

A Dimethylgallium Boryl Complex and Its Methyllithium Addition Compound

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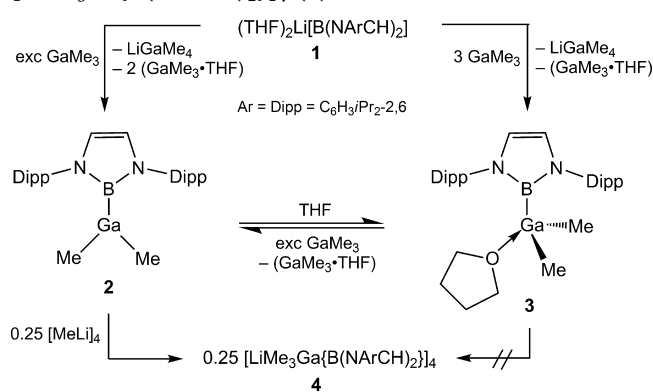
S Supporting Information

ABSTRACT: The three-coordinate complex $\text{Me}_2\text{Ga}[\text{B}(\text{NArCH})_2]$ ($\text{Ar} = \text{C}_6\text{H}_3i\text{Pr}_{2,6}$) is accessible via a tandem Lewis acid–base metathesis protocol employing $(\text{THF})_2\text{Li}[\text{B}(\text{NArCH})_2]$ and GaMe_3 . It features a very short Ga–B bond of 2.067(3) Å, which was further investigated by DFT calculations and the analysis of the electron density. Reaction of MeLi with $\text{Me}_2\text{Ga}[\text{B}(\text{NArCH})_2]$ forms tetrameric $[\text{LiMe}_3\text{Ga}\{\text{B}(\text{NArCH})_2\}]_4$ with a “nanowheel” structure.

The formation of direct metal (M)–boron bonds constitutes a key step in various catalytic organometallic transformations.¹ Hence, the synthesis and isolation of discrete organometallic species is crucial for assessing the nature of such M–B bonds, ultimately enhancing the knowledge of the respective mechanistic pathways involved. The isolation of a complex with a nucleophilic boron center, $(\text{THF})_2\text{Li}[\text{B}(\text{NArCH})_2]^{2,3}$ (**1**) ($\text{Ar} = \text{C}_6\text{H}_3i\text{Pr}_{2,6}$) in 2006 has given a new momentum to metal–boryl chemistry. Importantly, boryllithium **1** gave access to a series of complexes containing direct M–B bonds with main group (Mg, Al, Si, Ge, Sn),⁴ d-transition (Ti, Hf, Ir, Cu, Ag, Au, Zn),⁵ and smaller-sized rare-earth metals (Sc, Y, Gd, Er, Lu).⁶ The few structurally characterized boryl complexes featuring additional transition-metal M–carbon bonds comprise $[\text{B}(\text{NArCH})_2]\text{MIMes}$ and $[\text{B}(\text{NArCH}_2)_2]\text{MIMes}$ ($\text{Ar} = \text{C}_6\text{H}_3i\text{Pr}_{2,6}$; $\text{IMes} = 1,3$ -dimesityl-imidazole-2-ylidene; $\text{M} = \text{Cu, Ag, Au}$),^{5a,b} (η^5 - C_5Me_5) $\text{Hf}[\text{B}(\text{NArCH})_2](\text{CH}_2\text{Ph})_2$ ($\text{Ar} = \text{C}_6\text{H}_3i\text{Pr}_{2,6}$)^{5d} as well as complexes $\text{Ln}[\text{B}(\text{NArCH})_2](\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n$ ($\text{Ln} = \text{Sc}$ ($n = 1$); Y, Gd, Er, Lu ($n = 2$)).⁶ We recently isolated the organoaluminum boryl complexes $(\text{THF})\text{Me}_2\text{Al}[\text{B}(\text{NArCH})_2]$ and $[(\mu\text{-Me})\text{MeAl}\{\text{B}(\text{NArCH})_2\}]_2$ via reaction of trimethylaluminum with **1**. The boryl anion renders a highly Lewis acidic Al(III) center, which allowed for the synthesis of rare-earth metal heteroaluminate complexes $\text{Ln}[(\text{AlMe}_3)\{\text{B}(\text{NArCH})_2\}]_3$ ($\text{Ln} = \text{Y, Lu}$).^{4b} Having the distinct chemistry of the group 13 metals in mind,⁷ we have now investigated the reactivity of $(\text{THF})_2\text{Li}[\text{B}(\text{NArCH})_2]$ toward trimethylgallium.

