: δ 0.90 (d, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$, 12H), 1.98 (sept, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$, 2H), 3.20 (d, $^3J_{HH}$ = 6.8 Hz, $CHCH_2$, 4H). ^{13}C NMR: δ 19.91 ($CHCH_3$), 27.12 ($CHCH_3$), 58.16 (NCH_2). ^{11}B NMR: δ 25.9 ($h_{1/2}$ = 90 Hz).

Dibromo(di-*s*-butylamino)borane (B). Colorless liquid (bp 108 °C (7.5 Torr)). Anal. Calcd for $C_8H_{18}BBr_2N$ (298.86): Br, 53.47. Found: Br, 52.70. ^{1}H NMR: δ 0.90 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3, 6H), 1.05−1.75 (br, CH_3CH_2, $CHCH_3$, $CHCH_3$), 2.13 (br, $CHCH_3$), 3.12 (br, $CHCH_3$), 4.30 (br, $CHCH_3$). ^{13}C NMR: δ 11.72 (CH_2CH_3), 19.70 ($CHCH_3$), 27.57, 30.05 (CH_2CH_3), 54.02, 60.99 ($CHCH_3$). ^{11}B NMR: δ 24.0 ($h_{1/2}$ = 95 Hz).

1,3-Bis(dialkylamino)-1,3-dihalodiboroxanes (1a−h) and 2,4,6-Tris(diorganylamino)boroxines (2a−c,g,h). Typical Procedure for Cautious Hydrolysis of Dihalo(dialkyl-

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amino)boranes: Preparation of 1,3-Bis(diisopropylamino)-1,3-dichloro-1,3-diboroxane (1a) and 2,4,6-Tris(diisopropylamino)boroxine (2a). A mixture of 4.5 g (0.25 mol) H_2O, 50.5 g (0.5 mol) of triethylamine and 800 mL of dry diethyl ether was added within 3 h to a stirred solution of 91 g (0.5 mol) of dichloro(diisopropylamino)borane in 500 mL of hexane at −60 °C. Stirring was continued for 3 h at −60 °C and after warming to room temperature for another 10 h. Triethylammonium chloride was removed by filtration under N_2. The solvents were evaporated under reduced pressure and collected in a trap cooled by liquid N_2. From the remaining residue are recovered 12 g (13.2%) of dichloro(diisopropylamino)borane by distillation (bp 60 °C (7.5 Torr)) in a rotating three-bulb tube system. Yields of 59 g (76%) of **1a** (sublp 80−5 °C (0.001 Torr)) and **2a** (sublp 100−120 °C (0.001 Torr)) were obtained by subsequent sublimation in the three-bulb system.

1b−**h** and **2b**−**h** were prepared analogously in the 0.5 mol scale; the yields are summarized in Table 3.

Upon cautious hydrolysis of Me_2NBCl_2, Et_2NBCl_2, MeN-(C_6H_5)BCl_2, and Me(cyclo-C_6H_{11})$NBCl_2$, only the boroxine derivatives[$Me_2NBO]_3$,[$Et_2NBO]_3$,[Me(Ph)$NBO]_3$,and[Me(cyclo-$C_6H_{11}NBO]_3$ were obtained. These reactions were conducted starting from 100 mmol of the corresponding dichloro(diorganylamino)borane in 100 mL of hexane, 0.9 g (50 mmol) of H_2O, 10.1 g (100 mmol) of NEt_3 and 200 mL of Et_2O at −60 °C. The boroxine derivatives were isolated by sublimation and distillation, respectively, in the rotating three-bulb system. In the case of dichloro(dipropylamino)borane, the diboroxane derivative **1g** was obtained in a minute yield compared to the boroxine **2g**.

1,3-Dichloro-1,3-bis(diisopropylamino)-1,3-diboroxane (1a). White solid (sublp 80−85 °C (0.0075 Torr); mp (dec) from 185 °C). Anal. Calcd for $C_{12}H_{28}B_2Cl_2N_2O$ (308.89): C, 46.66; H, 9.14; Cl, 22.95; N, 9.06. Found: C, 46.66; H, 9.25; Cl, 22.70; N, 9.02. MS: EI *m*/*e* (rel intensity) 308 (10) [M^+], 293 (100); FI: 308 (100) [M^+]. ^{1}H NMR: δ 1.12 (d, $^3J_{HH}$ = 6.9 Hz, CHCH_3, 12H), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, CHCH_3, 12H), 3.40 (sept, $^3J_{HH}$ = 6.9 Hz, $CH$$CH_3$, 2H), 3.80 (sept, $^3J_{HH}$ = 6.8 Hz, 2H). ^{13}C NMR: δ 21.99 (CHCH_3), 23.14 (CHCH_3), 45.32 ($CH$$CH_3$), 47.46 ($CH$$CH_3$). ^{11}B NMR: δ 23.9 ($h_{1/2}$ = 230 Hz).

1,3-Dichloro-1,3-bis(di-i-butylamino)-1,3-diboroxane (1b). Colorless liquid (bp 105 °C (0.0075 Torr)). Anal. Calcd for $C_{16}H_{36}B_2Cl_2N_2O$ (365.00): C, 52.65; H, 9.94; Cl, 19.43; N, 7.67. Found: C, 52.41; H, 9.99; Cl, 19.11; N, 7.72. MS: EI *m*/*e* (rel intensity) 364 (7) [M^+], 321 (100); FI 364 (100) [M^+]. ^{1}H NMR: δ 0.86 (d, $^3J_{HH}$ = 6.6 Hz, CHCH_3, 12H), 0.88 (d, $^3J_{HH}$ = 6.7 Hz, CHCH_3, 12H), 1.80−1.95 (m, $CH$$CH_3$, 4H), 2.82 (d, $^3J_{HH}$ = 7.5 Hz, NCH_2, 4H), 2.91 (d, $^3J_{HH}$ = 7.60 Hz, NCH_2, 4H). ^{13}C NMR: δ 19.97, 20.08 (CHCH_3), 26.52, 26.73 ($CH$$CH_3$), 53.65, 54.61 (N$CH_2$). ^{11}B NMR: δ 24.4 ($h_{1/2}$ = 550 Hz).

