Synthesis and Characterization of Dialkylmetal Boryloxides $[(\mu\text{-9-BBN-9-O})MMe_2]_2$, M = Al, Ga, In

Romana Anulewicz-Ostrowska,[†] **Sergiusz Luliński,**[‡] **and Janusz Serwatowski***[,‡]

Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland, and
Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

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The treatment of trimethylaluminum with 9-hydroxy-9-borabicyclo[3.3.1]nonane 9-(OH)-9-BBN afforded a dimeric species $[(\mu\text{-9-BBN-9-O})AlMe_2]_2$ (**1**) in low yield and methylalumoxane $(MeAlO)_n$ as well as 9-Me-9-BBN as the major products. When the anhydride $(9\text{-BBN})_2O$ was used instead of 9-(OH)-9-BBN, the mixture of $(MeAlO)_n$ and 9-Me-9-BBN was formed exclusively. Contrary to this, reactions of $(9\text{-BBN})_2O$ with trimethylgallium and trimethylindium proceeded with the cleavage of only one metal−carbon bond. The compounds $[(\mu\text{-9-BBN-9-O})MMe_2]_2$, where M = Ga (**2**), In (**3**), were isolated in high yields. Reactions of tetraethyldiboroxane Et_4B_2O with trimethyl derivatives of aluminum, gallium, and indium were also studied. The structures of **1**−**3** were determined by X-ray diffraction showing a significant influence of the metal center on the pp(π) interaction between boron and oxygen. The molecular structure of the similar dimer $[(\mu\text{-9-BBN-9-O})GaBu^t_2]_2$ (**4**) is also reported.

Introduction

Metal diorganoboryloxides $[M(OBR_2)_n]_m$ may have interesting bonding properties due to expected weaker π-donor properties of the oxygen atom in the quasi-alkoxide R_2BO^- ligand when compared to typical alkoxide ligands. Another interesting aspect is a potential reactivity of these compounds arising from the presence of the coordinatively unsaturated boron atom. However, so far only a limited number of reports concerning the synthesis and structure of metal boryloxides have been published. In the case of alkaline metals, several species possessing the $R_2B{-}O{-}M$ moiety (M = Li, Na, K) have been synthesized and some of them, especially those containing bulky R substituents, have also been crystallographically characterized, e.g., $[9\text{-BBN-9-OLi}]_n$,[1] $[Mes_2BOLi(THF)]_2$,[2] $[((Me_3Si)_2CH)_2BOLi]_2$,[3] $[9\text{-BBN-9-ONa(THF)}]_4$.[4] From the viewpoint of our work the synthesis and structural characterization of dihalogenoaluminum derivatives of the general formula $[(\mu\text{-}R_2BO)AlX_2]_2$, where R = Et, R_2 = 1,5-cyclooctanediyl, X = Cl, Br, is especially noteworthy.[5] Some other examples are also known for silicon, tin, and mercury[6] but they have not been fully characterized, in particular by X-ray diffraction, or cannot be considered as simple metal or organometal boryloxides.[7] The chemistry of transition metal diorganoboryloxides is even less recognized as only two structures of homoleptic species $[Fe(OBMes_2)_2]_2$ and $[Mn(OBTrip_2)_2]_2$ were reported.[8]

We describe in this paper the preparation and structure of dialkylmetal diorganoboryloxides of the formula $[(\mu\text{-9-BBN-9-O})MMe_2]_2$ (M = Al, Ga, In). We also provide herein the new information about the reactivity of tetraalkyldiboroxanes toward trimethyl derivatives of group 13 metals, in particular of aluminum.

Experimental Section

General Comments. ^1H and ^{11}B NMR spectra were recorded at room temperature on a Varian Unity Plus 200 spectrometer using benzene-d_6 as the solvent. Chemical shifts are given relative to C_6D_5H (δ = 7.17 ppm) in ^1H NMR spectra and relative to $Et_2O{\cdot}BF_3$ in ^{11}B NMR spectra. Trimethylaluminum (Aldrich) was used as received. Trimethylgallium was a gift from Prof. K. Starowieyski from our university. Boron-containing reagents 9-(OH)-9-BBN,[9] $(9\text{-BBN})_2O$,[10] and Et_4B_2O,[11] trimethylindium,[12] and tris(*tert*-butyl)gallium[13] have been prepared according to the literature descriptions. Solvents were dried with sodium or potassium benzophenone ketyl, distilled, and stored under argon. All reactions were carried out under an argon atmosphere using standard Schlenk techniques.

