Diverse Reactivity of Dialkylaluminum Dimesitylboryloxides $[(\mu\text{-}Mes_2BO)AlR_2]_2$. Synthetic and Structural Study

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Several stable dimeric dialkylaluminum boryloxides of the formula $[(\mu\text{-}Mes_2BO)AlR_2]_2$ (R = Me (**1**), Et (**2**), ^iBu) have been prepared from dimesitylborinic acid Mes_2BOH and trialkylaluminums R_3Al. Compound **1** has been characterized by X-ray diffraction. These compounds exhibit diverse reactivity toward protonolytic reagents depending on the bulkiness of these reagents. Treatment of **1** with *tert*-butyl alcohol afforded crystalline species *trans*-$[(\mu\text{-}^tBuO)(Mes_2BO)AlMe]_2$ (**3**), which is the first example of a mixed system containing boryloxide and alkoxide ligands together. Most surprisingly, Mes_2BOH was found to undergo catalytic decomposition in the presence of $[(\mu\text{-}Mes_2BO)AlR_2]_2$ via the unexpected cleavage of one boron−carbon bond. The molecular structure of the decomposition product, i.e., trimesitylboroxin $[MesBO]_3$ (**4**) is reported.

Introduction

A number of reports concerning metal boryloxides have appeared since the 1970s.[1] However, up to now the chemical properties of these compounds have attracted only little attention when compared to synthetic and structural aspects. The recent interest in our laboratory has focused on the synthesis and full characterization of groups 12 and 13 alkylmetal boryloxides of type $[(\mu\text{-}R_2BO)MR'_2]_2$ (M = Al, Ga, In)[2] and $[(\mu\text{-}R_2BO)MR']_4$ (M = Zn, Cd).[3] These compounds can usually be prepared by the treatment of a metal alkyl with an appropriate diorganoborinic acid or tetraorganodiboroxane. However, this method generally does not work for alkylaluminum derivatives when the R substituent bonded to boron is not bulky, e.g., R = Et,[4] R_2 = cyclooctane-1,5-diyl.[2] The major drawback of such a procedure is the subsequent boron alkylation.[4] This results in poor yields of the corresponding alkylaluminum boryloxide. Similar or worse yields were obtained from reactions of aluminum alkyls with diboroxanes.[2] We were interested in a high-yield synthesis of alkylaluminum boryloxides in order to study their chemistry more extensively. It was found earlier that the use of mesityl groups gives the boron atom considerable protection from further reaction,[5] and indeed, we have found that the Mes_2B group is also resistant against alkylation on boron. Thus, dialkylaluminum dimesitylboryloxides $[(\mu\text{-}Mes_2BO)AlR_2]_2$ (R = Me, Et, ^iBu) are fairly stable and do not decompose even when heated in boiling toluene. In this paper, besides preparative and structural details, we describe some results concerning the diverse reactivity of these compounds.

Experimental Section

General Comments. All reactions were carried out under an argon atmosphere using the standard Schlenk techniques. Solvents were dried with sodium benzophenone ketyl, distilled and stored under argon. Aluminum alkyls (Aldrich) were used as received. Trimethylgallium was a gift from Prof. K. Starowieyski from our university. Boron-containing reagents Mes_2BOH,[6] 9-(OH)-9-BBN,[7] $(9\text{-BBN})_2O$,[8] have been prepared according to the literature descriptions. *tert*-Butyl alcohol was dried with sodium and freshly distilled prior to use. ^1H, ^{11}B, and ^{27}Al NMR spectra were recorded at room temperature on a Varian Unity Plus 200 spectrometer using benzene-d_6 as the solvent (unless otherwise noted). Chemical shifts are given in ppm relative to C_6D_5H (δ = 7.17 ppm), $Et_2O{\cdot}BF_3$, and $Al(acac)_3$ in ^1H, ^{11}B, and ^{27}Al NMR spectra, respectively. Elemental analyses were performed using a Perkin-Elmer 2400 apparatus.