1,3-Bis(di-*s*-butylamino)-1,3-dichloro-1,3-diboroxane (1c). Yellowish liquid (bp 100 °C (0.0075 Torr)). Anal. Calcd for $C_{16}H_{36}B_2Cl_2N_2O$ (365.00): C, 52.65; H, 9.94; Cl, 19.43; N, 7.67. Found: C, 52.43; H, 10.02; Cl, 19.12; N, 7.75. MS: EI *m*/*e* (rel intensity) 364 (5) [M^+], 321 (100); FI 364 (100) [M^+]. ^{1}H NMR: δ 0.80 (t, $^3J_{HH}$ = 6.7 Hz, CH_2CH_3, 6H), 0.82 (t, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3, 3H), 0.83 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3, 3H), 1.05−1.18 (m, CHCH_3, 12H), 1.33−1.60 (m, $CH_2$$CH_3$, 8H), 3.00 (br, N$CH$, 2H), 3.50 (br, N$CH$, 2H). ^{13}C NMR: δ 11.72, 11.88, 12.00, 12.24 (CH_2CH_3), 20.11, 20.64, 20.76, 20.96 (CHCH_3), 28.71, 29.67 ($CH_2$$CH_3$), 51.85, 52.16, 54.05 (NCH). ^{11}B NMR: δ 24.1 ($h_{1/2}$ = 390 Hz).

1,3-Dibromo-1,3-bis(diisopropylamino)-1,3-diboroxane (1d). White solid (sublp 80 °C (0.001 Torr); mp 137−146 °C). $C_{12}H_{28}B_2Br_2N_2O$ (397.78). MS: EI *m*/*e* (rel intensity) 398 (10), 383 (100); FI 383 (100, M^+). ^{1}H NMR: δ 1.17 (d, $^3J_{HH}$ = 6.7 Hz, CHCH_3, 12H), 1.26 (d, $^3J_{HH}$ = 6.7 Hz, CHCH_3, 12H), 3.55 (m, $CH$$CH_3$, 2H), 4.10 (m, $CH$$CH_3$, 2H). ^{13}C NMR: δ 21.73, 23.59 (CHCH_3), 45.48, 49.56 ($CH$$CH_3$). ^{11}B NMR: δ 22.3 $h_{1/2}$ = 300 Hz). **1d** contained boroxine **2a**.

1,3-Dibromo-1,3-bis(di-i-butylamino)-1,3-diboroxane (1e). Yellowish liquid (bp 130 °C (0.0075 Torr)). Anal. Calcd for $C_{16}H_{36}B_2Br_2N_2O$ (453.90): C, 42.34; H, 7.99; N, 6.17. Found: C, 42.75; H, 8.25; N, 6.30. MS: EI *m*/*e* (rel intensity) 454 [M^+], 411 (100); FI 454 (100) [M^+]. ^{1}H NMR: δ 0.83−0.90 (m, CHCH_3, 24H), 1.75−1.95 (m, $CH$$CH_3$, 4H), 2.75 (d, $^3J_{HH}$ = 7.4 Hz, NCH_2, 4H), 2.86 (d, $^3J_{HH}$ = 7.5 Hz, NCH_2, 2H), 2.98 (d, $^3J_{HH}$ = 7.5 Hz, NCH_2, 2H). ^{13}C NMR: δ 20.02, 20.15, 20.39 (CHCH_3), 26.55, 26.89, 27.20 ($CH$$CH_3$), 53.13, 53.90, 55.73 (NCH_2). ^{11}B NMR: δ 23.0 ($h_{1/2}$ = 720 Hz).

1,3-Dibromo-1,3-bis(di-*s*-butylamino)-1,3-diboroxane (1f). Yellowish liquid (bp 95 °C (0.001 Torr)). Anal. Calcd for $C_{16}H_{36}B_2Br_2N_2O$ (453.90): C, 42.34; H, 7.99; Br, 35.21; N, 6.17. Found: C, 42.84; H, 8.29; Br, 34.87; N, 6.26. MS: EI *m*/*e* (rel intensity) 425 (100) [$M - C_2H_5]^+$; FI 454 (100). ^{1}H NMR: δ 0.90 (t, $^3J_{HH}$ = 6.9 Hz, CH_2CH_3, 6H), 0.91 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3, 3H), 0.92 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3, 3H), 1.14 (d, $^3J_{HH}$ = 6.3 Hz, CHCH_3, 3H), 1.16 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.30 (d, $^3J_{HH}$ = 6.7 Hz, CHCH_3, 6H), 1.38−1.78 (m, CH_2-CH_3, 8H), 3.05 (br, $CH$$CH_3$, 2H), 3.86 (br, $CH$$CH_3$, 2H). ^{13}C NMR: δ 11.51, 11.65, 12.03, 12.09 (CH_2CH_3), 19.82, 20.36, 20.59, 20.95 (CHCH_3), 28.39, 30.02 ($CH_2$$CH_3$), 52.08, 55.98 ($CH$$CH_3$). ^{11}B NMR: δ 22.7 ($h_{1/2}$ = 450 Hz).

1,3-Dichloro-1,3-bis(dipropylamino)-1,3-diboroxane (1g). Yellowish liquid (bp 80 °C (0.001 Torr)). Anal. Calcd for $C_{12}H_{28}B_2Cl_2N_2O$ (308.89). C, 46.66; H, 9.14; N, 9.06. Found: C, 46.12; H, 9.19; N, 9.18. MS: EI 308 (10) [M^+], 279 (100); FI 308 (100). ^{1}H NMR: δ 0.85 (t, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3, 6H), 0.87 (t, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3, 6H), 1.50 (m, $CH_2$$CH_3$, 8H), 3.00 (4 overlaping d, NCH_2, 8H). ^{13}C NMR: δ 11.24, 11.30 (CH_2CH_3), 22.69, 22.73 ($CH_2$$CH_3$), 48.55, 49.60 (N$CH_2$). ^{11}B NMR: δ 23.6.