Preparation of $[(\mu\text{-9-BBN-9-O})AlMe_2]_2$ (1). A solution of 9-(OH)-9-BBN (1.50 g, 10.9 mmol) in toluene (20 mL) was added over 2−3 min to the stirred solution of Me_3Al (0.80 g, 11.1 mmol) in toluene (5 mL) at −70 °C. The resultant milky solution was allowed to warm slowly to room temperature with stirrring, and then it was left to stand for several hours. The supernatant liquid layer was decanted from over an amorphous precipitate and was concentrated to ca. one-half of the original volume. Crystals which separated during the concentration have been dissolved by warming up the solution to ca. 40 °C. Slow cooling

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[†] University of Warsaw.
[‡] Warsaw University of Technology.

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Table 1. Crystal Data and Structure Refinement for **1**−**4**

	1	**2**	**3**	**4**
compd	$[(\mu\text{-}9\text{-BBN-}9\text{-O})AlMe_2]_2$	$[(\mu\text{-}9\text{-BBN-}9\text{-O})GaMe_2]_2$	$[(\mu\text{-}9\text{-BBN-}9\text{-O})InMe_2]_2$	$[(\mu\text{-}9\text{-BBN-}9\text{-O})GaBu^t{}_2]_2$
emp form	$C_{20}H_{40}Al_2\ B_2O_2$	$C_{20}H_{40}\ B_2Ga_2O_2$	$C_{20}H_{40}B_2In_2O_2$	$C_{32}H_{64}\ B_2Ga_2\ O_2$
fw	388.10	473.58	563.78	641.90
cryst syst	orthorhombic	orthorhombic	orthorhombic	triclinic
space group	*Iba*2	*Ibam*	*Ibam*	$P\bar{1}$
a, Å	19.142(4)	19.063(4)	19.136(4)	9.209(2)
b, Å	9.876(2)	9.838(2)	9.830(2)	10.184(2)
c, Å	12.846(3)	12.934(3)	13.423(3)	10.503(2)
α, deg				69.55(3)
β, deg				67.75(3)
γ, deg				77.23(3)
V, Å^3	2428.5(9)	2425.7(9)	2525.0(9)	849.7(3)
Z	4	4	4	2
d (calcd), Mg/m^3	1.061	1.297	1.483	1.254
μ, mm^{-1}	1.146	2.786	14.656	2.117
F(000)	848	992	1136	344
cryst size, mm	0.5 × 0.3 × 0.2	0.7 × 0.5 × 0.3	0.6 × 0.4 × 0.3	0.4 × 0.2 × 0.2
θ range, deg	4.62 to 78.79	4.64 to 78.97	4.62 to 79.15	4.66 to 79.39
reflns collected	1511	1274	1300	3959
ind. reflns	1367	1268	1300	3959
GOF	1.082	1.118	1.076	1.036
R_w [$I > 2\sigma(I)$]	0.0568	0.0550	0.0751	0.0533
R_{all}	0.0700	0.0631	0.1072	0.0612
abs correction	none	empirical, $T_{min} = 0.99$, $T_{max} = 1.02$	empirical $T_{min} = 0.98$, $T_{max} = 1.00$	none
largest diff. peak and hole, e Å^{-3}	0.415 and −0.238	0.642 and −0.491	0.834 and −0.813 (near In)	0.847 and −0.826

