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Reactions of Hydroxymesitylboranes with Metal Alkyls: An Approach to New Sterically Hindered (Metaloxy)mesitylboranes

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Reactions of mesitylboronic acid with alkyl derivatives of aluminum R_3Al (R = Me, Et, Bu^i), gallium (Me_3Ga), and zinc (Et_2Zn) were investigated. The treatment of mesitylboronic acid, $MesB(OH)_2$, with trimethylgallium afforded the discrete dimer $[\mu\text{-}(MesB(OH)O)GaMe_2]_2$ (**1**), which is the simple example of a O-metalated boronic acid with no hydrogen bonding in the crystal lattice. In addition, the reaction of dimesitylborinic acid, Mes_2BOH, with diethylzinc produced the low-valent zinc compound $[(\mu\text{-}Mes_2BO)ZnEt]_2$ (**2**), which was also characterized by X-ray diffraction.

Introduction

It is well-known that the role of steric factors in boron chemistry is important. It was found earlier that the chemical properties of sterically hindered boron compounds may vary dramatically when compared to their nonhindered analogues. Obviously, it can be expected that the use of bulky substituents should reduce the reactivity of the boron center. A good example of such an effect is trimesitylborane, which, contrary to triphenylborane, is completely resistant against reactions involving the cleavage of the boron−carbon bond; e.g., this compound could not be hydrolyzed under normal conditions and is stable to air.[1] However, this compound does undergo some reactions but the boron environment remains unchanged.[2] Two mesityl groups provide still considerable protection to boron. This property was found earlier,[1] and then it was exploited by several research groups.[3]

Our work has focused on metal organoboryl oxides. Sterically hindered diorganoborinic acids were used successfully for the preparation of some systems possessing B−O−M linkage, and this involves also dimesitylborinic acid and the closely related compound $Trip_2BOH$ (Trip = 2,4,6-$Pr^i_3C_6H_2$).[4] Interesting results concerning diverse reactivity of dialkylaluminum dimesitylboryl oxides, $[(\mu\text{-}Mes_2BO)AlR_2]_2$, especially their catalytic activity, have been presented recently by our group[5] and independently by Gibson and co-workers.[6] This work is the continuation of our research on sterically hindered metal organoboryl oxides. We describe some results concerning mainly gallium and zinc derivatives of mesitylboronic and dimesitylborinic acids.

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 dimesitylborinic acid, Mes_2BOH,[1] and mesitylboronic acid, $MesB(OH)_2$,[7] have been prepared according to the literature descriptions. ^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 (unless otherwise noted). Chemical shifts are given in ppm relative to C_6D_5H (δ = 7.17 ppm) and $Et_2O{\cdot}BF_3$ in ^1H and ^{11}B spectra, respectively. Elemental analyses were performed using Perkin-Elmer 2400 apparatus.

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Table 1. Crystal Data and Structure Refinement for Compounds **1** and **2**

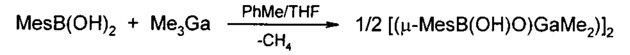
param	**1**	**2**
emp formula	$C_{22}H_{36}B_2Ga_2O_4$	$C_{47}H_{54}B_2O_2Zn_2$
fw	262.78	803.26
temp, K	293(2)	293(2)
λ, Å	1.541 78	0.710 73
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*n*
a, Å	10.864(2)	15.020(3)
b, Å	15.785(3)	10.740(2)
c, Å	16.703(3)	15.650(3)
β, deg	108.78(3)	117.83(3)
V, Å^3	2711.9(9)	2232.6(8)
Z	4	2
d(calcd), Mg/m^3	1.287	1.195
μ, mm^{-1}	2.608	1.108
F(000)	1088	844
cryst size, mm	0.32 × 0.24 × 0.20	0.30 × 0.24 × 0.10
reflcns collcd	2531	23 919
R [$I > 2\sigma(I)$]	0.0731	0.0901
largest diff. peak and hole, e Å^{-3}	0.683 and 1.758	2.549 and 0.591
GOF	1.191	1.162