1,3-Dichloro-1,3-bis(dicyclohexylamino)-1,3-diboroxane (1h). White solid (sublp 170 °C (0.001 Torr); mp dec starting at 320 °C). Anal. Calcd for $C_{24}H_{44}B_2Cl_2N_2O$ (469.15): C, 61.44; H, 9.45; N, 5.97. Found: C, 61.59; H, 9.62; N, 6.05. MS: EI *m*/*e* (rel intensity) 468 (50) [55]; FI 468 (100). ^{1}H NMR: δ 1.00−1.30 (m, CH_2, 8H), 1.45−1.90 (m, CH_2, 32H), 3.00 (br, CH, 2H), 3.40 (br, CH, 2H). ^{13}C NMR: δ 25.58, 26.38, 26.60, 32.41, 33.29 (CH_2), 55.45, 57.15 ($CH$$CH_2$). ^{11}B NMR: δ 23.9 ($h_{1/2}$ = 250 Hz).

2,4,6-Tris(diisopropylamino)boroxine (2a).[39,40] Colorless crystalline substance (sublp 100 °C (0.001 Torr); mp 204 °C). Anal. Calcd for $C_{18}H_{42}B_3N_3O_3$ (380.99): B, 8.51; N, 11.03. Found: B, 8.42; N, 11,12. MS: EI *m*/*e* (rel intensity) 381 (40) [M^+]; FI 381 (100). ^{1}H NMR: δ 1.16 (d, $^3J_{HH}$ = 7 Hz, CHCH_3, 36H), 3.57 (sept, $^3J_{HH}$ = 7 Hz, $CH$$CH_3$, 6H). ^{11}B NMR: δ 20.5 ($h_{1/2}$ = 120 Hz).

2,4,6-Tris(di-i-butylamino)boroxine (2b). Yellowish liquid (bp 120 °C (0.001 Torr)). Anal. Calcd for $C_{24}H_{54}B_3N_3O_3$ (465.14): C, 61.97; H, 11.70; N, 9.03. Found: C, 61.45; H, 11.86; N, 8.97. MS: EI *m*/*e* (rel intensity) 465 (5) [M^+], 422 (100); FI 465 (100). ^{1}H NMR: δ 0.86 (d, $^3J_{HH}$ = 6.6 Hz, CHCH_3, 36H), 1.84 (m, $CH$$CH_3$, 6H), 2.80 (d, $^3J_{HH}$ = 7.3 Hz, 12H). ^{13}C NMR: δ 20.47 (CHCH_3), 27.30 ($CH$$CH_3$), 53.22 (N$CH_2$). ^{11}B NMR: δ 23.9 ($h_{1/2}$ = 1700 Hz).

2,4,6-Tris(di-*s*-butylamino)boroxine (2c). Yellow oil (bp 165 °C (0.0075 Torr)). Anal. Calcd for $C_{24}H_{54}B_3N_3O_3$ (465.14): C, 61.97; H, 11.70; N, 9.03. Found: C, 61.39; H, 11.84; N, 9.01. MS: EI *m*/*e* (rel intensity) 465 (8) [M^+], 436 (100); FI 465 (100). ^{1}H NMR: δ 0.86 (t, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3, 18H), 1.12 (d, $^3J_{HH}$ = 6.5 Hz, CHCH_3, 9H), 1.14 (d, $^3J_{HH}$ = 6.0 Hz, CHCH_3, 9H), 1.45−1.65 (m, $CH_2$$CH_3$, 12H), 3.20 (br, N$CH$, 6H). ^{13}C NMR: δ 12.05, 12.10, 12.16, 12.22 (CH_2CH_3), 20.62, 20.74 (CHCH_3), 29.56, 29.69 ($CH_2$$CH_3$), 50.37, 50.62 (N$CH$). ^{11}B NMR: δ 22.6 ($h_{1/2}$ = 2200 Hz).

2,4,6-Tris(dipropylamino)boroxine (2g)[2]**.** Yellowish liquid (bp 85 °C (0.001 Torr)). $C_{18}H_{42}B_3N_3O_3$ (380.98). MS: EI *m*/*e* (rel intensity) 381 (5) [M^+], 352 (100); FI 381 (100). ^{1}H NMR: δ 0.85 (t, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3, 18H), 1.30−1.60 (m, $CH_2$$CH_3$, 12H), 2.75−2.95 (m, N$CH_2$, 12H). ^{13}C NMR: δ 11.64,

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(40) Bromm, D. Diplomarbeit Universität Göttingen, 1987.

11.69 (CH_2CH_3), 23.38, 23.47 (CH_2CH_3), 47.66, 49.15 (NCH_2). ^{11}B NMR: δ 22.30 ($h_{1/2}$ = 620 Hz).

2,4,6-Tris(dicyclohexylamino)boroxine (2h). White solid (sublp 270 °C (0.001 Torr), not melting below 310 °C). Anal. Calcd for $C_{36}H_{66}B_3N_3O_3$ (621.87): C, 69.54; H, 10.69; N, 6.76. Found: C, 70.21; H, 10.78; N, 6.69. MS: EI *m/e* (rel intensity) 621 (100); FI 621 (100). ^{1}H NMR: δ 1.10−1.30 (m, CH_2), 1.60 (m, CH_2), 1.72 (m, CH_2), 1.90 (m, CH_2), 2.62 (m, $CHCH_2$). ^{13}C NMR: δ 25.93, 26.82, 33.46 (CH_2), 53.30, 53.48 ($CHCH_3$). ^{11}B NMR: δ 20.9.