afforded well-developed colorless crystals of **1** (86 mg, yield 4%), mp (dec) > 210 °C. ^{1}H NMR δ/ppm: 1.78 (m, 10H, 9-BBN), 1.26 (m, 4H, 9-BBN), −0.35 (s, 6H, AlMe). ^{11}B NMR δ/ppm: 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 $[(\mu\text{-}9\text{-BBN-}9\text{-O})MMe_2]_2$, M = Ga (2), In (3). A solution of $(9\text{-BBN})_2O$ (0.80 g, 3.1 mmol) in toluene (5 mL) was added dropwise to the stirred solution of Me_3Ga (0.36 g, 3.1 mmol) in toluene (5 mL) at −40 °C. The resultant solution was allowed to warm slowly with stirrring. The precipitation of a white crystalline solid was observed at ca. 0 °C. Toluene (5 mL) was added, and the suspension was warmed to dissolve a precipitate (ca. 60 °C). Slow cooling afforded well-formed colorless crystals of **2** (450 mg, yield 62%), mp (dec) 260 °C. ^{1}H NMR δ/ppm: 1.82 (m, 10H, 9-BBN), 1.34 (m, 2H, 9-BBN), 1.03 (br, 2H, 9-BBN), 0.05 (s, 6H, GaMe). ^{11}B NMR δ/ppm: 57.4. Anal. Calcd for $C_{10}H_{20}BGaO$: C, 50.72; H, 8.51. Found: C, 50.68; H, 8.56.

The compound $[(\mu\text{-}9\text{-BBN-}9\text{-O})InMe_2]_2$ (**3**) was prepared similarly starting from $(9\text{-BBN})_2O$ (0.40 g, 1.55 mmol) and $InMe_3$ (0.26 g, 1.62 mmol), in toluene (5 mL). However, 15 min of heating at 50 °C was applied to complete the reaction. The yield of **3** was 260 mg (60%), mp 236−238 °C. ^{1}H NMR δ/ppm: 1.85 (m, 10H, 9-BBN), 1.39 (m, 2H, 9-BBN), 0.81 (br, 2H, 9-BBN), 0.09 (s, 6H, InMe). ^{11}B NMR δ/ppm: 56.3. Anal. Calcd for $C_{10}H_{20}BInO$: C, 42.61; H, 7.15. Found: C, 42.97; H, 7.13.

Preparation of $[(\mu\text{-}9\text{-BBN-}9\text{-O})GaBu^t{}_2]_2$ (4). The compound $[(\mu\text{-}9\text{-BBN-}9\text{-O})GaBu^t{}_2]_2$ (**4**) was isolated in low yield from the solution of $(9\text{-BBN})_2O$ (0.50 g, 1.94 mmol) and $GaBu^t{}_3$ (0.40 g, 1.66 mmol) in hexane (5 mL) as a white precipitate which was recrystallized from hot toluene (10 mL). The yield of **4** was 30 mg (6%), mp (dec) 290 °C. Anal. Calcd for $C_{16}H_{32}BGaO$: C, 59.88; H, 10.05. Found: C, 59.67; H, 10.39.

Crystal Structure Determination of 1−4. The crystals of compounds **1**−**4** were grown by slow cooling of their saturated toluene solutions. Selected monocrystals were sealed in glass capillaries under argon. The X-ray measurements were done on a KM-4 KUMA diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å). The data were collected at room temperature using $\omega-2\theta$ scan technique. The intensity of the control reflections varied by less than 3%, and the linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, and an absorption correction was applied for **2** and **3**.[14] The structures were solved by direct methods[15] and refined using full-matrix least-squares method based on F^2.[16] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted *R* factor, w*R* and all goodness-of-fit *S* values are based on F^2. The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions and their thermal parameters were refined isotropically. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[17] 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 Tables 2 and 3.

Results and Discussion

Synthesis. The reaction of 9-(OH)-9-BBN with Me_3Al proceeds smoothly at −70 °C. The ^{11}B NMR spectrum of the reaction mixture showed a major (ca. 90% of the total integration) signal of 9-Me-9-BBN at 88.5 ppm and a small signal at 60.5 ppm which was assigned to $[(\mu\text{-}9\text{-BBN-}9\text{-O})AlMe_2]_2$ (**1**). This result indicates clearly that the main pathway of the reaction is the formation of methylalumoxane $(MeAlO)_n$ as was shown in Scheme 1. However, the byproduct **1** could be isolated in low yield as a colorless crystalline material.[18] This compound was found to be stable in the solid state. Compounds of the type **1** were postulated previously[19] as unstable intermediates subsequently forming more stable alumoxane type species $(\mu\text{-}Et_2BO)AlR_2(OAlR)_2R_2Al(\mu\text{-}OBEt_2)$ (R= Me, Et, *i*-Bu) via intramolecular alkyl group transfer with

