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Benzoxaborolate ligands in group 13 metal complexes

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ABSTRACT

A series of group 13 metal benzoxaborolates $[R_2MOB(o-CH_2O)(C_6H_4)]_2$ $[R = {}^{t}Bu, M = Al$ (2), R = Me, M = Ga (3), $R = {}^{t}Bu, M = Ga$ (4), $R = {}^{t}Bu, M = In$ (5)] were synthesized in reactions of 1,3-dihydro-1-hydroxy-2,1-benzoxaborole (1) with group 13 metal trialkyls. The compounds were characterized by elemental analysis, melting point measurements, ${}^{1}H$, ${}^{13}C$ NMR, and IR spectroscopy. The molecular structure of 2–5 was determined by single-crystal X-ray diffraction. The structure of the compounds depends on the kind of metallic center. Reaction of ${}^{t}Bu_3Al$ with the benzoxaborole 1 leads to the aluminum derivative 2, similar to typical dialkylaluminum carboxylates, with a central eight-membered $B_2Al_2O_4$ ring, in which two oxygen atoms of the benzoxaborolate unit are bonded to aluminum atoms. In the presence of gallium and indium trialkyls, the benzoxaborola 1 acts as an alcohol yielding complexes 3–5, similar to dialkylmetal alkoxides, with a central M_2O_2 (where M = Ga, In) ring. Thermal decomposition of compounds 2 and 4 revealed the liberation of a mixture of organoboron compounds. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

Boronic acids, RB(OH)₂, have been attracting attention owing to their usefulness as organic reagents, catalysts, building blocks in crystal and material engineering, and molecular receptors [1]. Recently, they have been used in medicine as antifungal drugs and tested for the treatment of numerous diseases [2]. Their internal hemiesters, benzoxaboroles, have lately been reported as excellent potent antifungal, anti-inflammatory, and antibacterial drugs [3]. Crystal structure of the fluorinated benzoxaborole active against onychomycosis (AN-2690) has been recently reported [4]. The structure of benzoxaboroles, their chemical properties, applications, and methods of preparation have recently been reviewed by Sporzyński and coworkers [5].

Although benzoxaboroles can be regarded as electron donating ligands in complexes with aluminum, gallium, and indium alkyls due to the presence of two oxygen atoms in the benzoxaborole molecule, these benzoxaborolate complexes are unknown. Even reactions of group 13 metal compounds with other oxygen boron compounds have been largely unexplored. Until now, only several examples of aluminum-substituted boroxines have been reported [6,7]. Known complexes of aluminum containing OBR₂ units are limited to just a few examples [7,8]. Very recently, the first aluminum complex containing benzoxaborole moieties has been obtained in the reaction of 3-hydroxyphenylboronic acid with aluminum dihydride LAIH₂ (L = HC(CMeNAr)₂, Ar = 2,6-iPr₂C₆H₃) [7].

Although numerous inorganic compounds containing boron, gallium, and indium atoms, such as gallium and indium borates, are useful in materials engineering [9], the products of the reaction of benzoxaboroles and boronic acids with gallium and indium compounds are unknown.

For benzoxaborolate anions coordinated to metal atoms, there are several coordination modes possible, because of the presence of two potentially coordinating oxygen atoms in the benzoxaborolate units (Scheme 1). The aim of the present work was to study the benzoxaborolate complexes obtained in reactions of 1,3-dihydro-1-hydroxy-2,1-benzoxaborole (1) with aluminum, gallium, and indium trialkyls. Here, we demonstrate benzoxaborolate anions as difunctional and monofunctional ligands in the group 13 metal complexes depending on the kind of metal centers. Our study showed that, among the coordination modes in Scheme 1, structures with modes **A** and **B** were formed.

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Scheme 1. Possible coordination modes for benzoxaborolate anions coordinated to metal atoms.