X-ray Diffraction Studies. Crystal data regarding structures of **1** and **2** are given in Table 1 together with refinement details. X-ray measurements were performed on a Kuma KM-4 and KM4CCD κ-axis diffractometers with graphite-monochromated Cu Kα (**1**) or Mo Kα (**2**) radiation, respectively. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma diffraction programs. The structures were solved by direct methods[8] and refined using SHELXL.[9] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors, wR, and all goodness-of-fit *S* values are based on F^2. Conventional R factors are based on *F* with *F* set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from ref 10 Molecular diagrams were drawn using ORTEP.[11]

Preparation of [(*μ*-MesB(OH)O)GaMe$_2$]$_2$ (1). A solution of mesitylboronic acid (0.27 g, 1.65 mmol) in tetrahydrofuran (3 mL) was added dropwise during 2−3 min to a stirred solution of trimethylgallium (0.19 g, 1.65 mmol) in toluene (2 mL) at −70 °C. The resultant solution was allowed to warm slowly to room temperature. Solvents were evaporated under reduced pressure. A solid residue was washed with hexane (3 × 2 mL) and dried under reduced pressure. Compound **1** was obtained as a white powder in 0.27 g yield (62%), mp 152−154 °C (dec): ^{1}H NMR δ 6.67 (s, 2H, arom), 3.58 (s, 1H, OH), 2.26 (s, 6H, *o*-Me), 2.11 (s, 3H, *p*-Me), 0.07 (s, 6H, GaMe); ^{13}C{^{1}H} NMR δ 138.97, 138.46, 128.69, 127.63 (arom), 22.66 (*o*-Me), 21.64 (*p*-Me), −4.19 (GaMe); ^{11}B NMR δ 31.3. Anal. Calcd for $C_{11}H_{18}BGaO_2$: C, 50.28; H, 6.90. Found: C, 50.09; H, 6.69.

Preparation of [(*μ*-Mes$_2$BO)ZnEt]$_2$ (2). Diethylzinc (0.7 g, 5.5 mmol) was added during 2−3 min to the stirred solution of Mes$_2$BOH (1.33 g, 5.0 mmol) in toluene (10 mL) at 0 °C. The resultant solution was allowed to warm slowly to room temperature with stirring. A white precipitate was formed. It was dissolved by warming the suspension to ca. 50 °C. The solution was slowly cooled to room temperature. Colorless needles of compound were obtained. The supernatant solution was cooled to 0 °C, to give a further portion of crystals. They were washed with a small amount of hexane and dried under reduced pressure. The total amount of the product was 1.15 g (64%), mp 142−146 °C: ^{1}H NMR δ 6.76 (s, 4H, arom), 2.39 (s, 12H, *o*-Me), 2.14 (s, 6H, *p*-Me), 0.69 (t, 3H, ZnCH$_2$**C***H*$_3$), 0.06 (q, Zn*CH$_2$*CH$_3$); ^{13}C{^{1}H} NMR δ 140.97, 140.49, 137.96, 129.13 (arom), 23.39 (*o*-Me), 21.61 (*p*-Me), 11.51 (ZnCH$_2$*CH$_3$*), 1.05 (Zn*CH$_2$*CH$_3$); ^{11}B NMR δ 51.0. Anal. Calcd for $C_{20}H_{27}BOZn$: C, 66.80; H, 7.57. Found: C, 66.16; H, 7.28.