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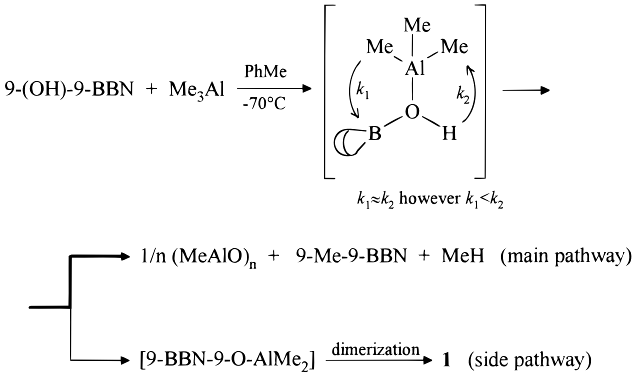
Table 2. Selected Bond Distances [Å], Angles and Torsion Angles [°] for **1**−**3**

1		2		3	
Al−C(1)	1.920(8)	Ga−C(6)	1.933(5)	In(1)−C(6)	2.170(13)
Al−C(2)	1.948(9)	Ga−C(6′)	1.933(5)	In(1)−C(6′)	2.170(13)
Al−O′	1.859(2)	Ga−O′	1.956(3)	In−O	2.174(10)
Al−O	1.863(2)	Ga−O	1.965(4)	In−O′	2.177(7)
B−O	1.375(4)	B O	1.356(7)	B−O	1.305(14)
C(1)−Al-C(2)	123.5(2)	C(6)−Ga-C(6′)	130.7(4)	C(6)−In-C(6′)	140.9(8)
O−Al−O′	81.11(9)	O−Ga−O′	79.4(2)	O−In−O′	76.7(4)
B−O−Al	129.9(2)	B−O−Ga	129.8(3)	B−O−In	130.3(8)
B−O−Al′	131.1(2)	B−O−Ga′	129.6(4)	B−O−In′	126.4(8)
Al−O−Al′	98.87(9)	Ga−O−Ga′	100.6(2)	In−O−In′	103.3(4)
O′-Al−O−B	−175.6(6)	O′-Ga−O−B	180.0	O′-In−O−B	180.0
Al−O−B−C(3)	−5.0(13)	Ga−O−B−C(1)	0.0	In−O−B−C(1)	180.0

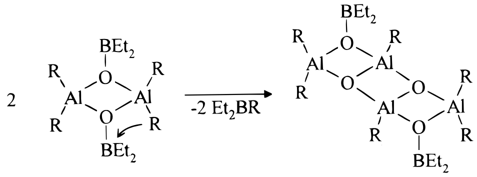
Table 3. Selected Bond Distances [Å], Angles and Torsion Angles [°] for **4**

Ga(1)−C(20)	1.973(11)
Ga(1)−O(1)	2.001(8)
Ga(1)−O(2)	2.025(7)
Ga(1)−C(19)	2.061(10)
Ga(2)−O(1)	1.994(8)
Ga(2)−C(18)	1.980(14)
Ga(2)−O(2)	2.009(8)
Ga(2)−C(17)	2.071(10)
O(1)−B(1)	1.372(12)
O(2)−B(2)	1.367(13)
O(1)−Ga(1)-O(2)	78.5(3)
C(20)−Ga(1)-C(19)	124.0(5)
Ga(1)−O(1)-Ga(2)	101.9(3)
B(1)−O(1)-Ga(1)	125.7(7)
Ga(1)−O(1)-B(1)−C(1)	0(2)
Ga(2)−O(1)-B(1)−C(1)	−178.7(9)