2. Experimental

2.1. Materials and instrumentation

All manipulations were carried out using standard Schlenk techniques under an inert gas atmosphere. Solvents were distilled over the blue benzophenone-K complex. 1,3-Dihydro-1-hydroxy-2,1-benzoxaborole (1) was synthesized as described in the literature [10]. ¹H and ¹³C NMR spectra were obtained on a Mercury-400BB Varian spectrometer. Chemical shifts were referenced to the residual proton signals of CDCl₃ (7.26 ppm). ¹³C NMR spectra were acquired at 100.60 MHz (standard: chloroform ¹³CDCl₃, 77.20 ppm). IR spectra were obtained using a Nicolet 6700 FT-IR (ATR) infrared spectrometer. Thermal stability and decomposition of compounds 2 and 4 were determined by an SDT Q600 V20.9 Build 20 derivatograph, recording TG, DTG, and DSC curves. The measurements were made at a heating rate of 2 K min⁻¹ with full scale recording. The samples (14.91-15.82 mg) were heated in ceramic crucibles in argon. Hydrolyzable alkyl groups and the aluminum content for compound 2 were determined according to the literature [11]. Elemental analyses of compounds 3-5 were obtained on a Perkin-Elmer 2400 analyzer.

2.2. Synthesis of $[R_2MOB(o-CH_2O)(C_6H_4)]_2$ $[R = {}^tBu, M = Al$ (2), R = Me, M = Ga (3), $R = {}^tBu, M = Ga$ (4), $R = {}^tBu, M = In$ (5)]: general procedure

A solution of R_3M (1 mmol) in 5 cm³ of CH₂Cl₂ was injected into a stirred solution of **1** (1.34 g, 1 mmol) in CH₂Cl₂ (20 cm³) at -76 °C. The reaction mixture was allowed to warm slowly to room temperature. A white solid appeared on the surface of the post-reaction solution. The solution was separated from the solid by an injector. The solvent was removed *in vacuo* from the post-reaction solution and a white product (**2–5**) was obtained.

2.3. $[{}^{t}Bu_{2}AlOB(o-CH_{2}O)(C_{6}H_{4})]_{2}$ (2)

Yield 85%. ¹H NMR (CDCl₃) δ : 1.00 [36H, s, AlC(CH₃)₃], 5.41 (4H, s, CH₂O), 7.38 (2H, m, H_{aromat}), 7.44 (2H, m, H_{aromat}), 7.59 (2H, m, H_{aromat}), 7.88 (2H, m, H_{aromat}). ¹³C NMR (CDCl₃) δ : 14.86 [AlC(CH₃)₃], 30.31 [AlC(CH₃)₃], 71.74 (CH₂O), 121.08, 128.34, 132.12, 132.26, 147.73 (C_{aromat}) ppm.

X-ray-quality crystals were obtained from the n-C₆H₁₄-CH₂Cl₂ solution at 10 °C. Decomposition (on the basis of DSC measurements): 247 °C. FTIR (nujol): $\nu = 1625.7$ (m), 1612.2 (m), 1562.1 (s), 1546.6 (s), 14.52.1 (m), 1353.8 (m), 1272.8 (m), 1168.7 (m), 966.2 (s), 946.9 (s), 811.9 (s), 794.5 (m), 761.7 (m), 723.2 (s), 709.7 (m), 632.5 (s), 599.8 (m), 568.9 (m), 491.8 (m) cm⁻¹. Elemental anal. Found: Al, 9.50; hydrolyzable ^tBu groups, 39.21; Calcd for C₃₀H₄₈Al₂B₂O₄: Al, 9.85; ^tBu, 39.40 wt.%.

2.4. $[Me_2GaOB(o-CH_2O)(C_6H_4)]_2$ (3)

Yield 81%. ¹H NMR (CDCl₃) δ : 0.07 (12H, s, GaCH₃), 5.08 (4H, s, CH₂O), 7.38 (4H, m, H_{aromat}), 7.50 (2H, m, H_{aromat}), 7.62 (2H, m, H_{aromat}). ¹³C NMR (CDCl₃) δ : -4.10 (GaCH₃), 70.70 (CH₂O), 121.40, 127.10, 130.22, 130.80, 154.50 (C_{aromat}) ppm.