Scheme 1



$$\mathrm{MesB(OH)_2 + Me_3Ga \xrightarrow[-CH_4]{PhMe/THF} 1/2\ [(\mu\text{-}MesB(OH)O)GaMe_2)]_2}$$

(Mes$_2$BO)ZnEt·2,2′-bipy (3) was prepared by the treatment of [(*μ*-Mes$_2$BO)ZnEt]$_2$ (0.90 g, 1.25 mmol), freshly prepared in tetrahydrofuran (7 mL), with 2,2′-bipyridine (0.42 g, 2.7 mmol). The resultant suspension was warmed to 50 °C to give the clear orange solution. Slow cooling to the room temperature afforded yellow needles of the complex **3**. Crystals were washed with a little cold THF (2 × 2 mL) and dried under reduced pressure. The yield of **3** was 0.81 g (63%), mp 165−168 °C: ^{1}H NMR (THF-d_8) δ 8.46 (d, 4H, bipy), 7.93 (t, 2H, bipy), 7.39 (t, 2H, bipy), 6.52 (s, 4H, arom), 2.19 (s, 6H, *p*-Me), 1.95 (s, 12H, *o*-Me), 1.02 (t, 3H, ZnCH$_2$*CH$_3$)*, 0.16 (q, Zn*CH$_2$*CH$_3$); ^{13}C{^{1}H} NMR δ 149.84, 140.66, 138.09, 135.22, 128.80, 128.05, 124.95, 121.62 (bipy, arom), 22.60 (*o*-Me), 21.20 (*p*-Me), 13.54 (ZnCH$_2$*CH$_3$)*, −1.55 (Zn*CH$_2$*CH$_3$); ^{11}B NMR δ 48.5. Anal. Calcd for $C_{30}H_{35}BN_2OZn$: C, 69.86; H, 6.84; N, 5.43. Found: C, 69.95; H, 6.89; N, 5.32.

Results and Discussion

Synthetic Details. The reaction of mesitylboronic acid with trimethylgallium proceeds cleanly as the selective protonolysis of one Ga−C bond occurs to yield the crystalline compound **1**. This is shown in Scheme 1. In this case the boron alkylation resulting from the transfer of methyl groups from gallium to boron does not proceed at all. The product is reasonably stable. The decomposition with gas evolution was observed only during melting (ca. 150 °C). The reaction of unsubstituted phenylboronic acid with GaMe$_3$ proceeded similarly but led to the formation of amorphous material whose structure was not determined.[12]

The reaction of mesitylboronic acid with diethylzinc proceeded with gas (ethane) evolution and afforded insoluble amorphous product. Similarly, reactions of mesitylboronic acid with aluminum alkyls do not yield well-defined products. In the case of trimethyl- and triethylaluminum insoluble amorphous materials were obtained. We suppose that oligomeric or polymeric B−O−Al type species are formed in these reactions.[13] However, the ^{11}B NMR analysis of the reaction mixture of MesB(OH)$_2$ and AlR$_3$, R = Me and Et (molar ratio 1:2, respectively), showed the presence

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(13) Very recently, the synthesis and characterization of related compounds obtained from the reactions of (2,6-diisopropylphenyl)boronic acid, 2,6-$Pr^i_2C_6H_3B(OH)_2$, with Bu^t_3Al were reported: Richter, B.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 1286.

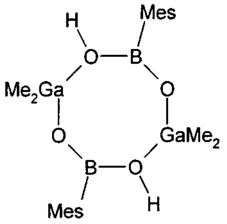
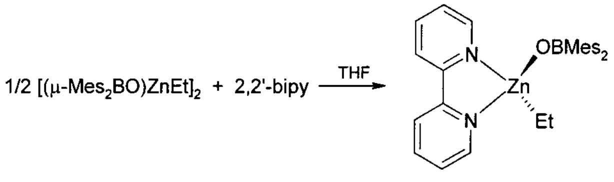


Figure 1. Hypothetical molecular structure of $[(\mu\text{-}MesB(OH)O)GaMe_2]_2$ (**1**).

Scheme 2

$$Mes_2BOH + Et_2Zn \xrightarrow[-C_2H_6]{PhMe} 1/2\ [(\mu\text{-}Mes_2BO)ZnEt)]_2$$

Scheme 3



of corresponding soluble mesityldialkylboranes $MesBR_2$, too. This is the evidence that the boron alkylation proceeds in these systems to a significant extent. Even the replacement of the mesityl group with the alkyl group was observed as the presence of trialkylboron in the reaction mixture was also established by the ^{11}B NMR measurement. Clearly, the redistribution reaction between $MesBR_2$ and AlR_3 is possible.