Dimethylgallium boryl $\text{Me}_2\text{Ga}[\text{B}(\text{NArCH})_2]$ (**2**) can be synthesized by treatment of boryllithium **1** with an excess of GaMe_3 , generating adduct $(\text{GaMe}_3\cdot\text{THF})$ and LiGaMe_4 as coproducts (Scheme 1). The same tandem Lewis acid–base metathesis protocol was already successfully employed for the synthesis of the aluminum congener.^{4b} However, as expected from Lewis acidity ($\text{Al(III)} > \text{Ga(III)}$) and electronegativity scales (Pauling: Al 1.61, Ga 1.81, C 2.55, B 2.04), the gallium

Scheme 1. Synthesis of $\text{Me}_2\text{Ga}[\text{B}(\text{NArCH})_2]^{4b}$ (2**), $(\text{THF})\text{Me}_2\text{Ga}[\text{B}(\text{NArCH})_2]^{4b}$ (**3**), and $[\text{LiMe}_3\text{Ga}\{\text{B}(\text{NArCH})_2\}]_4$ (**4**)**



derivative revealed distinct M–B bonding and hence reactivity features.

In agreement with the homoleptic group 13 methyl precursors (dimeric Al_2Me_6 ^{8a} vs monomeric GaMe_3),^{8b} three-coordinate gallium boryl complex **2** is monomeric in solution (according to low-temperature NMR spectra, see Figure S5) and in the solid state (Figure 1, top).⁹ Only one signal for both Ga-bonded methyl ligands was observed by a variable-temperature NMR spectroscopic study in the range 26 to -90°C , showing a chemical shift (-0.20 ppm, benzene- d_6 , 26°C) comparable to the ones of GaMe_3 (-0.15 ppm, benzene- d_6 , 26°C) and $[(\mu\text{-Me})\text{MeAl}\{\text{B}(\text{NArCH})_2\}]_2$ (-0.57 ppm, toluene- d_8 , 26°C).^{4b} A very short B–Ga bond length of 2.067(3) Å was revealed. Only in cluster compounds (vide infra), shorter B–Ga contacts were observed. The dimeric complex $[\text{Me}_2\text{Al}\{\text{B}(\text{NArCH})_2\}]_2$ featuring two four-coordinate aluminum centers displays a B–Al distance of 2.119(3) Å.^{4b} The few other monomeric complexes with GaMe_2 units reported in literature include $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{GaMe}_2$,¹⁰ the carbene-gallane complex $(\text{NR}_2)_2\text{MeP}=\text{C}(\text{SiMe}_3)(\text{GaMe}_2)$, $[\{(\text{DDP})\text{GaMe}\}\text{GaMe}_2]$ (DDP = bulky bisimidate),¹¹ and $\text{MeIr}(\text{PCy}_3)_2(\text{GaMe}_2)(\text{Cl}\cdot\text{GaMe}_3)$.¹²

The first direct B–Ga bonds were reported in 1969¹³ for the closed polyhedral gallacarborane $1\text{-CH}_3\text{GaC}_2\text{B}_4\text{H}_6$ revealing a B–Ga contact as close as 2.11(3) Å.¹⁴ Since then, several closo cluster compounds with B–Ga bonds in C_2B_9 and C_2B_4 cage systems have been described with shortest B–Ga contacts

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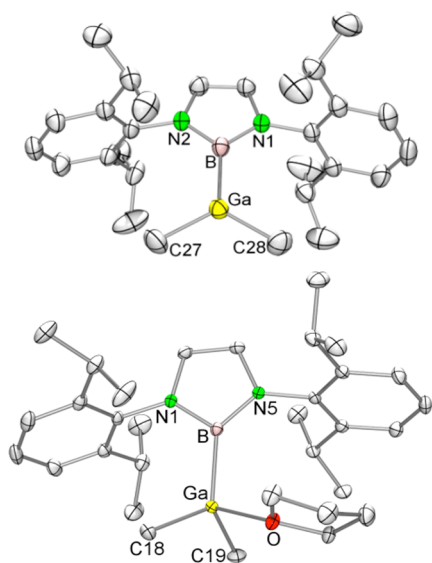


Figure 1. Molecular structures of **2** (top) and **3** (bottom) with atomic displacement parameters set at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: B–Ga 2.067(3); C27–Ga 1.968(3); C28–Ga 1.966(3); B–Ga–C27 122.1(2); B–Ga–C28 122.5(2); C27–Ga–C28 115.3(2). **3**: B–Ga 2.098(2); Ga–C18 1.984(2); Ga–C19 1.995(2); Ga–O 2.1116(8).

