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Syntheses and X-ray Structures of Monocyclic, Bicyclic, and Spirocyclic Gallium and Indium Boraamidinates

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The reactions of $\{Li_2[PhB(N^tBu)_2]\}_2$ with $GaCl_3$ in various stoichiometries yield $[Li(thf)_4][PhB(\mu\text{-}N^tBu)_2GaCl_2\cdot GaCl_3]$ (**1**), $[PhB(\mu\text{-}N^tBu)_2GaCl]_2$ (**2**), and $\{\mu\text{-}Li(OEt_2)[PhB(N^tBu)_2]Ga\}$ (**3a**), a series of complexes in which the three chloride ligands are successively replaced by the dianion $[PhB(N^tBu)_2]^{2-}$. The X-ray structures of **1**, **2**, and **3a** show that the boraamidinate ligand adopts an *N*,*N′*-chelating mode. In the ion-separated complex **1**, one of the nitrogen atoms is coordinated to a $GaCl_3$ molecule. The related indium complexes $[\mu\text{-}LiCl(thf)_2][PhB(\mu\text{-}N^tBu)_2InCl]_2$ (**4**) and $\{\mu\text{-}Li(OEt_2)[PhB(\mu\text{-}N^tBu)_2]In\}$ (**3b**) were obtained in a similar manner. Complex **4** is the indium analogue of **2** with the incorporation of a bissolvated LiCl molecule. In **3a** and **3b** the spirocyclic $\{[PhB(\mu\text{-}N^tBu)_2]_2M\}^-$ (M = Ga, In) anions are *N*,*N′*-chelated to the $[Li(OEt_2)]^+$ counterion. Prolonged reactions result in the formation of $[PhB(\mu\text{-}N^tBu)_2GaCl][^tBuN(H)GaCl_2]$ (**5**) and $\{[PhB(\mu\text{-}N^tBu)_2InCl][^tBuN(H)InCl_2][\mu\text{-}LiCl(OEt_2)_2]\}$ (**6**), respectively. The X-ray structures of **5** and **6** reveal bicyclic structures which formally involve the entrapment of the monomers $^tBuN(H)MCl_2$ by a four-membered BN_2M ring (M = Ga, In). The synthesis and X-ray structure of $Cl_2Ga[\mu\text{-}N(H)^tBu]_2GaCl_2$ are also reported.

Introduction

Complexes of amidinate anions $[RC(NR')_2]^-$ with main group elements[1a] or transition metals[1a,b] have been studied extensively. Recent work on group 13 systems has revealed novel structural chemistry for In[2] and catalytic activity for cationic Al or Ga complexes.[3] By contrast, previous investigations of the coordination chemistry of the isoelectronic boraamidinate dianion $[RB(NR')_2]^{2-}$ have been limited to group 4 for the transition metals and groups 14−16 in the case of p-block elements.[4] The most common route to aryl boraamidinate complexes has involved the preparation of $\{Li_2[PhB(NR')_2]\}_x$ (R = ^iPr, ^tBu) by dilithiation of $PhB(NHR')_2$ with Li^nBu followed by lithium−halogen exchange with the appropriate transition-metal or main group element halide.[5−7] This approach has also been applied to the pentafluorophenyl derivative $C_6F_5B(\mu\text{-}N^tBu)_2SnMe_2$.[8] More recently we have discovered a potentially versatile route to alkyl or aryl boraamidinates that involves the reaction of trisaminoboranes $B(NHR')_3$ with 3 equiv of an organolithium reagent RLi (R = alkyl, aryl).[9] In addition to effecting dilithiation, the RLi reagents serve as a nucleophile in the displacement of one NHR′ group by the substituent R. The dilithium derivatives $\{Li_2[RB(NR')_2]\}_x$ (R = Me, ^nBu, Ph; R′ = ^tBu) have dimeric ($x = 2$) cluster structures,[7,9] although a trimer ($x = 3$) has also been structurally characterized for R = Me, R′ = ^tBu.[7]