X-ray-quality crystals were obtained from the CH₂Cl₂ solution at 10 °C. Mp.: 191 °C. FTIR (nujol): ν = 1608.3 (m), 1452.1 (m), 1365.4 (s), 1286.3 (s), 1203.4 (m), 1182.2 (s), 1105.0 (m), 993.2 (m), 746.3 (m), 719.3 (s), 675.0 (m), 597.8 (s), 541.9 (s), 503.3 (s), 462.8 (s) cm⁻¹. Elemental anal.: Calcd for C₁₈H₂₄B₂Ga₂O₄: C, 46.41; H, 5.16. Found: C, 46.04; H, 5.21 wt.%.

2.5. $[{}^{t}Bu_{2}GaOB(o-CH_{2}O)(C_{6}H_{4})]_{2}$ (4)

Yield 86%. ¹H NMR (CDCl₃) δ : 1.22 [36H, s, GaC(*CH*₃)₃], 5.04 (4H, s, *CH*₂O), 7.38 (4H, m, *H*_{aromat}), 7.48 (2H, m, *H*_{aromat}), 7.76 (2H, m, *H*_{aromat}). ¹³C NMR (CDCl₃) δ : 26.30 [GaC(*CH*₃)₃], 31.47 [GaC(*CH*₃)₃], 69.66 (*CH*₂O), 121.45, 126.83, 130.63, 131.16, 155.30 (*C*_{aromat}) ppm.



Scheme 2. Reaction of benzoxaborole 1 with one equivalent of ^tBu₃Al.

Crystals were obtained from the post-reaction solution at 10 °C. Mp.: 232–236 °C. FTIR (nujol): $\nu = 1608.3$ (w), 1469.5 (m), 1452.1 (m), 1365.4 (s), 1355.7 (s), 1282.4 (m), 1176.4 (m), 1101.2 (m), 1000.9 (s), 813.8 (m), 757.9 (m), 738.6 (m), 725.1 (s), 678.8 (m), 653.8 (m), 636.4 (s), 594.0 (s), 540.0 (m), 493.7 (s), 466.7 (s) cm⁻¹. Elemental anal.: Calcd for C₄₆H₄₂B₂Ga₂N₂O₄: C, 67.33; H, 5.13. Found: C, 66.98; H, 5.34 wt.%.

2.6. $[{}^{t}Bu_{2}InOB(o-CH_{2}O)(C_{6}H_{4})]_{2}$ (5)

Yield 76%. ¹H NMR (CDCl₃) δ : 1.30 [36H, s, InC(CH₃)₃], 5.01 (4H, s CH₂O), 7.38 (4H, m, H_{aromat}), 7.46 (2H, m, H_{aromat}), 7.62 (2H, m, H_{aromat}). ¹³C NMR (CDCl₃) δ : 32.37 [InC(CH₃)₃], 36.02 [InC(CH₃)₃], 69.37 (CH₂), 121.53, 126.94, 130.04, 130.39, 154.92 (C_{aromat}) ppm.

X-ray-quality crystals were obtained from the CH₂Cl₂ solution at -15 °C. Decomposition at 205 °C. FTIR (nujol): $\nu = 1606.4$ (m), 1479.1 (m), 1461.8 (m), 1454.1 (m), 1390.4 (s), 1357.6 (s), 1278.6 (m), 1160.9 (m), 1093.4 (m), 1070.3 (m), 997.0 (s), 810.0 (m), 756.0 (m), 723.2 (s), 638.3 (s), 582.4 (m), 464.8 (s) cm⁻¹. Elemental anal.: Calcd for C₃₀H₄₈B₂In₂O₄: C, 49.73; H, 6.63. Found: C, 49.37; H, 6.81 wt.%.