ranging from 2.062(11)¹⁵ to 2.125(10) Å.¹⁶ Besides boron cluster compounds, gallium(I) complexes have been combined with electron-deficient perfluorinated B(C₆F₅)₃. Hardman et al. synthesized HC[MeC(C₆H₃iPr₂-2,6)N]₂Ga → B(C₆F₅)₃ (B–Ga 2.142(3), 2.156(1) Å) (**A**), molecular drawings of **A–F** are shown in Supporting Information, SI¹⁷ and (η⁵-C₅Me₅)Ga → B(C₆F₅)₃ (**B**).¹⁷ The latter complex **B** was also independently synthesized by Jutzi et al.¹⁸ (B–Ga 2.160(2),¹⁷ 2.153(6)¹⁸ Å). Utilization of differently substituted aryl ligands afforded similar Ga(I) → B(C₆F₅)₃ bonding (2.108(2)–2.129(3) Å) (**C**).¹⁹ Moreover, Yurkerwich et al. obtained complexes LGaB(C₆F₅)₃ (L = tris(2-mercapto-1-*R*-imidazolyl)hydroborato (**D**),²⁰ tris-(pyrazolyl)hydroborato (**E**) (B–Ga 2.158(3)–2.185(2) Å).²¹ The list is completed by (η⁵-C₅H₅)Ga → B(C₆F₅)₃ (**F**) (B–Ga 2.154(3) Å).²²

The presence of three-coordinate boron atoms in complexes **2** and (THF)₃Me₂Ga[B(NArCH)₂] (**3**) (vide infra) is corroborated by ¹¹B NMR signals at 31.3 and 32.0 ppm, respectively (see Figures S4 and S9).^{4–6} For comparison, complexes **A–C** and **F** with four-coordinate boron centers display boron shifts in the range –20.3 (**A**) to –3 (**F**) ppm, due to a higher shielding of the ¹¹B nuclei.²³ In contrast to the aforementioned adduct complexes where the gallium(I) fragment serves as an electron donor, in complex **2** the boron now acts as a donor to the acceptor Ga in GaMe₃. In order to explore the bonding between B and Ga in more detail, we carried out DFT calculations²⁴ on **2** (henceforth denoted as model system **2a**), the uncoordinated boryl anion [B(NArCH)₂][–] (**1a**), and complex **C** (aryl = C₆H₃iPr₂-2,6; Dipp = C₆H₃iPr₂-2,6; ¹¹B, –17.73 ppm),¹⁹ accompanied by a topological analysis of the electron density, ρ(r), thus derived, using the “atoms in molecules” approach.²⁵

In accordance with earlier reports on hydroborane^{2b} and transition-metal boryl complexes,^{5d} it is the HOMO-1 that displays most of the mixing of B and Ga in **2a** (Figure 2a). The HOMO mainly consists of π-bonding contributions within the boron heterocycle (see SI for details). The nature and strength

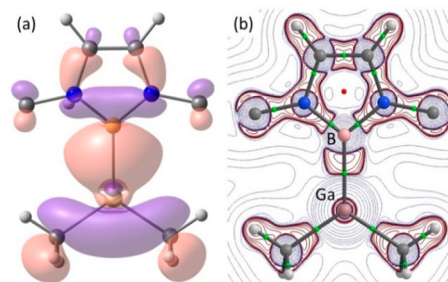


Figure 2. (a) HOMO-1 orbital and (b) contour plot of the negative Laplacian of the electron density, $-\nabla^2\rho(\mathbf{r})$, in the molecular plane of **2a**; in (b) bond paths and BCPs (green points) are superimposed.

of the B–Ga bond are revealed through the topological parameters of ρ(r) listed in Table 1. A relatively large ρ(r) at

Table 1. Selected Atomic Charges, $q(\Omega)$, and Topological Parameters at the BCPs for the Electron Densities of **2a**, **1a**, and **C**

	d [Å]	ρ_b [$e\text{Å}^{-3}$]	$\nabla^2\rho_b$ [$e\text{Å}^{-3}$]	ϵ	H_b [haÅ^{-3}]	δ
2a [$q(\text{B}) = +1.09$, $q(\text{Ga}) = +1.10$, $q(\text{N}) = -1.42$]						
B–Ga	2.095	0.656	–0.817	0.02	–0.321	0.78
Ga–C	2.000	0.733	+2.965	0.03	–0.341	0.76
B–N	1.449	1.235	+12.109	0.01	–1.082	0.65
1a [$q(\text{B}) = +0.76$, $q(\text{N}) = -1.38$]						
B–N	1.497	1.070	+10.859	0.19	–0.854	0.65
C [$q(\text{B}) = +1.48$, $q(\text{Ga}) = +0.95$]						
B–Ga	2.163	0.571	–1.999	0.01	–0.264	0.55