Scheme 1

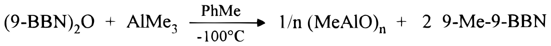


Scheme 2



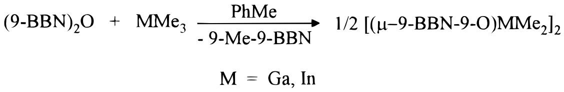
elimination of Et_2BR and dimerization (Scheme 2). In fact, decomposition of **1** occurs in solution at room temperature only very slowly to give undefined methylalumoxane type species and 9-Me-9-BBN,[20] which indicates that the formation of $(MeAlO)_n$ as a main product in this reaction cannot be explained by the decomposition of **1**. Assuming the formation of the unstable complex 9-(OH)-9-BBN·Me_3Al in the first step (Scheme 1), a rapid one-step decomposition of this complex to form $(MeAlO)_n$ must apparently be involved. The above observations suggest that the rate of the protonolysis is probably only slightly higher than the rate of the methyl group transfer. This suggestion is strongly supported by the investigation of the reaction of $(9\text{-BBN})_2O$ with Me_3Al (Scheme 3). In this case only traces of **1** were detected in the reaction mixture by the ^{11}B NMR analysis, which means that the tranfer of both methyl groups from aluminum to boron in the complex $(9\text{-BBN})_2O$·$AlMe_3$ occurs almost simultaneously. If the transfer of the second methyl group were considerably slower, the dimerization of the initially formed monomeric species [9-BBN-9-OAlMe_2] would result in good yield on the relatively stable compound **1**. Unfortunately, the full analysis of the main product of this reaction, i.e., methylalumoxane $(MeAlO)_n$, was impossible. The evaporation of the solvent and the byproduct 9-Me-9-BBN afforded an amorphous residue which still contained a large amount of 9-Me-9-BBN whose complete removal was difficult. However, the ^1H NMR spectrum of this material showed in the region 0.1−0.3 ppm the broad resonance typical for $(MeAlO)_n$.[21]

Scheme 3



$$(9\text{-BBN})_2O + AlMe_3 \xrightarrow[-100°C]{PhMe} 1/n\,(MeAlO)_n + 2\ 9\text{-Me-9-BBN}$$

Scheme 4



$$(9\text{-BBN})_2O + MMe_3 \xrightarrow[-\,9\text{-Me-9-BBN}]{PhMe} 1/2\,[(\mu\text{-9-BBN-9-O})MMe_2]_2$$

$$M = Ga, In$$

In addition, we were interested in synthesis and characterization of heavier group 13 analogues of **1**. It is well-known that in contrast to aluminum alkyls trialkylgallium and trialkylindium compounds have a tendency to split off readily only one alkyl group. Indeed, we found that the treatment of trimethylgallium and trimethylindium with $(9\text{-BBN})_2O$ afforded in high yields crystalline compounds $[(\mu\text{-9-BBN-9-O})GaMe_2]_2$ (**2**) and $[(\mu\text{-9-BBN-9-O})InMe_2]_2$ (**3**), respectively (Scheme 4). This result is the obvious evidence for the selective cleavage of one metal−carbon bond. The compounds **2** and **3** were also found to be stable not only in the solid state but also in solution. Reactions of tetraethyldiboroxane Et_4B_2O with Me_3Ga and Me_3In proceeded similarly as was proved by the ^{11}B NMR analysis of the corresponding reaction mixtures showing two resonances of Et_2MeB at 86.9 ppm and the corresponding $[Et_2BOMMe_2]_n$ (M = Ga, In) species at ca. 54 ppm. The compound $[(\mu\text{-}Et_2BO)GaMe_2]_2$ (**5**) has been isolated as a colorless oil, and its dimeric structure was established from the mass spectrum. In addition, we have found that the examined diboroxanes are

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[20] The ^{11}B NMR spectrum of a diluted solution of **1** in benzene-d_6 recorded after 24 h the solution had been prepared, showed signals of 9-Me-9-BBN and **1** with an integral ratio of ca. 1:8, respectively.

[21] Sinn, H. *Macromol. Symp.* **1995**, *97*, 27.