Interesting results obtained previously for alkylaluminum dimesitylboryl oxides, $[(\mu\text{-}Mes_2BO)AlR_2]_2$,[5,6] have prompted us to investigate their zinc analogues. In fact the treatment of Mes_2BOH with diethylzinc led to gas (ethane) evolution and the high-yield formation of the soluble dimeric ethylzinc dimesitylboryl oxide, $[(\mu\text{-}Mes_2BO)ZnEt]_2$ (**2**) (Scheme 2).

Ethane was not evolved when dimesitylborinic acid was added to the toluene solution of **2** at room temperature. In addition, the catalytic decomposition of Mes_2BOH which is known to proceed in the presence of $[(\mu\text{-}Mes_2BO)AlR_2]_2$ (R = Me, Et)[5,6] is not the case, apparently because of the weaker Lewis acidity of zinc with respect to aluminum. However, compound **1** reacts easily with 2,2′-bipyridine at room temperature to form the 1:1 addition complex $Mes_2BOZnEt\cdot bipy$ (**3**) as yellow crystals (Scheme 3). The steric hindrance at zinc was apparently not sufficient to prevent the donor coordination. Unfortunately, the quality of crystals was too low to perform an X-ray diffraction study of this interesting compound.

Structural Description. Initially, we considered the structure of the dimer **1** in which gallium atoms are donated by the hydroxyl oxygens. This would lead to the formation of the eight-membered BOGaOBOGaO ring as shown in Figure 1.

However, the X-ray analysis of **1** revealed that the central four-membered planar Ga_2O_2 ring is formed. Gallium atoms are bridged by the boryl oxide oxygen atoms as shown in Figure 2. Selected bond distances and angles are presented in Table 2. The Ga−O(1) bond distances are 1.972(5) Å. The Ga−O−Ga and O−Ga−O angles are 101.0(2) and 79.0(2)°, respectively. The metric features of the Ga_2O_2 core are very similar to those found for related gallium boryl oxide $[(\mu\text{-}9\text{-}BBN\text{-}9\text{-}O)GaMe_2]_2$.[14] The Ga···O(2) distance in **1** is large (3.094 Å), and there is no deviation from the tetrahedral environment typical for gallium atoms in related compounds. Hence, hydroxyl oxygens are not engaged in any interaction with gallium. The Ga−C bond distances as well as the C−Ga−C angle are also typical. The B−O bond distances are almost equal to one another (1.346(8) Å for boryl oxide oxygen and 1.351(10) Å for hydroxyl oxygen) and correspond well to the value found in $[(\mu\text{-}9\text{-}BBN\text{-}9\text{-}O)GaMe_2]_2$ (1.356(7) Å). The O(1)−B−O(2) angle is 115.6(6)°. It should be noted that the X-ray diffraction determination of the structure of the dibutyltin derivative of phenylboronic acid $[Ph(OH)O]_2SnBu^t_2$ showed the very large variation of B−O bond distances as well as O−B−O angles.[7] On the other hand, the quality of the refinement suggests some care in using those results.

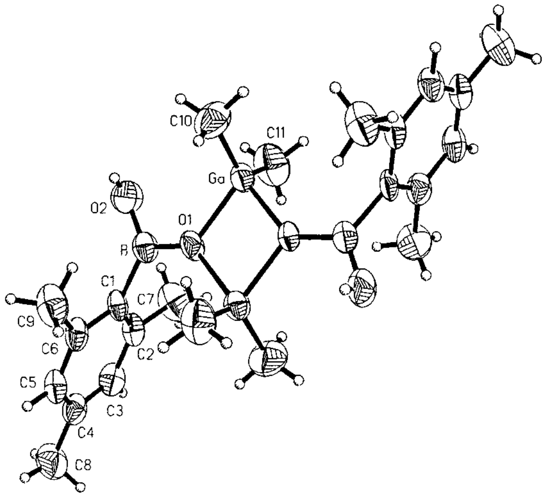


Figure 2. Molecular structure of of $[(\mu\text{-}MesB(OH)O)GaMe_2]_2$ (**1**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1** and **2**