Preparation of $[(\mu\text{-}Mes_2BO)AlR_2]_2$ (R = Me (1), Et (2)). A solution of Mes_2BOH (0.95 g, 3.57 mmol) in toluene (10 mL) was added fot 2−3 min to a stirred solution of Me_3Al (0.30 g, 4.17 mmol) in toluene (2 mL) at −70 °C. The resultant solution was allowed to warm slowly to room temperature with stirring. Toluene was removed under reduced pressure, and the residue was washed with hexane (3 × 5 mL) to yield **1** (0.90 g, 78%), mp 225−230 °C. ^1H NMR: δ 6.69 (s, 4H, arom), 2.49 (s, 12H, *o*-Me), 2.04 (s, 6H, *p*-Me), −0.47 (s, 6H, AlMe). ^{11}B NMR: δ 57.3. ^{27}Al NMR: δ 160. Anal. Calcd for $C_{20}H_{28}AlBO$: C, 74.55; H, 8.76. Found: C, 74.65; H, 8.81.

Compound $[(\mu\text{-}Mes_2BO)AlEt_2]_2$ (**2**) was prepared similarly starting from Mes_2BOH (1.38 g, 5.19 mmol) and Et_3Al (0.60 g, 5.26 mmol).

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(8) See ref 1, p 816.

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Table 1. Crystal Data and Structure Refinement of **1**, **3**, **4**

	1	**3**	**4**
compd	$[(\mu\text{-Mes}_2\text{BO})\text{AlMe}_2)]_2$	*trans*-$[(\mu\text{-}^t\text{BuO})(\text{Mes}_2\text{BO})\text{AlMe}]_2$	$[\text{MesBO}]_3$
empirical formula	$C_{40}H_{56}Al_2B_2O_2$	$C_{46}H_{68}Al_2B_2O_4$	$C_{27}H_{33}B_3O_3$
fw	644.43	380.29	437.96
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	*Pbca*	$C2/c$
a, Å	11.2190(2)	17.2070(3)	8.991(2)
b, Å	16.5510(5)	8.6950(4)	14.081(3)
c, Å	11.6130(4)	31.413(1)	20.024(4)
β, deg	114.049(1)		101.36(3)
V, Å3	1969.2(1)	4699.9(3)	2485.4(9)
Z	2	8	4
d (calcd), Mg/m^3	1.087	1.075	1.170
temp, K		293(2)	
λ, Å		0.710 73	
μ, mm^{-1}	0.105	0.100	0.072
F(000)	696	1648	936
cryst size, mm	0.92 × 0.30 × 0.40	0.95 × 0.32 × 0.44	0.72 × 0.60 × 0.45
θ range, deg	2.13−27.52	2.70−23.81	2.73−30.09
reflns collected	8324	6775	6536
reflns unique	4506 [$R_{int} = 0.025$]	3502 [$R_{int} = 0.029$]	3316 [$R_{int} = 0.0694$]
GOF	1.030	1.013	0.993
R_w [$I > 2\sigma(I)$]^a	R1 = 0.0599	R1 = 0.0569	R1 = 0.0681
R_{all}	R1 = 0.1171	R1 = 0.1368	R1 = 0.1693
abs correction	none	none	none
largest diff peak and hole, e Å^{-3}	0.357 and −0.257	0.142 and −0.182	0.369 and −0.215

[a] $R1 = \sum| |F_o| - |F_c||/|F_o|$.

The yield of **2** was 1.06 g, 58%, mp 195−210 °C. ^{1}H NMR: δ 6.72 (br, 4H, arom), 2.48 (br, 12H, *o*-Me), 2.07 (s, 6H, *p*-Me), 0.74 (t, 6H, $AlCH_2CH_3$), 0.34 (q, 4H, $AlCH_2$). ^{11}B NMR: δ 57.3. ^{27}Al NMR: δ 160. Anal. Calcd for $C_{22}H_{32}AlBO$: C, 75.44; H, 9.21. Found: C, 75.28; H, 9.42.