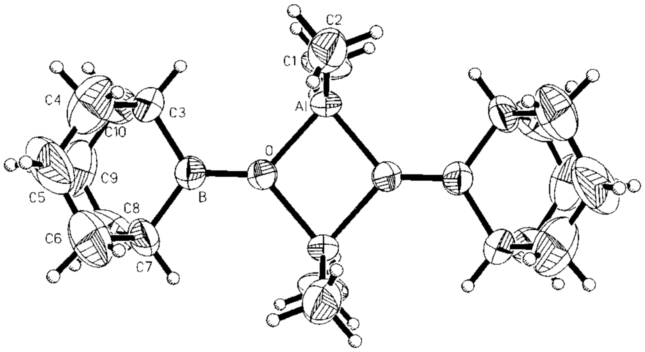
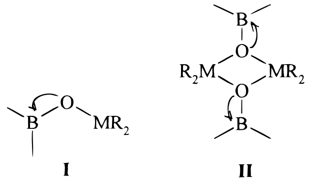


Figure 1. The molecular structure of $[(\mu\text{-9-BBN-9-O})AlMe_2]_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 5



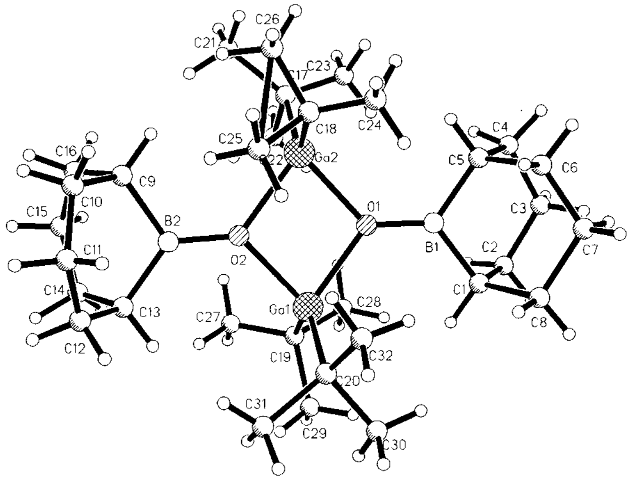


Figure 2. The molecular structure of $[(\mu\text{-9-BBN-9-O})GaBu^t{}_2]_2$ (**4**).

unreactive toward tris(*tert*-butyl)gallium which can be explained by the steric hindrance precluding the formation of the $R_4B_2O\cdot GaBu^t{}_3$ complex. This is not surprising since the importance of steric factors in boron chemistry is well-known. The low yield isolation of crystalline $[(\mu\text{-9-BBN-9-O})GaBu^t{}_2]_2$ (**4**) from the reaction of $(9\text{-BBN})_2O$ with $GaBu^t{}_3$ is probably due to the presence of a small amount of a 9-(OH)-9-BBN impurity in the used anhydride.