Typical Dehalogenation Reaction of Bis(dialkylamino)dihalo-1,3-diboroxanes: Preparation of 2,3,5,6-Tetrakis(di-*s*-butylamino)-1,4-dioxa-2,3,5,6-tetraborinane (3c) and 2,3-Bis(di-*s*-butylamino)-1-oxa-2,3-diborirane (4c). A 73 g (200 mmol) sample of **1c** was added under vigorous stirring to a suspension of 500 mmol of Na/K alloy (13 g of K, 4 g of Na) in 650 mL of hexane at 25 °C within 1 h. After refluxing the reaction mixture for 60 h, the excess of alkali metals and salts was removed by filtration. The solvent was evaporated under reduced pressure and collected in a trap cooled by liquid N_2. The residue was fractionated by distillation and sublimation, respectively, in a rotating three-bulb system at 0.001 Torr to give four fractions with the following boiling point ranges: 50−100, 100−120, 140−150, and 165−170 °C. The first fraction (50−100 °C) contained bis(di-*s*-butylamino)borane, bis(di-*s*-butylamino)chloroborane, and **4c**. A 1.3 g (4.5%) sample of **4c** (bp 60 °C, 0.001 Torr) was obtained by redistillation of this fraction in a microdistillation apparatus. The fraction bp 100−120 °C contained a mixture of bis(di-*s*-butylamino)-1,3-diboroxane and bis(di-*s*-butylamino)-1-chlorodiboroxane, which were identified by their mass spectra. Attempted separation was unsuccessful. Redistillation of the fraction bp 140−150 °C afforded 27 g (45%) of tris(di-*s*-butylamino)boroxine **2c** (a yellow, viscous liquid), bp 145−150 °C (0.001 Torr). Resublimation of the fraction bp 165−170 °C gave 4.7 g (7.99%) of **3c** (sublp 170 °C (0.001 Torr)). Certainly there are considerable losses in the purification process by distillation and sublimation. Replacing the solvent by octane did not change the composition of the obtained fractions significantly, the main product in this case was also tris(di-*s*-butylamino)boroxine, **2c**.

Syntheses of 3a and 3b. A 61.6 g (0.2 mol) sample of **1a** and 73 g (0.2 mol) of **1b**, respectively, were treated with 0.5 mol of Na/K alloy (13 g of K, 4 g of Na) in 650 mL of hexane. The reactions were carried out as described for **3c**. However, **4a** and **4b** could not be obtained in a pure state (identification by mass spectrometry) by the subsequent distillation and sublimation process. The other byproducts of these reactions are the corresponding bis(dialkylamino)boranes and bis(dialkylamino)chloroboranes (bp 50−70 °C (0.001 Torr)), bis(dialkylamino)-1,3-diboroxanes and bis(dialkylamino)-1-chloro-1,3-diboroxanes (fraction bp 70−90 °C (0.001 Torr)). As for **3c**, the main products are the boroxines **2a** (19.5 g, 39%) and **2b** (28.9 g, 47%). **3a** (sublp 175 °C (0.001 Torr); 5.46 g, (11.47%) and **3b** (sublp 200 °C (0.001 Torr); 6.12 g, (10.41%), which are both colorless solids, were obtained by sublimation. Crystals for the X-ray structure of **3b** were obtained by crystallization from hexane.

2,3,5,6-Tetrakis(diisopropylamino)-1,4-dioxa-2,3,5,6-tetraborinane (3a). White solid (sublp 175 °C (0.001 Torr); mp 185 °C (dec)). Anal. Calcd for $C_{24}H_{56}B_4N_4O_2$ (475.97): C, 60.56; H, 11.86; N, 11.77. Found: C, 60.32; H, 12.05; N, 11.72. MS: EI *m/e* (rel intensity) 476 (45) [M^+], 433 (100); FI 476 (100). ^{1}H NMR (toluene-d_8): δ 1.06 (d, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$, 12H), 1.09 (d, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$, 12.H), 1.43 (d, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$, 12H), 1.51 (d, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$, 12H), 3.05 (sept, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$, 4H), 3.78 (sept, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$, 4H). ^{13}C NMR: δ 21.53, 23.53, 23.91, 25.00 ($CHCH_3$), 43.95, 50.62 ($CHCH_3$). ^{11}B NMR: δ 35.6 ($h_{1/2}$ = 480 Hz).

2,3,5,6-Tetrakis-(di-i-butylamino)-1,4-dioxa-2,3,5,6-tetraborinane (3b). White solid (sublp 200 °C (0.001 Torr); mp (dec) from 245 °C). Anal. Calcd for $C_{32}H_{72}B_4N_4O_2$ (588.19): C, 65.34; H, 12.34; N, 9.52. Found: C, 65.76; H, 12.45; N, 9.51. MS: EI *m/e* (rel intensity) 588 (15) [M^+], 545 (100); FI 588 (100). ^{1}H NMR (toluene-d_8): δ 0.72 (d, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$, 24H), 0.84 (d, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$, 24H), 1.70−1.90 (m, $CHCH_3$, 8H), 2.78 (d, $^3J_{HH}$ = 7.3 Hz, NCH_2, 16H). ^{13}C NMR: δ 19.92, 20.52, 20.71 ($CHCH_3$), 25.96, 27.10 ($CHCH_3$), 50.62, 56.70 (CH_2CH). ^{11}B NMR: δ 34.6 ($h_{1/2}$ = 1150 Hz).

Table 4. Educts and Products to 5−7

compd	g (mmol) of aromatic educt	g (mmol) of 1,3-dichloro-1,3-diboroxane **1**	yield (g (%))
5c	25.6 (200)	36.5 (100) **1c**	12.6 (30.0)
6a	36.5 (200)	30.8 (100) **1a**	14.5 (35.0)
6b	36.5 (200)	36.5 (100) **1b**	13.7 (29.0)
6c	36.5 (200)	36.5 (100) **1c**	12.35 (26.2)
6h	36.5 (200)	46.9 (100) **1h**	18.10 (31.4)
7	36.5 (200)	36.5 (100) **1b**	16.30 (34.5)

2,3,5,6-Tetrakis-(di-*s*-butylamino)-1,4-dioxa-2,3,5,6-tetraborinane (3c). White solid (sublp 170 °C (0.001 Torr); mp (dec) at 243 °C). Anal. Calcd for $C_{32}H_{72}B_4N_4O_2$ (588.19): C, 65.34; H, 12.34; N, 9.52. Found: C, 65.80; H, 12.41; N, 9.48. MS: EI *m/e* (rel intensity) 588 (20) [M^+], 559 (100); FI 588 (100). ^{1}H NMR: δ 0.75−1.40 (m, CH_3, CH_2, 64H), 1.50 (br, NCH, 2H), 1.95 (m, NCH, 2H), 2.65 (m, NCH, 2H), 3.35 (br, NCH, 2H). ^{13}C NMR: δ 12.34, 12.40, 12.56, 12.61, 12.77, 12.90, 12.97, 13.03 (CH_2CH_3), 20.09, 20.40, 20.62, 20.71, 20.86, 20.88, 21.11, 21.32 ($CHCH_3$), 50.22, 50.78, 50.95, 51.04, 56.67, 56.74, 56.81, 56.89 ($CHCH_3$). ^{11}B NMR: δ 35.7 ($h_{1/2}$ = 1200 Hz).