Although the use of the reagents $\{Li_2[RB(NR')_2]\}_x$ in metathetical reactions is the most versatile route to boraamidinate complexes,[5−7] several other synthetic approaches have been reported. These include the preparation of (a) the dimeric Sn(II) complex $[PhB(\mu\text{-}N^tBu)_2Sn]_2$ by the reaction of $SnCl_2$ with $Me_3SiN(Li)BMe_2$,[10] (b) sulfur(II) complexes

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of the type $RB(\mu\text{-}NR')(\mu\text{-}NR'')S$ by treatment of sulfur(IV) diimides with $RB(SMe)_2$,[11] (c) $C_6F_5B(\mu\text{-}N^tBu)_2CPh_2$[12] and $^tBuB(\mu\text{-}N^tBu)_2P^tBu(N^tBu)$[13] by [2 + 2] cycloaddition reactions of the appropriate iminoborane with $^tBuN{=}CPh_2$ or $^tBuN{=}P^tBu$, respectively, (d) $MesB(\mu\text{-}N^tBu)_2Si(Mes)SiMe_3$ by the reaction of the iminoborane $Me_3Si(^tBu)NB{=}N^tBu$ with the photochemically generated silylene $SiMes_2$,[14] (e) $MeB(\mu\text{-}NAr)_2SiMe_2$ (Ar = 2,6-diisopropylphenyl) from the isomerization of $ArN{=}BN(Ar)SiMe_3$ formed by the lithiation of $Ar(H)NB(F)N(R)SiMe_3$ with Li^tBu,[15] and (f) $PhB(\mu\text{-}N^tBu)_2TeN^tBu$ by the reaction of $PhBCl_2$ with $\{Li_2[Te(N^tBu)_3]\}_2$.[16]

In view of the current interest in the catalytic activity of aluminum and gallium amidinates, as well as the potential importance of group 13 complexes of nitrogen-centered ligands as precursors of electronic materials such as gallium nitride, we have initiated an investigation of boraamidinate complexes of group 13 metals. In this paper we describe the synthesis, spectroscopic characterization, and X-ray structures of $[Li(thf)_4][PhB(\mu\text{-}N^tBu)_2GaCl_2{\cdot}GaCl_3]$ (**1**), $[PhB(\mu\text{-}N^tBu)_2GaCl]_2$ (**2**), $[\mu\text{-}Li(OEt_2)\{PhB(\mu\text{-}N^tBu)_2\}_2M]$ (**3a**, M = Ga; **3b**, M = In), and $[\mu\text{-}LiCl(thf)_2][PhB(\mu\text{-}N^tBu)_2InCl]_2$ (**4**), the first boraamidinate complexes of group 13 elements. The spectroscopic and structural characterizations of the novel bicyclic complexes $\{[PhB(\mu\text{-}NBu^t)_2GaCl][^tBuN(H)GaCl_2]\}$ (**5**) and $\{[PhB(\mu\text{-}NBu^t)_2InCl][Bu^tN(H)InCl_2][\mu\text{-}LiCl(OEt_2)_2]\}$ (**6**) and the dimer $Cl_2Ga[\mu\text{-}N(H)^tBu]_2GaCl_2$ (**7**) are also reported.

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled before use: tetrahydrofuran, toluene, *n*-hexane, diethyl ether (all from Na/benzophenone); *n*-pentane (Na). $^tBuNH_2$ (99.5%), ^nBuLi (2.5 M solution in hexanes), $PhBCl_2$ (97%), $GaCl_3$ (99.99%), and $InCl_3$ (99.999%) were commercial samples (Aldrich) and used as received. The reagent $Li_2[PhB(N^tBu)_2]$ was prepared from $PhB(NH^tBu)_2$ and 2 equiv of Li^nBu[7] or by the reaction of $B(NH^tBu)_3$ with 3 equiv of LiPh.[7] The handling of air- and moisture-sensitive reagents was performed under an atmosphere of argon gas using Schlenk techniques or a glovebox.