2.7. Thermal decomposition of $[{}^{t}Bu_{2}GaOB(o-CH_{2}O)(C_{6}H_{4})]_{2}$ (4)

For 2 h, a 0.50 g sample of compound **4** was heated without any solvent at ca. 250–280 °C, followed by distillation under high vacuum at ca. 250 °C. A yellow liquid (0.21 g) obtained as the distillate was studied by NMR spectroscopy. ¹H NMR (CDCl₃) δ : 1.23, 1.06, 1.04 [(CH₃)₃C, three singlets], 1.40–0.90 (numerous small signals), 5.30, 5.28, 5.25 (CH₂O, three singlets), 8.30–7.10 (H_{aromat}, m). ¹¹B NMR (CDCl₃) δ : –23.7, 33.1, 50.8.

2.8. Crystallographic data

The X-ray measurement of compound **2** was performed at 100(2) K on a KUMA CCD *k*-axis diffractometer with graphitemonochromated MoK α radiation (0.71073 Å). The crystal was positioned at 61.2 mm from the KM4CCD camera; 703 frames were measured at 0.7° intervals on a counting time of 25 s. Data reduction and analysis were carried out with the Kuma Diffraction programs. The data were corrected for Lorentz and polarization effects and multi-scan absorption correction [12] was applied. The structure was solved by direct methods [13] and refined by using SHELXL [14]. The refinement was based on F² for all reflections except for those with very negative F². The weighted *R* factor, w*R*, and all goodness-of-fit *S* values are based on F². The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a difference map and refined isotropically. The atomic scattering factors were taken from the International Tables [15].

The data for compounds **3–5** were collected at 100(2) K on a Nonius Kappa CCD diffractometer [16] using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package) [17]. The structure was solved by direct methods using the SHELXS97 [13] program and refined by full matrix least-squares on F² using the program SHELXL97 [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. To improve



Fig. 1. (*top*) Molecular structure of (**2**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al(1)-O(2) 1.727(1), Al(1)-O(1a) 1.934(1), O(1)-B(1) 1.444(2), O(2)-B(1) 1.298(2), O(2)-Al(1)-O(1a) 102.18(6), B(1)-O(2)-Al(1) 169.7(1), O(2)-B(1)-O(1) 121.0(2), B(1)-O(1)-Al(1a) 129.5(1), O(2)-B(1)-C(7) 133.4(2), O(1)-B(1)-C(7) 105.6(2). (*bottom*) View of a molecule of **2** showing that the central $B_2Al_2O_4$ ring adapts a flattened chair conformation.

the geometrical parameters, ultimately restrained instructions DFIX and SIMU were applied in the refinement.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 901057 (**2**), CCDC 901058 (**3**), CCDC 902032 (**4**), CCDC 901059 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

Treatment of the benzoxaborole **1** with one equivalent of ^tBu₃Al in methylene dichloride, followed by crystallization from CH_2Cl_2 -n- C_6H_{12} solution at 10 °C, afforded a white crystalline compound, whose characterizing data are consistent with the dimeric species [^tBu₂AlOB(o-CH₂O)(C_6H_4)]₂ (**2**) (Scheme 2).

The compound was characterized by NMR and IR spectroscopies, elemental analysis, and thermogravimetric analysis. The molecular structure was determined on the basis of an X-ray diffraction study and is shown in Fig. 1 (*top*). Data collection and structure analyses are listed in Table 1. Crystals of **2** suitable for Xray structure determination were grown from a n-C₆H₁₄-CH₂Cl₂ solution at 10 °C. The molecular studies showed that the centrosymmetric molecule of **2** consists of a central eight-membered B₂Al₂O₄ ring adapting a flattened chair conformation (Fig. 1 *bottom*).

The molecule is composed of two monoanion benzoxaborolate ligands, two four-coordinate aluminum atoms and four ^tBu groups bonded to the aluminum atoms. The structure of aluminum benzoxaborolate 2 is similar to the structure of typical carboxylates of group 13 metal alkyls obtained in reaction of trialkylaluminum and trialkylgallium with monocarboxylic acids. These carboxylates have

been	reported	as	dimeric	complexes	of	the	formula	$[R_2M(\mu -$
$O_2 CR'$)] ₂ (where	M	= Al, Ga)	that consist o	of co	entra	l eight-m	embered
rings $M_2C_2O_4$ with bridging carboxylate anions [19].								