Preparation of $[(\mu\text{-}^t\text{BuO})(\text{Mes}_2\text{BO})\text{AlMe}]_2$ (3). A solution of *tert*-butyl alcohol (0.16 g, 2.16 mmol) in toluene (2 mL) was added for 2−3 min to a stirred solution of **1** (0.70 g, 1.09 mmol) in toluene (10 mL) at 0 °C. The resultant solution was allowed to warm slowly to room temperature with stirring. Toluene was removed under reduced pressure. The oily residue was recrystallized from a hexane/toluene mixture (2:1, 15 mL) to yield **3** (0.40 g, 48%), mp 240−242 °C. ^{1}H NMR: δ 6.80 (s, 4H, arom), 2.49 (s, 12H, *o*-Me), 2.18 (s, 6H, *p*-Me), 1.03 (s, 9H, Bu^t), −0.21 (s, 3H, AlMe). ^{11}B NMR: δ 49.0. ^{27}Al NMR: δ 95.9. Anal. Calcd for $C_{23}H_{34}AlBO_2$: C, 72.64; H, 9.01. Found: C, 72.44; H, 9.07.

Catalytic Decomposition of Mes_2BOH. A solution of Me_3Al (0.05 g, 0.69 mmol) in toluene (1 mL) was added to a solution of Mes_2BOH (1.33 g, 5.0 mmol) in toluene (10 mL). The resultant solution was heated at 100 °C for 1 h with stirrring. Toluene and the byproduct mesitylene were removed under reduced pressure. The residue was washed with warm hexane (4 × 5 mL) and dried in vacuo to yield trimesitylboroxin $[MesBO]_3$ (**4**) (0.50 g, 68%), mp 227−230 °C. ^{1}H NMR ($CDCl_3$): δ 6.85 (s, 6H, arom), 2.46 (s, 18H, *o*-Me), 2.28 (s, 9H, *p*-Me). ^{11}B NMR: ($CDCl_3$) δ 31.3. Anal. Calcd for $C_9H_{11}BO$: C, 74.55; H, 8.76. Found: C, 74.65; H, 8.81.

Preparation of $[(\mu\text{-9-BBN-9-O})\text{AlMe}_2]_2$ (5). A solution of 9-(OH)-9-BBN (0.44 g, 3.19 mmol) in toluene (5 mL) was added to a stirred solution of **1** (0.98 g, 1.52 mmol) in toluene (10 mL) at −70 °C. The resultant solution was allowed to warm slowly to 0 °C. A white precipitate was formed. It was dissolved by warming the solution to ca. 40 °C. Slow cooling afforded colorless crystals of **5** (0.31 g, yield 52%), mp >210 °C (dec). ^{1}H NMR: δ 1.78 (m, 10H, 9-BBN), 1.26 (m, 4H, 9-BBN), −0.35 (s, 6H, AlMe). ^{11}B NMR: δ 60.9. Anal. Calcd for $C_{10}H_{20}AlBO$: C, 61.89; H, 10.39. Found: C, 61.69; H, 10.44.

Preparation of $[(\mu\text{-Mes}_2\text{BO})\text{GaMe}_2]_2$ (6). Compound **6** was obtained by the treatment of Me_3Ga (0.52 g, 4.52 mmol) in toluene (5 mL) with Mes_2BOH (1.16 g, 4.36 mmol) in toluene (5 mL) at ca. 0 °C. Toluene was removed, and the residue was recrystallized from hexane (10 mL). The yield of **6** was 0.94 g, 59%), mp 186−188 °C. ^{1}H NMR: δ 6.71 (s, 4H, arom), 2.48 (s, 12H, *o*-Me), 2.08 (s, 6H, *p*-Me), −0.04 (s, 6H, GaMe). ^{11}B NMR: δ 50.0. Anal. Calcd for $C_{20}H_{28}BGaO$: C, 65.82; H, 7.73. Found: C, 65.47; H, 8.00.

Crystal Structure Determination of 1, 3, and 4. The crystals of compounds **1**, **3**, and **4** were grown by slow cooling of their saturated hexane (**1**) or toluene (**3**, **4**) solutions. Selected monocrystals were sealed in glass capillaries under argon. X-ray data for **1** and **3** were collected on a Nonius KappaCCD and for **4** on a KM-4 KUMA diffractometers. For structure **1**, 98 frames with φ scan and 18 frames with ω scan were collected (scan angle, 2°; scan time, 80 s/frame). For the structure **3**, 146 frames with φ scan and 34 frames with ω scan were collected (scan angle, 1°; scan time, 20 s/frame). The measurements were done using the diffractometer control program COLLECT,[9] and unit cell parameters were determined and data reduction was done with DENZO and SCALEPAK programs.[10] The structures were solved by direct methods using SHELXS-97[11] and refined using the full-matrix least-squares method based on F^2.[12] Molecular diagrams were drawn using ATOMS.[13] The details of X-ray measurements, structural computations, and crystal data are given in Table 1. Selected bond lengths, bond angles, and torsion angles are presented in Table 2.