	Compound **1**		
Ga−C(11)	1.928(9)	B−O(1)	1.346(8)
Ga−C(10)	1.941(8)	B−O(2)	1.352(10)
Ga−O(1)	1.972(4)	B−C(1)	1.585(9)
Ga−O(1)	1.972(5)		
C(11)−Ga−C(10)	130.2(5)	B−O(1)−Ga	124.7(5)
O(1)−Ga−O(1)	79.0(2)	B−O(1)−Ga	134.0(4)
Ga−O(1)−Ga	101.0(2)	O(1)−B−O(2)	115.5(6)
	Compound **2**		
Zn(1)−O(1)	1.972(4)	B(1)−O(1)	1.345(10)
Zn(1)−O(1)	1.969(5)	B(1)−C(13)	1.572(12)
Zn(1)−C(20)	1.941(8)	B(1)−C(6)	1.574(11)
Zn(1)···Zn(1)	3.0047(18)		
O(1)−Zn(1)−O(1)	80.6(2)	O(1)−B(1)−C(13)	117.1(7)
Zn(1)−O(1)−Zn(1)	99.4(2)	O(1)−B(1)−C(6)	118.4(7)
C(20)−Zn(1)−O(1)	139.6(3)	C(13)−B(1)−C(6)	124.5(7)
B(1)−O(1)−Zn(1)	130.1(5)		

The C_2BO plane in **1** is slightly twisted (by ca. 10°) with respect to the Ga_2O_2 plane. An interesting structural feature is that B−O(1)−Ga and B−O(1)−Ga′ angles vary significantly (124.7(4) and 134.0(4)°, respectively). This effect can

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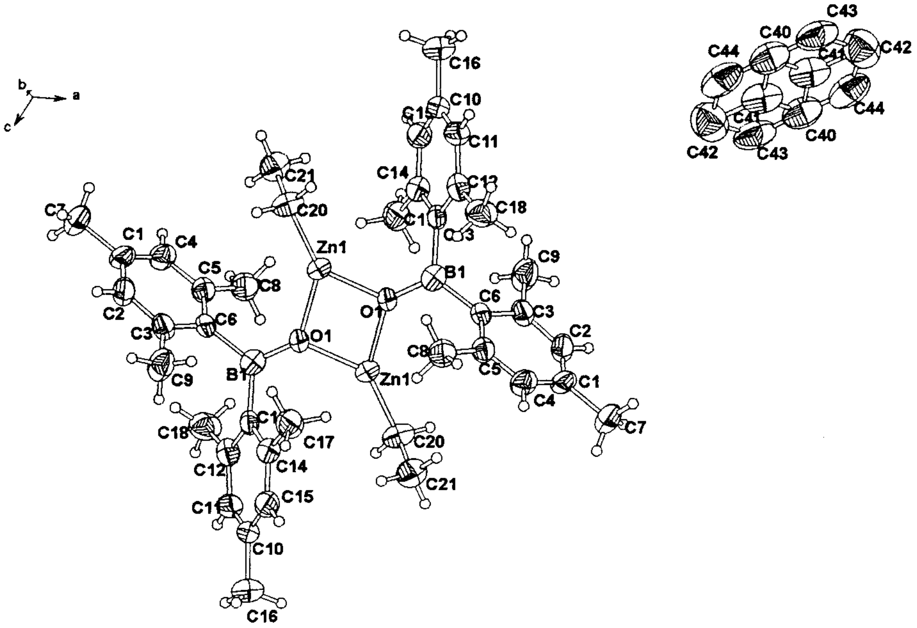