The significant difference between B(1)-O(2) and B(1)-O(1) bond lengths (0.146 Å) is indicative of the lack of electron delocalization within the OBO group in compound **2**, whereas the difference between C–O bond lengths in the group 13 metal carboxylates is situated in the region of 0.01–0.03 Å, showing an appreciable degree of delocalization within the carboxylate groups [19b-f, 20]. We cannot exclude, that according to the Bent's rule, the electron withdrawing effect caused by aluminum atom results in increasing of p-character of the B–O bond and elongation of B(1)-O(1) bond in the compound **2**.

The sum of the angles about the boron atom $\Sigma[B(1)]$, 360.0°, indicates a trigonal planar boron. The same boron coordination was observed in compound **1** and other benzoxaboroles, and in phenylboronic acids [5,10,21,22]. The Al(1)–O(2) [1.727(1) Å] bond length is comparable to that in aluminum alkoxide derivatives.

In contrast to the reaction of compound **1** with ^tBu₃Al, the treatment of **1** with gallium and indium trialkyls leads to the formation of dimeric compounds [$R_2MOB(o-CH_2O)(C_6H_4)$]₂ [M = Ga, R = Me (**3**), M = Ga, R = ^tBu (**4**), M = In, R = ^tBu (**5**)], analogs of group 13 metal alkoxides (Scheme 3).

The molecular structures of compounds **3** and **5** are shown in Figs. 2–4. Data collection and structure analyses of **3–5** are listed in Table 1. The crystal structure of **4** was insufficiently solved $[R_1 = 0.0711, WR_2 = 0.1478$ for 4904 reflections with $I_o > 2\sigma(I_o)]$ because of a disorder and high thermal motion associated with ^tBu groups bonded to gallium atoms. The crystallographic data support the isostructurality of the gallium compound **4** to the indium compound **5**. Crystals of **4** and **5** contain two kinds of molecules in a cell, differing in bond lengths and angles. In contrast to the structure of **2**, the molecules of **3–5** consist of a central four-

Table 1	
Crystal data and data collection parameters for	2-5

	2	3	4	5
Empirical formula	C ₃₀ H ₄₈ Al ₂ B ₂ O ₄	$C_{18}H_{24}B_2Ga_2O_4$	$C_{30}H_{48}B_2Ga_2O_4$	C ₃₀ H ₄₈ B ₂ In ₂ O ₄
Formula weight	548.26	465.43	633.74	723.94
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P-1	P 2(1)/c	P2(1)/c
<i>a</i> (Å)	9.1147(8)	7.4330(4)	14.7901(5)	15.0815(2)
b(Å)	16.331(1)	8.2430(3)	12.6179(3)	12.7725(2)
<i>c</i> (Å)	11.1717(8)	10.0220(5)	21.0951(5)	21.5260(3)
α(°)	90	111.377(3)	90	90
β(°)	105.440(9)	95.082(2)	125.951(2)	126.134(1)
γ(°)	90	109.238(3)	90	90
$V(Å^3)$	1602.9(2)	524.45(4)	3186.9(2)	3348.90(9)
Ζ	2	1	4	4
$D_{\rm calc}({\rm g~cm^{-3}})$	1.136	1.474	1.321	1.436
Absorption	0.122	2.587	1.722	1.407
coefficient (mm ⁻¹)				
F(000)	592	236	1328	1472
Crystal size (mm)	$0.20 \times 0.10 \times 0.10$	$0.46 \times 0.36 \times 0.28$	0.58 imes 0.44 imes 0.26	$0.36 \times 0.20 \times 0.14$
range for data collection (°)	2.86–25.50	0.998–27.485	0.998–27.485	0.998–27.485
Index ranges	$-11 \le h \le 8, -19 \le k \le 19,$ 13 < 1 < 13	$-9 \le h \le 9, -10 \le k \le 10,$ 13 < 1 < 12	$-17 \le h \le 18, -15 \le k \le 15,$	$-17 \le h \le 17, -15 \le k \le 14,$
Reflections collected	10 974	4163	11 145	9978
Independent reflections	$2955 [R_{\odot} - 0.0143]$	$2375 [R_{\odot} = 0.0313]$	$5982 [R_{\odot} - 0.0441]$	$5650 [R_{\odot} = 0.0235]$
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data/restraints/parameters	2955/0/178	2375/0/121	5982/60/405	5650/0/355
$Goodness-of-fit on F^2$	1 129	1 082	1 168	1 271
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0453 \text{ w} R_2 = 0.1398$	$R_1 = 0.0427 \text{ w} R_2 = 0.1090$	$R_1 = 0.0711 \text{ w} R_2 = 0.1478$	$R_1 = 0.0563 \text{ w} R_2 = 0.1427$
R indices (all data)	$R_1 = 0.0522, wR_2 = 0.1449$	$R_1 = 0.0475$, $wR_2 = 0.1124$	$R_1 = 0.1216$, $wR_2 = 0.1798$	$R_1 = 0.0580, wR_2 = 0.1432$
Max/Min of residual	0.841 and -0.221	0.622 and -0.607	0.83 and -0.74	0.749 and -0.629
electron density				