the bond critical point (BCP), ρ_b , along with a negative Laplacian $\nabla^2\rho_b$ and a negative total energy H_b , indicates a clearly covalent B–Ga bond, only slightly weaker than the more polar Ga–C bonds in **2a**. As can be seen in Figure 2b, for both the Ga–C and Ga–B bonds, the electron density is predominantly concentrated on the more electronegative atoms, C and B, leaving Ga with a charge of +1.10. It is interesting to note, that upon coordination to Ga the now greater charged boron atom moves closer toward the heterocyclic ring which leads to a noticeable increase in ρ_b for the B–N bonds (see data for **1a** vs **2a** in Table 1).

The bonding charge concentration on boron facing the gallium atom (Figure 2b) deviates from cylindrical symmetry about the B–Ga bond, with the major axis of ρ(r) perpendicular to the molecular plane (bond ellipticity $\epsilon \leq 0.07$). This might indicate a weak π-contribution to the B–Ga bonding which would also explain the coplanar arrangement of the GaMe₂ moiety with the boron heterocycle. While the NBO scheme²⁶ also denotes a donor–acceptor interaction in **2a**, in which a partially filled p orbital on B (occupancy: 0.53) acts as a donor to a parallel p orbital on Ga (occupancy: 0.08), the distribution of the electron density suggests that such an interaction, if any, should only be very modest: the value of ϵ drops to 0.02 at the B–Ga BCP. This interpretation is confirmed by the change in energy calculated for a modified complex **2a**, in which the GaMe₂ moiety is rotated by 90° relative to the heterocyclic ring. Here, the energy increases by only 5 kJ/mol which therefore rules out any significant π interactions. Slightly greater energy differences, however, are found for intermediate dihedral angles which points to sterics as the true reasons for the observed coplanarity in **2** (see SI for

details). In Table 1, the topological parameters for the B–Ga bond in complex **C** are also included, which is representative for the aforementioned systems with a larger separation between the two atoms. The values show that the greater bond length is also reflected in a slightly reduced value of ρ_b , indicative of a somewhat weaker bond. DFT calculations, however, revealed that it requires <2.5 kJ/mol to stretch the B–Ga bond in **2a** by 7 pm. The shorter bond distance in **2** might therefore simply be a consequence of the reduced coordination number of the boron atom (three in **2** vs four in **C**).

The distinct reactivity of gallium boryl **2** compared to its aluminum counterpart is already observed for the respective THF donor adducts. While displacement of THF from (THF)₂Me₂Al[B(NArCH)₂]₂ is very difficult to achieve in the presence of excess of AlMe₃, formation of **2** from (THF)-Me₂Ga[B(NArCH)₂]₂ (**3**, Figure 1, bottom) is straightforward when utilizing a small excess of GaMe₃ or vacuum treatment (Scheme 1). The changed bonding situation and most likely the drastically decreased Lewis acidity of the gallium boryl is made responsible for the lack of reactivity toward polymeric [LnMe₃]_n.^{4b} However, gallium boryl **2** can disrupt the Li₄C₄ heterocubane framework of methyllithium. In the absence of donor solvents, an equimolar reaction of **2** and MeLi in toluene at ambient temperature affords tetrameric [LiMe₃Ga{B(NArCH)₂}]₄ (**4**) featuring a 16-membered ring structure (see Figure 3). Bridging between Ga and Li centers is