Figure 3. Molecular structure of $[(\mu\text{-Mes}_2\text{BO})\text{ZnEt}]_2$ (**2**). The disordered molecule of toluene has also been shown.

be explained in terms of steric interaction between mesityl groups and methyl groups at gallium. Alternatively, an interaction between hydroxyl oxygen and gallium could also be considered as a reason for the mentioned difference. However, as was mentioned above, this is not the case since such an interaction should result in a more acute O(1)−B−O(2) angle and/or significantly shorter Ga···O(2) distance.

It should be stressed that the hydroxyl group does not form any intra- and/or intermolecular hydrogen bonds. This observation was confirmed by the IR spectrum showing the sharp band at 3630 cm^{-1}, i.e., in the range typical for the nonassociated hydroxyl group. Apparently the steric hindrance provided by the bulky mesityl groups together with dimethylgallium moieties results in the lack of association. In fact, the orientation of mesityl rings is specific as they are located almost perpendicular to the Ga_2O_2 plane. The lack of association in **1** is again in contrast to the existence of extensive hydrogen-bonding network in $[\text{Ph(OH)O}]_2\text{SnBu}^t{}_2$.[7]

Molecular structure of **2** is depicted in Figure 3. Compound **2** crystallizes with one molecule of toluene. Selected bond distances and angles are given in Table 2. The central Zn_2O_2 is planar. The Zn−O bond distance are 1.969(5) and 1.972(4) Å; i.e., they are significantly shorter than those found in the tetrameric zinc boryl oxide $[(\mu_3\text{-9-BBN-9-O})\text{ZnEt}]_4$,[15] where the Zn−O distances vary in the range 2.07−2.14 Å. However, they are comparable with the values measured in related dimeric alkoxides $[(\mu\text{-2,6-Pr}^i{}_2\text{C}_6\text{H}_3\text{O})\text{ZnCH}_2\text{SiMe}_3]_2$ and $[(\mu\text{-2,4,6-Bu}^t{}_3\text{C}_6\text{H}_2\text{O})\text{ZnCH}_2\text{SiMe}_3]_2$.[16] The Zn−O−Zn (99.4(2)°) and O−Zn−O (80.6(2)°) angles in **2** are also similar to those found in the mentioned dimers. The shortening of Zn−O distances in **2** is due to the decreasing the coordination number of zinc from 4 to 3. The B−O bond distance is 1.345(10) Å and is also shorter (but only slightly) than the mean value in $[(\mu_3\text{-9-BBN-9-O})\text{ZnEt}]_4$. It should be noted that the torsion angle between the C_2BO and Zn_2O_2 planes is about 15°. This nonplanar conformation probably reflects steric requirements of mesityl groups. In the related aluminum compound $[(\mu\text{-Mes}_2\text{BO})\text{AlMe}_2]_2$,[5] the analogous torsion angle is even larger (ca. 30°), but this is in accord with the smaller size of the Al_2O_2 core vs Zn_2O_2 core.

The dimeric structure of **2** is not typical for alkylzinc alkoxides and also boryl oxides. It is clear that the presence of bulky mesityl groups prevents the formation of a tetramer. Obviously, the boryl oxide ligand is expected to be a less effective π-donor with respect to typical alkoxide ligands. However, the tetrameric structure of other alkylzinc boryl oxides[12] lends strong support to the conclusion that in the case of **2** steric factors are crucial for the stabilization of the dimeric structure.

In conclusion, mesitylboronic acid was used succsessfully in synthesis of a new gallium boryl oxide. However, generally dimesitylborinic acid seems to be a more versatile reagent in the synthesis of metal boryl oxides.

Acknowledgment. We gratefully acknowledge the support by Aldrich Chemical Co., Inc., Milwaukee, WI, through continuous donation of chemicals and equipment. We also thank the State Committee for Scientific Research for financial support.

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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