Scheme 3. Reactions of benzoxaborole 1 with gallium- and indium trialkyls.

membered ring M_2O_2 (M = Ga, In) and two benzoxaborolate moieties. In spite of the similarity between the chemistry of benzoxaboroles and that of organoboronic acids [23], the structures of **3–5** indicate that the benzoxaborole **1** acts with gallium and indium trialkyls as alcohol involving a reaction of the OH group only and yielding products similar to typical alkylmetal alkoxides. The M–O (M = Ga, In; O = oxygen atom of the oxaborole ring) distances are about 3.1 Å, indicative of the lack of an M–O coordinative bond. Boron atoms in all molecules show a planar trigonal coordination (the sum of the angles around boron is 360°).

The ¹H NMR spectra of compounds **2–5** reveal the following signals: multiplets of aromatic protons at approximately 7.30–7.90 ppm, one singlet of CH_2O protons at approximately 5.00–5.50 ppm and one singlet of the protons of alkyl groups bonded to metal atoms (at approximately 1.00–1.30 ppm in **2**, **4**, and **5**; at 0.07 ppm in **3**). The appearance of only one signal of protons of alkyl groups bonded to metal atoms indicates an equivalence of these groups in accordance with the crystal structures. On the basis of the integration ratio of the CH_2O protons and the alkyl group protons, we found that in the molecules there are two alkyl groups bonded to metal atoms per one benzoxaborolate unit.

Complexes **2** and **4** were characterized by thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) in argon atmosphere. Thermoanalytical curves are presented in Figs. 5 and 6. The beginning of the compound's **2** thermal decomposition is observed at ca. 200 °C, and in the range up to ca. 260 °C, an exothermal transformation occurs, which is accompanied by an approximately 55% mass loss of the sample on the TGA diagram. In the thermogram, a sharp peak with a maximum at 247 °C appears. Upon increasing the temperature, intermediates undergo further decomposition with a total mass loss of 76.36%. Measurements of the melting point of compound **2** in



Fig. 2. (*top*) Molecular structure of (**3**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): O(1)–B(1) 1.374(4), O(2)–B(1) 1.347(4), O(2)–Ga(1) 1.962(2), O(2a)–Ga(1) 1.971(2), B(1)–O(2)–Ga(1) 125.0(2), B(1)–O(2)–Ga(1a) 134.7(2), Ga(1)–O(2)–Ga(1a) 100.3(1), O(2)–Ga(1)–O(2a) 79.7(1). (*bottom*) View of a molecule of **3** showing that two benzoxaborolate units and the central Ga₂O₂ ring are coplanar.



Fig. 3. Molecular structure of (**4**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for one molecule in a cell: O(1)–Ga(1a) 1.997(6), O(1)–Ga(1) 2.002(5), O(1-B(1)) 1.36(1), O(1)–Ga(1)–O(1a) 77.3(2), Ga(1a)–O(1)–Ga(1) 102.7(2), B(1)–O(1)–Ga(1a) 122.2(6), B(1)–O(1)–Ga(1) 135.1(6).