2,3-Bis(di-*s*-butylamino)-1-oxa-2,3-diborirane (4c). Colorless liquid (bp 60 °C (0.075 Torr)). Anal. Calcd for $C_{16}H_{36}B_2N_2O$ (294.09). C, 65.35; H, 12.34; N, 9.52. Found: C. 65.15; H, 12.52; N, 9.43. MS: EI *m/e* (rel intensity) 265 (100) [$M - C_2H_5]^+$; FI 294 (100). ^{1}H NMR: δ 0.88 (t, $^3J_{HH}$ = 7.3 Hz, CH_2CH_3, 12H), 1.17 (d, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$, 3H), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$, 6H), 1.23 (d, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$, 3H), 1.35−1.75 (m, CH_2CH_3, 8H), 2.90 (sept, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$, 1H), 2.92 (sept. $^3J_{HH}$ = 6.7 Hz, $CHCH_3$, 1H), 3.42 (sept, $^3J_{HH}$ = 6.5 Hz, $CHCH_3$, 2H). ^{13}C NMR: δ 11.35, 11.37, 11.39, 11.76 (CH_2CH_3), 20.97, 21.04, 24.01, 24.10 (CH_2CH_3), 29.35, 29.37, 31.77, 32.10 (CH_2CH_3), 53.30, 54.03, 55.23, 55.87 (NCH). ^{11}B NMR: δ 36.2 ($h_{1/2}$ = 490 Hz).

Typical Reaction of Alkali Metal Complexes of Aromatic Compounds with Bis(dialkylamino)dihalo-1,3-diboroxanes: 1,3-Bis(diisopropylamino)(1,2-dihydronaphthalene-1,2-diyl)-1,3-diboroxane (5a). A 25.6 g (200 mmol) sample of naphthalene was added during 30 min to a stirred suspension of 200 mmol Na/K alloy (5.2 g K, 1.6 g Na) in a solvent mixture of 1,2-dimethoxyethane (250 mL) and hexane 250 mL) at 25 °C. The start of the reaction was indicated by black coloring of the suspension. Stirring was continued for 24 h at room temperature. In due course, 30.8 g (100 mmol) of **1** in 200 mL of hexane was added within 1 h. The exothermic reaction was accompanied by a color change from black to grey. After refluxing for 6 h the slurry was filtered, the solvents were evaporated from the filtrate under reduced pressure, and the residue fractionated by sublimation in a rotating three-bulb system. As a first fraction, 12.5 g of a mixture of naphthalene and dihydronaphthalene sublimed/distilled, respectively, at 60−80 °C (0.001 Torr); 11.7 g, (32%) **5a** was obtained by subsequent sublimation at 120 °C (0.001 Torr).

5c, **6a**−**c**, **6h**, and **7** were prepared in the same manner. For educt quantities and product yields, see Table 4. As for **5a** for **5c**, the color turns from black to grey by addition of the 1,3-dihalo-1,3-diboroxane derivative; in the reactions of anthracene and phenanthrene, respectively, it turns from black to green. The starting materials were partially recovered in the low subliming fractions at 60−80 (for **5** and **7**) and 100−120 °C (0.001 Torr) (for **6**). Dihydronaphthalene and dihydroanthracene were identified by their mass spectra in these

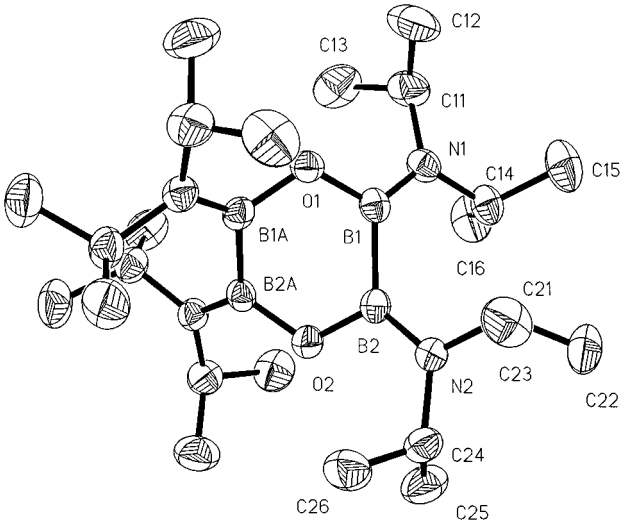

Figure 2. Crystal structure of **3a** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

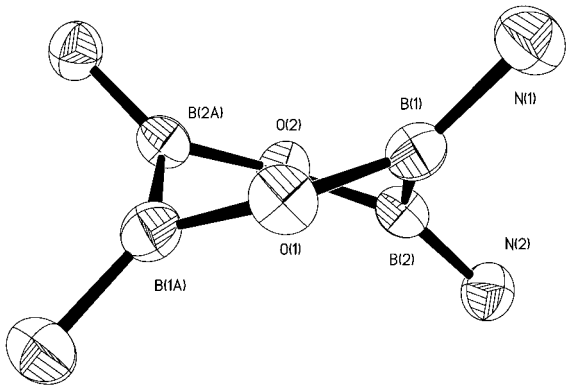

Figure 3. Crystal structure of the skeleton of **3a** seen from the direction of the 2-fold axis (tilted by 5°). Anisotropic displacement parameters depicting 50% probability.