Results and Discussion

Synthesis. Dimesitylborinic acid cleaves readily one Al−C bond of trialkylaluminum at low temperature. The steric hindrance of mesityl groups prevents the boron alkylation, allowing high-yield formation of the corresponding dialkylaluminum dimesitylboryloxide (Scheme 1). Contrary to the previously reported analogues, e.g., $[(\mu\text{-9-BBN-9-O})\text{AlMe}_2]_2$ (**5**),[2] these compounds are more stable and do not show a tendency to undergo decomposition via alkyl group transfer from aluminum to boron even when prolonged heating of the toluene solution was applied. We have chosen compound **1** as the model to study the chemical properties of this class of compounds.

Protonolysis. The treatment with water or an alcohol resulted in the evolution of alkane due to the common cleavage of the

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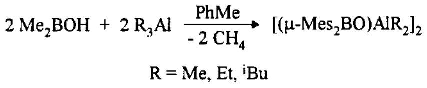
Table 2. Selected Bond Distances [Å] and Angles [deg] for Compounds **1**, **3**, **4**

compound **1**		compound **3**		compound **4**	
Al(1)···Al(1′)	2.858(1)	Al(1)···Al(1′)	2.779(2)	B(1)−O(1)	1.380(3)
Al(1)−O(1′)	1.8741(1)	Al(1)−O(1′)	1.826(2)	B(1′)−O(2)	1.377(3)
Al(1)−O(1)	1.882(1)	Al(1)−O(1)	1.828(2)	B(2)−O(1)	1.375(3)
Al(1)−C(1)	1.933(2)	Al(1)−O(2)	1.709(2)	B(1)−O(2)	1.377(3)
Al(1)−C(2)	1.939(3)	Al(1)−C(1)	1.924(3)	B(1)−C(1)	1.546(4)
B(1)−O(1)	1.389(2)	O(1)−C(2)	1.470(3)	B(2)−O(1′)	1.375(3)
B(1)−C(21)	1.577(3)	O(2)−B(1)	1.348(4)	B(2)−C(10)	1.564(5)
B(1)−C(11)	1.593(3)	B(1)−C(11)	1.587(5)		
		B(1)−C(21)	1.597(5)	B(2)−O(1)−B(1)	122.3(2)
O(1′)−Al(1)−O(1)	80.89(6)			B(1′)−O(2)−B(1)	123.6(3)
Al(1′)−O(1)−Al(1)	99.11(6)	O(2)−Al(1)−O(1′)	108.24(9)	O(2)−B(1)−O(1)	116.8(3)
O(1′)−Al(1)−C(1)	117.09(9)	O(2)−Al(1)−O(1)	111.4(1)	O(2)−B(1)−C(1)	121.7(2)
O(1)−Al(1)−C(1)	118.8(1)	O(1′)−Al(1)−O(1)	80.97(9)	O(1)−B(1)−C(1)	121.4(3)
O(1′)−Al(1)−C(2)	110.09(9)	Al(1′)−O(1)−Al(1)	99.03(9)	O(1)−B(2)−O(1′)	118.2(3)
O(1)−Al(1)−C(2)	108.84(8)	O(2)−Al(1)−C(1)	118.9(1)	O(1)−B(2)−C(10)	120.9(2)
C(1)−Al(1)−C(2)	116.0(1)	O(1′)−Al(1)−C(1)	116.0(1)	O(1′)−B(2)−C(10)	120.9(2)
B(1)−O(1)−Al(1′)	132.5(1)	O(1)−Al(1)−C(1)	115.2(1)		
B(1)−O(1)−Al(1)	128.4(1)	C(2)−O(1)−Al(1)	130.1(2)		
O(1)−B(1)−C(21)	118.5(2)	B(1)−O(2)−Al(1)	150.7(2)		
O(1)−B(1)−C(11)	118.9(2)				

