Journal of Organometallic Chemistry 732 (2013) 8–14

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Benzoxaborolate ligands in group 13 metal complexes

Eliza Jaśkowska [a], Iwona Justyniak [b], Michał K. Cyrański [c], Agnieszka Adamczyk-Woźniak [d], Andrzej Sporzyński [d], Ewa Zygadło-Monikowska [a], Wanda Ziemkowska [a,*]

[a] Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland
[b] Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
[d] Warsaw University of Technology, Faculty of Chemistry, Department of Physical Chemistry, Noakowskiego3, 00-664 Warsaw, Poland

ARTICLE INFO

Article history:
Received 23 October 2012
Received in revised form
10 January 2013
Accepted 14 January 2013

Keywords:
Aluminum
Gallium
Indium
Benzoxaborole
Thermogravimetric analysis

ABSTRACT

A series of group 13 metal benzoxaborolates $[R_2MOB(o\text{-}CH_2O)(C_6H_4)]_2$ [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$_3$Al 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 benzoxaborole **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.

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].

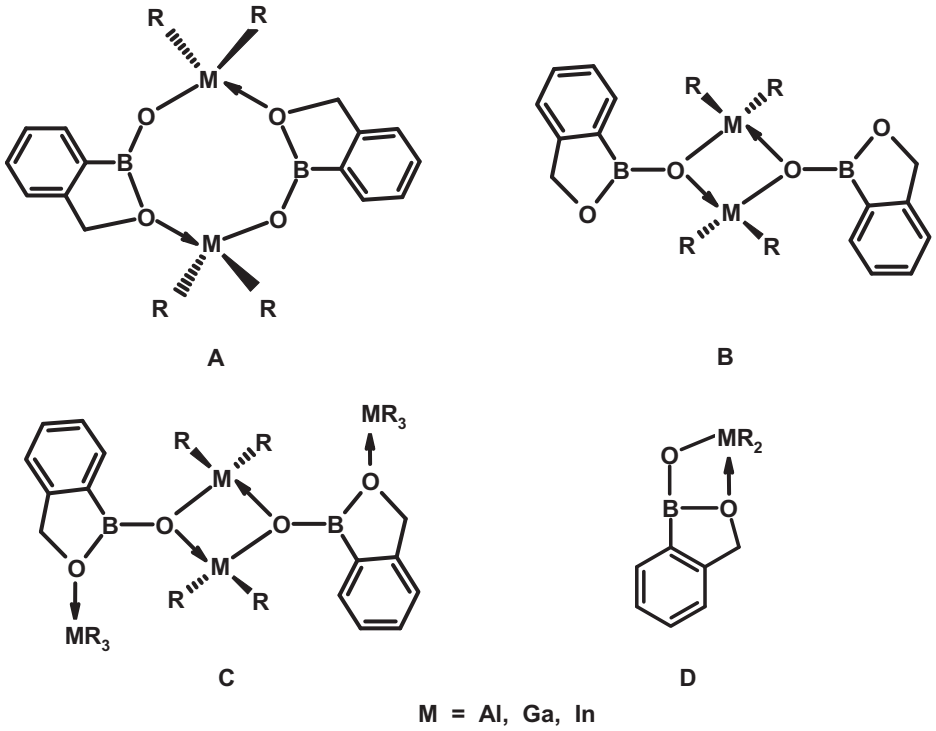
Although benzoxaboroles can be regarded as electron donating ligands in complexes with aluminum, gallium, and indium alkyls due to the presence of two oxygen atoms in the benzoxaborole molecule, these benzoxaborolate complexes are unknown. Even reactions of group 13 metal compounds with other oxygen 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 OBR_2 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 $LAlH_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-i$Pr_2C_6H_3$) [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.

* Corresponding author. Tel.: +48 22 2347316.
E-mail address: ziemk@ch.pw.edu.pl (W. Ziemkowska).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.01.023



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]. ^{1}H and ^{13}C NMR spectra were obtained on a Mercury-400BB Varian spectrometer. Chemical shifts were referenced to the residual proton signals of $CDCl_3$ (7.26 ppm). ^{13}C NMR spectra were acquired at 100.60 MHz (standard: chloroform $^{13}CDCl_3$, 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 $[R_2MOB(o\text{-}CH_2O)(C_6H_4)]_2$ [R = ^{t}Bu, M = Al (**2**), R = Me, M = Ga (**3**), R = ^{t}Bu, M = Ga (**4**), R = ^{t}Bu, M = In (**5**)]: general procedure

A solution of R_3M (1 mmol) in 5 cm^3 of CH_2Cl_2 was injected into a stirred solution of **1** (1.34 g, 1 mmol) in CH_2Cl_2 (20 cm^3) 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. $[^{t}Bu_2AlOB(o\text{-}CH_2O)(C_6H_4)]_2$ (**2**)

Yield 85%. ^{1}H NMR ($CDCl_3$) δ: 1.00 [36H, s, AlC(CH_3)$_3$], 5.41 (4H, s, CH_2O), 7.38 (2H, m, H_{aromat}), 7.44 (2H, m, H_{aromat}), 7.59 (2H, m, H_{aromat}), 7.88 (2H, m, H_{aromat}). ^{13}C NMR ($CDCl_3$) δ: 14.86 [AlC(CH_3)$_3$], 30.31 [AlC(CH_3)$_3$], 71.74 (CH_2O), 121.08, 128.34, 132.12, 132.26, 147.73 (C_{aromat}) ppm.

X-ray-quality crystals were obtained from the *n*-C_6H_{14}–CH_2Cl_2 solution at 10 °C. Decomposition (on the basis of DSC measurements): 247 °C. FTIR (nujol): ν = 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 ^{t}Bu groups, 39.21; Calcd for $C_{30}H_{48}Al_2B_2O_4$: Al, 9.85; ^{t}Bu, 39.40 wt.%.

2.4. $[Me_2GaOB(o\text{-}CH_2O)(C_6H_4)]_2$ (**3**)

Yield 81%. ^{1}H NMR ($CDCl_3$) δ: 0.07 (12H, s, GaCH_3), 5.08 (4H, s, CH_2O), 7.38 (4H, m, H_{aromat}), 7.50 (2H, m, H_{aromat}), 7.62 (2H, m, H_{aromat}). ^{13}C NMR ($CDCl_3$) δ: −4.10 (GaCH_3), 70.70 (CH_2O), 121.40, 127.10, 130.22, 130.80, 154.50 (C_{aromat}) ppm.

X-ray-quality crystals were obtained from the CH_2Cl_2 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 $C_{18}H_{24}B_2Ga_2O_4$: C, 46.41; H, 5.16. Found: C, 46.04; H, 5.21 wt.%.

2.5. $[^{t}Bu_2GaOB(o\text{-}CH_2O)(C_6H_4)]_2$ (**4**)

Yield 86%. ^{1}H NMR ($CDCl_3$) 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}). ^{13}C NMR ($CDCl_3$) 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.