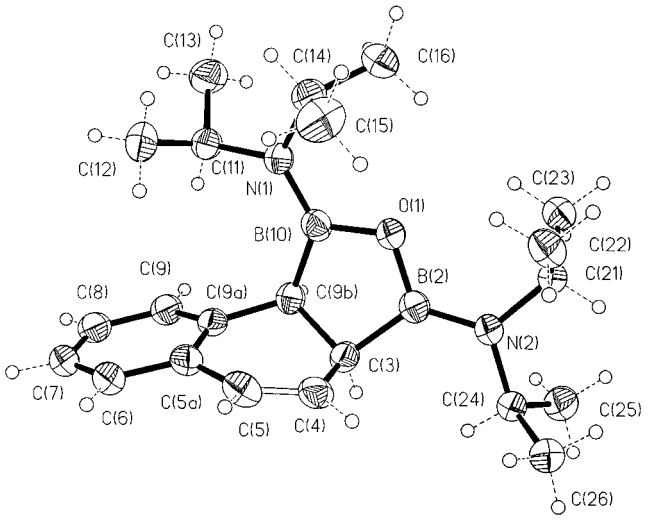

Figure 4. Crystal structure of **5a** with anisotropic displacement parameters depicting 50% probability.

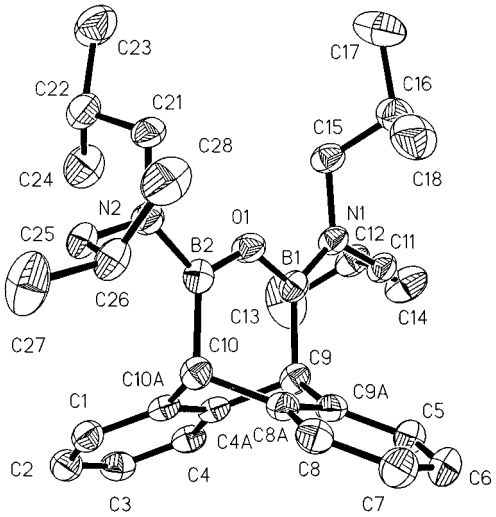

Figure 5. Crystal structure of **6b** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

fractions. The yields are summarized in Table 4. Crystals for the X-ray analysis of **5a** and **6b** were obtained by crystallization from *n*-hexane.

1,3-Bis(diisopropylamino)-(1,2-dihydronaphthalene-1,2-diyl)-1,3-diboroxane (5a). Colorless crystals (sublp 120 °C (0.001 Torr); mp 116−119 °C). Anal. Calcd for $C_{22}H_{36}B_2N_2O$ (366.16): C, 72.16; H, 9.92; N, 7.65. Found: C, 72.25; H, 10.04; N, 7.72. MS: EI *m/e* (rel intensity) 366 (10) [M^+]; FI 366 (100). ^{1}H NMR: δ 0.46 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.98 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.12 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H), 1.33 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 2.35 (dvt, 2H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 2.7 Hz, $^4J_{HH}$= 2.8 Hz, 1H), 2.66 (d, 1H, $^3J_{HH}$ = 8.5 Hz, 1H), 3.03 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, *CH*CH$_3$), 3.24 (sept, $^3J_{HH}$ = 6.8 Hz, CH*CH*$_3$, 1H), 3.65 (sept, $^3J_{HH}$ = 6.7 Hz, *CH*CH$_3$, 1H), 3.70 (sept, $^3J_{HH}$ = 6.7 Hz, *CH*CH$_3$, 1H), 5.78 (dvd, 3-H, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 2.7 Hz, 1H), 6.37 (dvd, 4-H, $^3J_{HH}$ = 9,5 Hz, $^4J_{HH}$= 2.8 Hz, 1H), 6.90−7.10 (m, possible 5−8, 4H). ^{13}C NMR: δ 21.2, 21.7, 22.4, 22.5, 24.0, 24.1 (CH*CH*$_3$), 29.2 (br, 2-C), 33.2 (br, 1-C), 43.6, 43.9, 47.2, 48.4 (*CH*CH$_3$), 126.9 (4-C), 124.8, 125.3, 126.2, 128.2 (5-C to 8-C), 130.7 (3-C), 133.5, 138.5 (C_q). ^{11}B NMR: δ 36.3 ($h_{1/2}$ = 500 Hz).

1,3-Bis(di-*s*-butylamino)-(1,2-dihydronaphthalene-1,2-diyl)-1,3-diboroxane (5c). White solid (sublp 140 °C (0.001 Torr); mp (dec) from 196 °C). Anal. Calcd for $C_{26}H_{44}B_2N_2O$ (422.26): C, 73.96; H, 10.50; N, 6.63. Found: C, 73.45; H, 10.70; N, 6.55. MS: EI *m/e* (rel intensity) 422 (15) [M^+], 393 (100),; FI 393 (100). ^{1}H NMR: δ 0.85 (m, CH$_2$*CH*$_3$, 12H), 1.05−1.30 (m, CH*CH*$_3$, 12H), 1.55 (m, *CH*$_2$CH$_3$, 8H), 2.35 (br, B*CH*, 1H), 2.65 (m, N*CH*, 2H), 2.85 (br, B*CH*×e2 1H), 3.35 (m, N*CH*, 2H), 5.70−5.90 (m, 3-H, 1H), 6.30−6.40 (m, 4-H, 1H), 6.85−7.05 (m, 5-H bis 8-H, 4H). ^{13}C NMR: δ 11.84, 11.89, 11.95, 12.01 (CH$_2$*CH*$_3$), 19.26, 20.50, 20.62, 20.78 (CH*CH*$_3$), 21.31, 27.91, 27.95, 29.10 (*CH*$_2$CH$_3$), 33.0 (br, B-C), 50.31, 50.39, 50.49, 50.55 (*CH*CH$_3$), 124.67, 125.21, 127.25, 128.28, 128.31, 130.93 (3-C bis 8-C), 133.49, 139.12 (C_q). ^{11}B NMR: δ 36.3 ($h_{1/2}$ = 940 Hz).