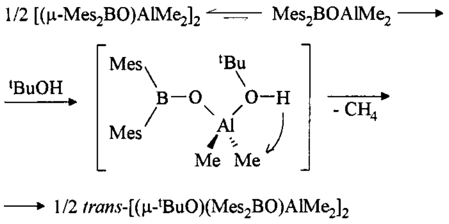
Scheme 1



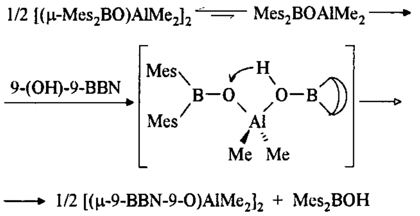
$$2\,Me_2BOH + 2\,R_3Al \xrightarrow[-2\,CH_4]{PhMe} [(\mu\text{-}Mes_2BO)AlR_2]_2$$

R = Me, Et, ^{i}Bu

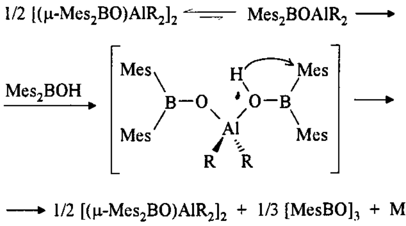
Scheme 2



Scheme 3



Scheme 4



Al−C bond. Unfortunately, products of these reactions could not be well defined in most cases, i.e., when water, methanol, and ethanol were used. In all these cases amorphous or oily materials were obtained. Their NMR spectra exhibit broad resonances, suggesting some dynamic processes involving different type species. The only exception was the treatment of **1** with *tert*-butyl alcohol, which led to the isolation of the crystalline compound *trans*-[(μ-^{t}BuO)(Mes$_2$BO)AlMe]$_2$ (**3**) in moderate yield (Scheme 2).

Exchange of Boryloxide Ligands. We also attempted to obtain species possessing two boryloxide ligands per one aluminum using a quasi-alcohol reagent, i.e., hydroxydialkylborane for the cleavage of the second aluminum−carbon bond in **1**. However, the reaction of **1** with 9-(OH)-9-BBN in toluene afforded [(9-BBN−O)AlMe$_2$]$_2$ (**5**) as the main product. Methane evolution was observed only to a little extent. Apparently the main pathway mechanism involves the initial coordination of 9-(OH)-9-BBN followed by the rapid exchange of diorganoboryloxide ligands and dimerization of the monomeric species 9-BBN-9-OAlMe$_2$ as shown in Scheme 3. The driving force of the reaction is the low solubility of the product **5** in toluene. It should be noted that the yield is much higher than that obtained from the simple treatment of 9-(OH)-9-BBN with Me$_3$Al. The reaction of **1** with diboroxane (9-BBN)$_2$O proceeds similarly to give **5**, and the mechanism should be analogous. However, this reaction proceeds significantly more slowly than that discussed above.

Catalytic Formation of Trimesitylboroxin. We have also investigated the reaction of **1** with Mes$_2$BOH. In this case methane evolution was not observed even when the toluene solution was heated at 100 °C; i.e., protonolysis of the aluminum−carbon bonds does not take place. This could resemble the behavior of the dimer [(μ-ArCH$_2$O)AlMe$_2$]$_2$ (Ar = 2,4,6- ^{t}Bu$_3$C$_6$H$_2$).[14] This compound is also resistant against further protonolysis using an excess of ArCH$_2$OH because of the postulated enhanced stability of the dimer and the relatively weak nucleophilicity of the alcohol. However, unexpectedly, in our reaction we observed the formation of mesitylene and boroxin **4** due to the cleavage of one boron−carbon bond. The equimolar amounts of **1** and Mes$_2$BOH were dissolved in toluene at room temperature; the ^{11}B NMR spectrum of the reaction mixture shows two signals of equal intensity at 56 and 31 ppm. The former can be assigned to **1**, while the latter corresponds to **4**. We have also found that the reaction has catalytic character; i.e., Mes$_2$BOH decomposes in the presence of a catalytic amount of **1**. The mechanism apparently involves the coordination of Mes$_2$BOH and subsequent protonation of the mesityl ipso carbon (Scheme 4). We suppose that the steric interactions of mesityl groups favor the conformation in which the cleavage of the Al−C bond is difficult. Moreover, we have found that the gallium analogue [(μ-Mes$_2$BO)GaMe$_2$)]$_2$ (**6**) does not catalyze this reaction. This is presumably due to the lower Lewis acidity of gallium,[15,16] which is unable to coordinate the molecule of Mes$_2$BOH.