Fig. 4. Molecular structure of (**5**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for one molecule in a cell: O(1)-ln(1) 1.206(5), ln(1)-O(1a) 1.199(5), B(1)-O(1) 1.325(11), B(1)-O(2) 1.395(10), O(1)-ln(1)-O(1a) 74.8(2), ln(1)-O(1)-ln(1a) 105.2(2), B(1)-O(1)-ln(1a) 139.9(5), B(1)-O(1)-ln(1a) 139.9(5), O(1)-ln(1) 114.7(5), O(1)-B(1)-O(2) 118.4(7), O(1)-B(1)-C(9) 134.0(8), O(2)-B(1)-C(9) 107.6(7).



Fig. 5. Thermogravimetric analysis traces showing the decomposition of compound **2** in an inert (Ar) atmosphere.

a capillary tube show decomposition in the region 240–250 °C without melting, which is in agreement with the thermoanalysis.

The decomposition of compound **4** begins at ca. 110 °C. The DTA curve shows one sharp endothermic peak at 232.4 °C, which is attributed to melting followed by decomposition. The melting point found on the DTA curve confirms the melting point determined by a capillary tube system under argon (232–236 °C). Besides the endothermic peak at 232.4 °C, the first weight loss step is accompanied by a sharp exothermic peak at 272.8 °C, whereas the remainder of the decomposition process in the range 280–500 °C is characterized by a broad endothermic feature with a total mass loss of 71.27%.

On the basis of the thermogravimetric studies, it is difficult to link different areas of mass loss to a specific way of the decomposition of the compounds. To gain a better understanding of the decomposition process, the structure of the volatile decomposition products was studied. These products were obtained by heating compound **4** in the region 250–280 °C under argon. The decomposition products were isolated by distillation under vacuum as a yellow liquid. The NMR analysis shows a mixture of products. In the ¹H NMR spectrum, the presence of signals of aromatic protons (8.30–7.10 ppm) and signals at 1.40–0.90 ppm indicates phenyl



Fig. 6. Thermogravimetric analysis traces showing the decomposition of compound **4** in an inert (Ar) atmosphere.



Scheme 4. Structure of the compound **E** formed as a result of a transition of ^tBu groups from gallium to boron.

and alkyl groups of organic compounds. Three intensive singlets at 1.23, 1.06, and 1.04 ppm can be assigned to the protons of ^tBu groups bonded to metal atoms, whereas three singlets at 5.30, 5.28, and 5.25 ppm of CH₂O protons indicate compounds similar to the benzoxaborole 1. The mixture of the decomposition products consists of boronic compounds, which was evidenced by the green color of the flame during combustion and the presence of boron signals in the ¹¹B NMR spectrum. Based on the literature data [23], the signal at 33.1 ppm originates from the boron atom of the benzoxaborole 1, whereas the signal at 50.8 ppm is typical for boron bonded to two carbon atoms and one oxygen atom [24]. The signal is assigned to the boron atom of a compound E (Scheme 4), which is formed as a result of a transition of ^tBu groups from gallium to boron. Additional signal at -23.7 ppm can be attributed to the borate ion [25], but it is difficult to determine its structure on the basis of the presented results.

Summarizing, the study has revealed the nature of benzoxaborolate ligand in group 13 metal complexes. In the reaction with the trialkylaluminum compound, the benzoxaborole **1** acts as an acid yielding a product similar to dimeric dialkylaluminum carboxylates, in which two oxygen atoms of the benzoxaborolate moiety are bonded to aluminum atoms. Gallium and indium trialkyls react with the OH group of **1** only to form complexes similar to alkoxides. Coordination of an oxygen atom of the oxaborole ring to the gallium and indium centers was not observed, which indicates lower coordination abilities of these metal centers in comparison with an aluminum center. Thermogravimetric studies revealed that group 13 metal benzoxaborolates undergo thermal decomposition with liberation of organoboron compounds mainly and probably a small amount of organic compounds is formed.

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