Instrumentation. ^1H NMR spectra were collected on Bruker AM-200 and Bruker DRX 400 spectrometers operating at 200 and 400 MHz, respectively, and chemical shifts are reported relative to that of Me_4Si in $CDCl_3$. ^{11}B, ^{13}C, ^{71}Ga, and ^7Li NMR spectra were measured at 25 °C in C_6D_6 or C_4D_8O on a Bruker DRX 400 spectrometer using a 5 mm broad-band (BBO) probe operating at 128.336, 100.594, 122.014, and 155.459 MHz, respectively. Chemical shifts are reported relative to those of $BF_3{\cdot}Et_2O$ in C_6D_6, $Ga(NO_3)_3$ in D_2O, and 1.0 M LiCl in D_2O, respectively. FTIR spectra were obtained as Nujol mulls between KBr plates on a Mattson 4030 FTIR or Nicolet Nexus 470 spectrometer in the range 4000−350 cm^{-1}. Elemental analyses and mass spectra were obtained by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of $(thf)_4Li\{[PhB(\mu\text{-}N^tBu)_2GaCl_2]GaCl_3\}$ (1). A colorless solution of $Li_2[PhB(N^tBu)_2]$ (0.541 g, 2.215 mmol) in thf (20 mL) was added to solid $GaCl_3$ (0.780 g, 4.430 mmol) cooled to −78 °C, whereupon a dark purple solution was obtained. The reaction mixture was allowed to reach 23 °C after 30 min, and a colorless solution was obtained after another 30 min. After 3.5 h the volatile materials were removed under vacuum to give a sticky white solid. Et_2O (10 mL) was added, and the pale yellow solution was filtered through a PTFE filter disk into a Schlenk glass tube to remove LiCl. The formation of two phases was observed. The upper colorless phase was removed and discarded. The remaining yellow liquid was transferred into a test tube. Colorless blocklike crystals of **1** (0.764 g, 0.907 mmol, 82% based on $GaCl_3$) were obtained after 7 d at −19 °C. ^1H NMR (C_4D_8O, 23 °C, δ): 7.78−7.15 (m, 5 H, C_6H_5), 3.60 (m, 16 H, CH_2CH_2O), 1.75 (m, 16 H, CH_2CH_2O), 1.25 (s, 18 H, C_4H_9). ^{13}C NMR (C_4D_8O, 23 °C, δ): 134.35, 127.95, 127.34 (C_6H_5), 56.12 (br) (CMe_3), 33.82 (CMe_3). ^{11}B NMR (C_4D_8O, 23 °C, δ): 36.4. ^{71}Ga NMR (C_4D_8O, 23 °C, δ): 247.8 ($\Delta\nu_{1/2}$ = 49 Hz). ^7Li NMR (C_4D_8O, 23 °C, δ): −0.71. Several attempts to obtain CHN analyses gave inconsistent results owing to the loss of thf from the complex.

From a second crystallization colorless platelike crystals of $(thf)_3(Et_2O)\{Li[PhB(N^tBu)_2]GaCl_2{\cdot}GaCl_3\}$ were obtained. ^1H NMR (C_4D_4O, 23 °C, δ): 7.85−7.18 (m, 5 H, C_6H_5), 3.63 (m, 12 H, CH_2CH_2O), 3.36 (q, 4 H, CH_3CH_2O), 1.78 (m, 12 H, CH_2CH_2O), 1.308 (s, 18 H, C_4H_9), 1.11 (t, 6 H, CH_3CH_2O). ^{13}C NMR (C_4D_8O, 23 °C, δ): 134.51, 127.78, 127.29 (C_6H_5), 68.27 (CH_2CH_2O), 66.36 (CH_3CH_2O), 56.05 (CMe_3), 33.88 (CMe_3), 26.43 (CH_2CH_2O), 15.72 (CH_3CH_2O). ^{11}B NMR (C_4D_8O, 23 °C, δ): 37.4. ^{71}Ga NMR: 247.8. ^7Li NMR (C_4D_8O, 23 °C, δ): 0.91.