1,3-Bis(diisopropylamino)-(9,10-dihydroanthracene-9,10-diyl)-1,3-diboroxane (6a). Light brown solid (bp 135 °C (0.001 Torr); mp 174−6 °C). Anal Calcd for $C_{26}H_{38}B_2N_2O$ (416.22): C, 75.04; H, 9.32; N, 6.69; Found: C, 74.67; H, 9.42; N, 6.69. MS: EI *m/e* (rel intensity) 416 (30) [M^+]; FI 416 (100). ^{1}H NMR: δ 0.98 (d, $^3J_{HH}$ = 6.9 Hz, CH*CH*$_3$, 12H), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, CH*CH*$_3$, 12H), 3.80 (m, *CH*CH$_3$, 4H), 4.12 (s, 9-H and 10-H, 2H), 6.98−7.40 (m, 1-H to 4-H and 5-H to 8-H, 8H). ^{13}C NMR: δ 22.26, 25.00 (CH*CH*$_3$), 43.21, 44.45 (*CH*CH$_3$), 43.70 (br, B-C, 9-C and 10-C), 124.85, 125.53 (1-C, 2-C), 140.85 (C_q). ^{11}B NMR: δ 28.2 ($h_{1/2}$ = 680 Hz).

1,3-Bis(di-i-butylamino)-(9,10-dihydroanthracene-9,10-diyl)-1,3-diboroxane (6b). Yellowish, highly viscous substance (bp 150 °C (0.001 Torr)) which crystallizes slowly (mp 112−3 °C) after crystallization from n-hexane. Anal. Calcd for $C_{30}H_{46}B_2N_2O$ (472.31): C, 76.29; H, 9.82; N, 5.93. Found: C, 75.98, H, 10.02; N, 5.97. MS: EI *m/e* (rel intensity) 472(20)

Table 5. Crystal Data and Structure Refinement for 1a, 3a, 5a, and 6b

	1a	3a	5a	6b
formula	$C_{12}H_{28}B_2Cl_2N_2O$	$C_{24}H_{56}B_4N_4O_2$	$C_{22}H_{36}B_2N_2O$	$C_{30}H_{46}B_2N_2O$
fw	308.88	475.97	366.15	472.31
temp (K)	153(2)	213(2)	153(2)	153(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/c$
a (Å)	10.992(1)	9.673(1)	11.236(5)	18.317(2)
b (Å)	15.150 (1)	28.584(8)	6.163(3)	9.080(1)
c (Å)	11.063(1)	12.6070(1)	32.606(9)	18.930(3)
α (deg)	90	90	90	90
β (deg)	94.16(1)	111.55(1)	97.17(9)	111.81(1)
γ (deg)	90	90	90	90
volume (Å^3), Z	1837.5(3), 4	3242.1(10), 4	2240(2), 4	2923.0(6), 4
density (calcd) (Mg m^{-3})	1.117	0.9756	1.086	1.073
abs coeff (mm^{-1})	0.348	0.059	0.064	0.063
F(000)	664	1056	800	1032
crystal size (mm)	0.70 × 0.70 × 0.50	0.50 × 0.40 × 0.40	0.70 × 0.70 × 0.50	0.80 x 0.80 × 0.70
θ-range for data coll (deg)	3.69−24.98	3.76−22.53	3.54−22.54	3.59−22.46
limiting indices	$-13 \le h \le 13$	$-10 \le h \le 10$	$-12 \le h \le 2$	$-19 \le h \le 19$
	$-8 \le k \le 18$	$-3 \le k \le 30$	$-6 \le k \le 6$	$-3 \le k \le 9$
	$-13 \le l \le 13$	$-13 \le l \le 13$	$-35 \le l \le 35$	$-12 \le l \le 20$
no. of rflns coll	5195	2440	3379	3822
no. of indep rflns	3206	2125	2874	3788
R(int)	0.0293	0.0629	0.0744	0.1022
refinement method full-matrix-least squares on F^2				
g_1	0.030	0.076	0.110	0.066
g_2	2.050	2.260	1.830	0.954
data/restraints/parameters	3200/0/180	2121/0/163	2869/0/252	3782/0/324
goodness of fit on F^2	1.118	1.038	1.040	1.038
final R indices [$I > 2\sigma(I)$]	R1 = 0.0488	R1 = 0.0545	R1 = 0.0662	R1 = 0.0417
	wR2 = 0.1167	wR2 = 0.1327	wR2 = 0.1730	wR2 = 0.1066
R indices (all data)	R1 = 0.0571	R1 = 0.0804	R1 = 0.0802	R1 = 0.0473
	wR2 = 0.1276	wR2 = 0.1576	wR2 = 0.1963	wR2 = 0.1161
largest diff peak and hole (e Å^{-3})	0.390 and −0.215	0.209 and −0.187	0.344 and −0.267	0.181 and −0.185

[M$^+$], 429(100); FI 472(100). ^{1}H NMR: δ 0.60 (d, $^3J_{HH}$ = 6.7 Hz, CHCH_3, 12H), 0.96 (d, $^3J_{HH}$ = 6.7 Hz, CHCH_3, 12H), 1.76 (sept v. t, CHCH$_3$, zu d bei 0.60, 2H), 1.91 (sept v. t, CHCH$_3$, zu d. bei 0.96, 2H), 4.03 (s, 9-H, 10-H, 2H), 2.75 (d, $^3J_{HH}$ = 7.6 Hz, NCH_2, zu 1.76, 4H), 3.05 (d, $^3J_{HH}$ = 7.4 Hz, NCH_2, zu 1.91, 4H), 7.03 (m, 2-H, 4H), 7.13 (m, 1-H, 4H). ^{13}C NMR: δ 19.9, 20.6 (CHCH_3), 26.8, 28.2 (CHCH$_3$), 41.4 (B-C), 52.6, 55.0 (NCH_2), 125.0 (2-C), 125.3 (1-C), 140.2 (C$_q$). ^{11}B NMR: δ 28.2 ($h_{1/2}$ = 1000 Hz).