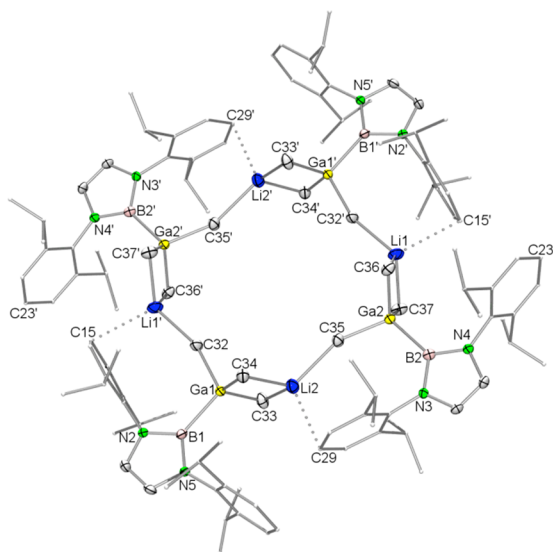


Figure 3. Molecular structure of **4** with atomic displacement parameters set at the 50% level. Hydrogen atoms are omitted and the aromatic parts shown with reduced radii for clarity. Selected bond lengths [Å] and angles [°]: Ga1–B1 2.099(3), Ga1–C32 2.029(2), Ga1–C33 2.067(2), Ga1–C34 2.050(2), Li1...C15' 2.669(5), Li2...C29 2.545(5); C12–N2–B1 127.6(2), C26–N3–B2 127.2(3), C6–N5–B1 129.4(3); C20–N4–B2 130.1(2).

accomplished in an alternating fashion by μ -Me and $(\mu$ -Me)₂ groups. Two cocrystallized benzene molecules (not shown) are either located in or outside the nanosized rings (Ga₂–Ga₂', 0.9313 nm; C₂₃–C₂₃', 1.9768 nm; see Figure 3).²⁷ MeLi addition results in four-coordinate Ga centers showing slightly longer B–Ga distances compared to **2** (**2**: 2.067(3) Å; **4**: 2.099(3); 2.091(3) Å). The *para*-C atom of one of the two Dipp groups of each boryl unit is characterized by a short Li–C contact (Li₂–C₂₉, 2.545(5) Å; Li₁–C₁₅', 2.669(5) Å), which

also affects the B–N–C_{ipso} angles. Only one proton signal was observed for the LiGaMe₃ units (–1.14 ppm, benzene-*d*₆, 26 °C) indicative of a rapid methyl group exchange in solution. The ¹¹B NMR signal is detected at 34.3 ppm (see Figure S15).

Organolithium compounds are known to occur in a large variety of structural types, including heterocubanes, pseudooctahedra, polymeric chains, and stacked and isolated rings.²⁸ While MeLi itself adopts a heterocubane structure,²⁹ heterometallic **4** is intriguing from the point of view that the sterically nondemanding MeLi units combine with **2** to an unprecedented (M–CH₃)₈ ring structure (M = Li, Ga).^{30,31} The cyclic “octamer” seems to be enforced by the bulky boryl ligand, which is prone to secondary metal interactions through the Dipp substituents. The [GaMe₃Li] unit is also found in the infinite chain structure of [LiN(SiMe₃)₂GaMe₃]_∞, which is formed in the equimolar reaction of LiN(SiMe₃)₂ with GaMe₃.³²

In conclusion, Me₂Ga[B(NArCH)₂]₂ (Ar = C₆H₃iPr₂-2,6) is monomeric in solution and in the solid state. The very short B–Ga bond of 2.067(3) Å can be ascribed to three-coordinate group 13 metal centers, on the basis of DFT calculations. Me₂Ga[B(NArCH)₂]₂ completely disaggregates the [MeLi]₄ heterocubane structure. The 16-membered ring-structure of the 1:1 addition compound [LiMe₃Ga{B(NArCH)₂}]₄ is directed by the bulky carbanion-like boryl ligand.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (9) Compound **2** ($C_{28}H_{42}BGaN_2$, $M_r = 587.18$): $Pcab$, $a = 14.7354(5)$, $b = 18.7239(6)$, $c = 20.3319(8)$ Å, $V = 5609.7(3)$ Å³, $d_{\text{calcd}} = 1.154$ g cm⁻³, $Z = 8$, $wR2 = 0.1031$, $R1 = 0.0475$. Compound **3** ($C_{32}H_{50}BGaN_2O$, $M_r = 559.27$): $P21/c$, $a = 12.1653(9)$, $b = 10.6931(8)$, $c = 25.5308(19)$ Å, $V = 3159.2(4)$ Å³, $d_{\text{calcd}} = 1.176$ g cm⁻³, $Z = 4$, $wR2 = 0.0690$ and $R1 = 0.0255$. Compound **4** ($C_{134}H_{198}B_4Ga_4Li_4N_8$, $M_r = 2270.87$): $P21/c$, $a = 19.5718(10)$, $b = 18.8267(11)$, $c = 20.2279(10)$ Å, $V = 6655.0(6)$ Å³, $d_{\text{calcd}} = 1.133$ g cm⁻³, $Z = 2$, $wR2 = 0.0878$ and $R1 = 0.0420$. CCDCs 949222 (2), 949223 (3), and 972035 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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