Molecular Structure of $[(\mu\text{-9-BBN-9-O})MMe_2]_2$ (M = Al (1), Ga (2), In(3)). The structure of compound **1** is depicted in Figure 1. The structures of **2** and **3** are not presented as they are very similar to the structure of **1**. A comparison of selected bond distances, angles, and torsion angles for compounds **1**−**3** is given in Table 2. The weaker (with respect to typical alkoxides) π-donor properties of the oxygen atom in the boryloxide ligand might lead to the stabilization of the monomeric structure of type **I** (Scheme 5) but they are apparently still too strong to prevent the formation of typical dimers **II** with bridging R_2BO groups. The main structural feature of these dimers is the planar arrangement of the metal, oxygen, and boron atoms as well as the carbon atoms bonded to the boron atoms. Thus, the oxygen atom may be considered as sp^2 hybridized and its lone electron pair on the remaining 2p orbital is engaged in the interaction with the vacant 2p orbital on the neighboring boron atom. However, in the case of **1** a slight deviation from planarity is observed, e.g. the torsion angle Al−O−B−C(3) is −5.0(13)°, suggesting a slightly weaker pp(π) interaction in **1** than that in **2** and **3**. The B−O bond distances decrease in the order **1** (1.375(4) Å) > **2** (1.356(7) Å) > **3** (1.305(14) Å). Obviously, these distances could be significantly less different within 3σ, but the trend is not questionable, since the elongation of the metal−oxygen bond should result in shortening the boron−oxygen bond. We suppose that this shortening corresponds to the increasing B−O bond order arising from the increasing π-bonding.[2] ^{11}B NMR spectroscopy is a valuable tool used to determine and characterize π-bonding in boron compounds.[22] In case of **1**−**3**, we have found that the boron shielding inreases in row (60.9, 57.4, and 56.3 ppm, respectively), which may reflect the better pp(π) interaction for heavier analogues. Alternatively, the B−O distance as well as $\delta^{11}B$ changes are not only due to pp(π) type interactions as they could also be a result of other factors: in particular metal−oxygen σ-interaction influence should be considered.[23] However, we believe that the metal center affects the B−O pp(π) interaction to a significant extent. For comparison, the B−O distances ($\delta^{11}B$ in ppm) in related compounds $[(\mu\text{-}Et_2BO)AlCl_2]_2$ and $[(\mu\text{-9-BBN-9-O})AlBr_2]_2$ are 1.420(5) Å (60.6) and 1.392(8) Å (59.5), respectively.[5] It should be noted that the correlation between the B−O bond length and the $\delta^{11}B$ NMR chemical shift is not simple and can only be made for closely related species such as **1**−**3**. The elongation of the B−O distances in dihalogenoaluminum derivatives can clearly be explained by the effect of a strongly electronegative halogen atom reducing the charge density on the aluminum atom which in turn leads to the stronger interaction between aluminum and oxygen. In fact, Al−O bonds in these compounds are shorter by about 0.03−0.04 Å than that in **1**.

Another important structural aspect of **1**−**3** is the geometry around the metal atom. Among group 13 metals aluminum has the greatest tendency to form sp^3 hybridized orbitals. This tendency is weaker for gallium and still weaker for indium. In fact, the deviation from the ideal tetrahedral environment increases significantly from **1** to **3** which is reflected by the rather large C−In−C angle 140.9(8)° in **3**. The O−M-O angles as well as M−C and M−O bond lengths are, however, in the range observed for related alkoxides. The structure of the dimer **4** (Figure 2) corresponds to the structures **1**−**3** except for the lack of symmetry arising from the replacement of methyl groups with *tert*-butyl groups. Comparing the data for **2** and **4** (Table 3), the elongation of the central $B_2O_2Ga_2C_2$ core bond distances in **4** with respect to **2** should be noted. It is also noteworthy that the C−Ga−C bond angle in **4** is slightly smaller than that in **2** which can be explained by the steric influence of the 9-BBN moiety on the bulky *tert*-butyl groups.

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(22) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectra of Boron Compounds*; Springer-Verlag: Berlin, Heidelberg, New York, 1978.

(23) For example, see: (a) Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137. (b) *Gmelin Handbook of Inorganic Chemistry, Gallium, Organogallium Compounds, Part 1*; Springer-Verlag: Berlin, New York, 1987. (c) *Gmelin Handbook of Inorganic Chemistry, Indium, Organoindium Compounds, Part 1*; Springer-Verlag: Berlin, New York, 1991. (d) Power, M. B.; Cleaver, W. M.; Apblett, A. W.; Barron, A. R.; Ziller, J. W. *Polyhedron* **1992**, *11*, 477. (e) Bradley, D. C.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *Organometallics* **1988**, *7*, 1112.

In conclusion, a triad of dimeric metal boryloxides of the formula $[(\mu\text{-9-BBN-9-O})\text{MMe}_2]_2$ (M = Al, Ga, In) have been synthesized and characterized. In principle, they are isostructural, however, a significant variation of the corresponding bond distances and angles is observed. The aluminum derivative **1** is especially interesting as it slowly eliminates 9-Me-9-BBN to yield methylalumoxane and therefore it may be regarded as a precursor for this important species. Recently, we have undertaken a more detailed study on the reactivity of alkylaluminum boryloxides which also might be interesting from the practical point of view.

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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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