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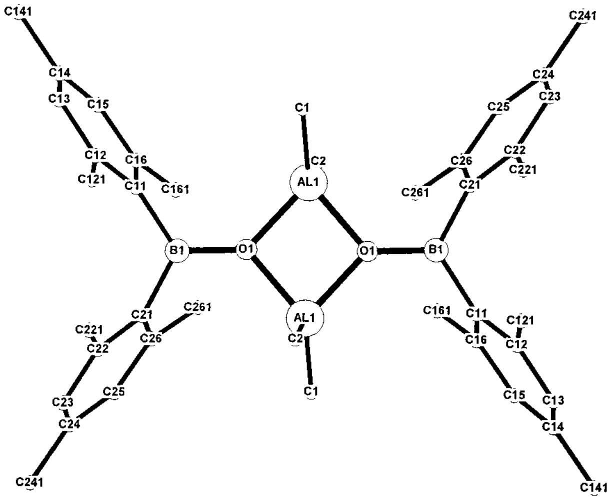

Figure 1. Molecular structure of $[(\mu\text{-Mes}_2\text{BO})\text{AlMe}_2)]_2$ (**1**). Hydrogen atoms are omitted for clarity.

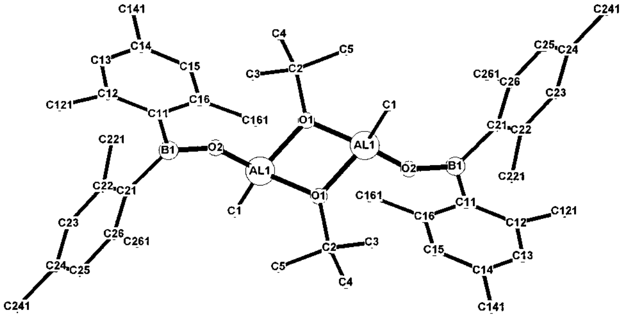

Figure 2. Molecular structure of *trans*-$[(\mu\text{-Bu}^t\text{O})(\text{Mes}_2\text{BO})\text{AlMe}]_2$ (**3**). Hydrogen atoms are omitted for clarity.

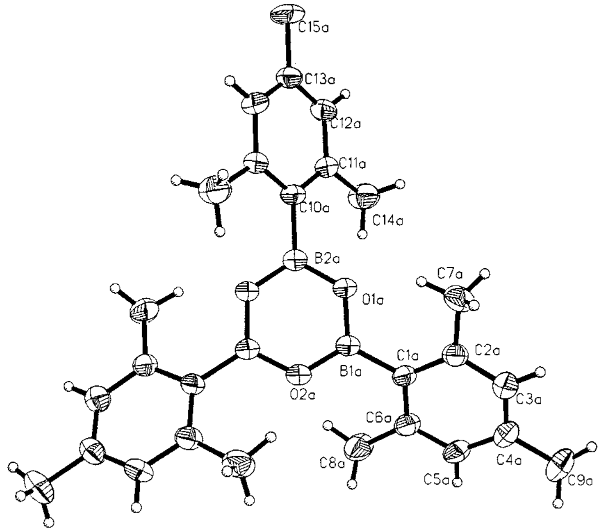

Figure 3. Molecular structure of $[\text{MesBO}]_3$ (**4**).