1,3-Bis(di-*s*-butylamino)-(9,10-dihydroanthracene-9,10-diyl)-1,3-diboroxane (6c). Ockre oil, solidifies upon storing (bp 170 °C (0.001 Torr); mp 101−4 °C). Anal. Calcd for $C_{30}H_{46}B_2N_2O$ (472.31): C, 76.29; H, 9.82; N, 5.93. Found: C, 76.55; H, 9.97; N, 5.84. MS: EI m/e (rel intensity) 472 (35) [M$^+$], 443 (100); FI 472 (100). ^{1}H NMR: δ 0.50−2.00 (m, CH$_3$, CH$_2$, 32H), 3.60 (br, NCH, 4H), 4.10 (s, 9-H, 10-H, 2H). ^{13}C NMR: δ 11.62, 12.13, 12.53, 12.71, 14.10 (CH$_3$), 22.68, 29.74, 31.62 (CH$_2$), 43.19 (BC), 50.25, 50.48, 51.03, 51.27 (NCH), 124.81, 125.45 (1-C, 2-C), 140.77 (C$_q$). ^{11}B NMR: δ 28.3 ($h_{1/2}$ = 1300 Hz).

1,3-Bis(dicyclohexylamino)-(9,10-dihydroanthracene-9,10-diyl)-1,3-diboroxane (6h). White solid (sublp 250 °C (0.001 Torr); mp 213−218 °C). Anal. Calcd for $C_{38}H_{54}B_2N_2O$ (576.48): C, 79.17; H, 9.44; N, 4.86. Found: C, 78.63; H, 9.52; N, 4.69. MS: EI m/e (rel intensity) 576 (5) [M$^+$], 138 (100). ^{1}H NMR: δ 0.95−2.25 (m, CH$_2$, 40 H), 2.95 (br, CHCH$_2$, 2H), 3.60 (br, CHCH$_3$, 2H), 4.20 (s, 9-H and 10-H, 2H), 7.05 (m, 2-H, 4H), 7.27 (m, 4-H, 4H). ^{13}C NMR: δ 25.60, 26.13, 26.33, 32.30, 36.17 (CH$_2$), 43.70 (br, BCH), 54.39 (9-C, 10-C), 124.80 (1-C), 125.56 (2-C), 141.02 (C$_q$). ^{11}B NMR: δ 29.3 ($h_{1/2}$ = 1000 Hz).

1,3-Bis(di-i-butylamino)-(9,10-dihydrophenanthrene-9,10-diyl)-1,3-diboroxane (7). Yellowish, viscous liquid (bp 180 °C (0.001 Torr)). Anal. Calcd for $C_{30}H_{46}B_2N_2O_2$ (472.33): C, 76.29; H, 9.82; N, 5.93. Found: C, 75.89; H, 9.85; N, 5.86. MS: EI m/e (rel intensity) 472 (5) [M$^+$], 178 (100); FI 472 (100). ^{1}H NMR: δ 0.50−0.95 (m, CHCH_3, 24H), 1.65−1.85 (m, CHCH$_3$, 4H), 2.60 (d, $^3J_{HH}$ = 6.6 Hz, 2H), 2.65 (d, $^3J_{HH}$ = 6.6 Hz, 4H), 2.76 (d, $^3J_{HH}$ = 7.3 Hz, 4H), 2.83 (s, B-CH, 2H), 7.05−7.60 (m, 1-H bis 8-H). ^{13}C NMR: δ 19.64, 19.73, 19.86, 20.50 (CHCH_3), 33.1 (br, BC), 53.02, 53.07 (NCH_2), 123.80, 125.84, 126.96, 128.76 (1-C bis 8-C), 134.65, 139.80 (C$_q$). ^{11}B NMR: δ 35.90 ($h_{1/2}$ = 750 Hz).

Hydrolytic reactions of 5a, 6a and 7. To 5 g **5a**, **6a**, and **7**, respectively, dissolved in *n*-hexane, 50 mL of 30 °C aqueous, KOH was added and the mixture refluxed for 8 h. The hexane phase was separated and the aqueous phase extracted with diethyl ether. The etheric phase and the hexane phase were combined and dried by $MgSO_4$. After filtration from $MgSO_4$ and removal of the solvents, the residue was distilled and yielded 1,2-dihydronaphthalene for the reaction of **5a**, 9,10-dihydroanthracene for **6a**, and 9,10-dihydrophenanthrene for **7**, identified by their mass spectra.

X-ray Structure Determinations for 1a, 3a, 5a, and 6b. Data were collected on a Stoe-Siemens diffractometer with monochromated Mo Kα radiation (λ = 71.073 pm). The temperatures of the measurements are listed in Table 3. The structures were solved by direct methods using SHELXS-90.[41] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms the riding model was used. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g^2P$, with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93.[42] The R values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$. Figures 1 −5 (hydrogen atoms omitted) show 50% probability displacement ellipsoids. Crystal data and structure refinement details are listed in Table 5.

(41) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(42) Sheldrick, G. M. SHELXL-93, program for crystal structure refinement, University of Göttingen, 1993.

Summary. Bis(dialkylamino)dihalogenodiboroxanes, **1**, are obtained together with the corresponding tris(dialkylamino)-boroxines, depending upon the steric requirement of the *N*-alkyl substituents. Upon dehalogenation of **1** with Na/K alloy, tetrakis(dialkylamino)-1,4-dioxa-2,3,5,6-tetraborinanes **3** were formed, and in the case of the sterically most demanding di-*s*-butylamino substituents, the corresponding 1-oxa-2,3-diborirane, **4c**, was isolated. Dehalogenation of **1** in the presence of naphthalene, anthracene, or phenanthrene resulted in the 1,2-(dihydronaphthalene-1,2-diyl), (9,10-dihydroanthrancene-9,10-diyl)-, or (9,10-dihydrophenanthrene-9,10-diyl)-1,3-diboroxane derivatives, respectively.

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Supporting Information Available: Tables of crystal data, complete fractional coordinates and *U* values, bond lengths and angles, and anisotropic displacement parameters and fully labeled figures of 50% anisotropic displacement parameters of the structures **1a**, **3a**, **5a**, and **6b** (28 pages). Ordering information is given on any current masthead page.

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