Molecular Structures of $[(\mu\text{-Mes}_2\text{BO})\text{AlMe}_2)]_2$ (1), *trans*-$[(\mu\text{-Bu}^t\text{O})(\text{Mes}_2\text{BO})\text{AlMe}]_2$ (3), and $[\text{MesBO}]_3$ (4). The structure of compound **1** is depicted in Figure 1. In principle, it is similar to structure **5**.[2] The metric features of the central $\text{B}_2\text{O}_2\text{Al}_2$ core in **1** are close to those found in **5** and related dimeric dialkylaluminum alkoxides.[17] The B−O distance in **1** is slightly longer than that in **5** ($d_{\text{B-O}}$ = 1.389(2) and 1.375(4) Å, respectively) and is also the longest among structurally characterized derivatives of dimesitylborinic acid, i.e., $[\text{Fe}(\mu\text{-OBMes}_2)(\text{OBMes}_2)]_2$,[18] $[(\mu\text{-Mes}_2\text{BO})\text{Li(THF)}]_2$, and $[\text{Co}(\mu\text{-OBMes}_2)_2\text{Li(THF)}_2\text{Cl}_2\text{Li(THF)}_2]$.[19] In addition, it should be noted that in **1** the C_2BO plane is twisted by ca. 30° relative to the Al_2O_2 plane while in **5** the corresponding conformation angle is very small (ca 5°). This effect can apparently be attributed to the steric requirements of mesityl groups.

Structure **3** is shown in Figure 2. The structure of the central Al_2O_2 core in **3** is typical. The average internal Al−O distance is 1.827(2) Å, while the terminal Al−O distance is 1.709(2) Å. This is in agreement with results obtained for related aluminum alkoxides, e.g., $[(^t\text{BuO})_2\text{AlH}]_2$,[20] $[(^t\text{BuO})_3\text{Al}]_2$,[21] $[(\text{ArO})_2\text{Al}(\text{OEt})]_2$ (Ar = 2,4,6-$^t\text{Bu}_3\text{C}_6\text{H}_2$).[22] It should be noted that the bridging oxygens in **3** show slight deviation from the strictly planar coordination ($\sum$°O(1) ≅ 358.5). Contrary to **1** the Mes_2BO^- ligand does not occupy the bridging position but is located in the terminal position. This could be expected for steric as well as electronic reasons because the quasi-alkoxide Mes_2BO^- ligand is more bulky and is also a less effective π donor than the alkoxide ^{t}BuO ligand. We believe that presumably steric rather than electronic factors account for the large B(1)−O(2)−Al(1) angle of 150.7(2)°. For comparison, the terminal C−O−Al angle in the less crowded compound $[(^t\text{BuO})_2\text{AlH}]_2$ is 144.3(4)°.[20] However, an alternative explanation involving π interactions between oxygen and aluminum should also be considered.[23] On the other hand, we suppose that π interactions may affect more strongly the B−O bonding situation in **3.** In fact, the different coordination mode of the boryloxide ligand is reflected by the shortening of the B−O distance in **3** with respect to **1** ($d_{\text{B-O}}$ = 1.348(2) and 1.389(2) Å, respectively) as well as the distinct difference of the ^{11}B NMR chemical shifts. The ^{11}B NMR δ values for **1** and **3** are 57.3 and 49.0 ppm, respectively; i.e., the boron atom in **3** is significantly shielded relative to **1**, which can be some evidence for the increased B−O bond order.

Structure **4** (Figure 3) resembles the structure of triphenylboroxin.[24] The central B_3O_3 ring is strictly planar. Fairly large dihedral angles between the mesityl rings and the B_3O_3 plane (35−41°) again reflect steric crowding of mesityl groups. This propeller-like structure indicates clearly that the conjugation energy does not compensate for repulsions between ortho Me groups. A different situation is observed in $[\text{PhBO}]_3$ where phenyl rings are almost coplanar with the central B_3O_3 ring.

In conlusion, it should be noted that the stabillity of aluminum boryloxides varies significantly depending mainly on the kind of substituent on the boron atom. Dialkylaluminum dimesitylboryloxides are a thermally stable but still reactive species. Their reactivity arises from the Lewis acid properties of aluminum

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but is also notably determined by steric interactions with the participation of bulky mesityl groups.

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Supporting Information Available: Listings of crystal and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for all non-hydrogen atoms as well as hydrogen atom coordinates with isotropic displacement parameters and an X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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