Preparation of $\{[PhB(\mu\text{-}N^tBu)_2]GaCl\}_2$ (2). A colorless solution of $Li_2[PhB(N^tBu)_2]$ (0.500 g, 2.049 mmol) in thf (20 mL) was added to solid $GaCl_3$ (0.360 g, 2.049 mmol) cooled to −78 °C. The formation of a pink solution was observed. The reaction mixture was allowed to reach 23 °C over a period of 50 min and then stirred for 3 h. The volatile materials were removed under vacuum, and Et_2O (5 mL) was added. The solution was filtered through a syringe filter PTFE disk (pore size 0.45 μm). The solution was concentrated to 3 mL and filtered again, and *n*-pentane was added, whereupon a white microcrystalline precipitate was formed. The solution was stored at −20 °C to give an additional amount of white crystalline solid. The total yield was 0.223 g. The product was a mixture of **2** and $(Et_2O)Li[PhB(\mu\text{-}N^tBu)_2]_2$ (**3**). Attempts to separate the two products through fractional crystallization were unsuccessful. The NMR resonances for **2** were identified by subtraction of those for **3** (vide infra). ^1H NMR (C_4D_8O, 23 °C, δ): 7.5−7.1 (m, C_6H_5), 1.29 (s, C_4H_9). ^{13}C NMR (C_4D_8O, 23 °C, δ): 133.0, 128.8, 128.4 (C_6H_5), 54.1 (CMe_3), 34.4 (CMe_3). ^{11}B NMR (C_4D_8O, 23 °C, δ): 35.0.

Preparation of $(Et_2O)\mu\text{-}Li\{Ga[PhB(\mu\text{-}N^tBu)_2]_2\}_2$ (3a). A colorless solution of $Li_2[PhB(N^tBu)_2]$ (0.500 g, 2.049 mmol) in Et_2O/*n*-hexane (30 mL, 2:1) was added to solid $GaCl_3$ (0.180 g, 1.024 mmol) cooled to −78 °C. An immediate exothermic reaction occurred, and the formation of a dark purple solution was observed. The reaction mixture was allowed to reach 23 °C after 15 min. After 4.5 d the pale yellow solution was filtered through an Acrodisc syringe PTFE filter to remove LiCl. Solvent was removed under

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vacuum to give sticky white crystals. Addition of diethyl ether (5 mL) followed by cooling to −19 °C gave blocklike crystals of **3a** in two crops (0.254 g, 0.371 mmol, 36%). Anal. Calcd for $C_{32}H_{56}B_2GaLiN_4O$: C, 62.91; H, 9.25; N, 9.18. Found: C, 62.28; H, 9.62; N, 9.06. ^{1}H NMR (C_4D_8O, 23 °C, δ): 7.38−6.92 (m, 10 H, C_6H_5), 3.38 (q, 4 H, OCH_2CH_3), 1.11 (t, 6 H, OCH_2CH_3), 1.05 (s, 36 H, C_4H_9). ^{13}C NMR (C_4D_8O, 23 °C, δ): 133.6, 126.5, 124.3 (C_6H_5), 66.3 (OCH_2CH_3), 50.9 (CMe_3), 36.3 (CMe_3), 15.7 (OCH_2CH_3). ^{11}B NMR (C_4D_8O, 23 °C, δ): 32.5. ^{7}Li NMR (C_4D_8O, 23 °C, δ): −0.67.

Preparation of Li(OEt$_2$){PhB(μ-N^{t}Bu)$_2$}$_2$In (3b). The addition of a solution of $Li_2[PhB(N^tBu)_2]$ (1.00 g, 4.10 mmol) in Et_2O (50 mL) to a stirred solution of $InCl_3$ (0.50 g, 2.26 mmol) in Et_2O (50 mL) at −78 °C produced a cloudy, bright pink solution. The reaction mixture was heated at reflux for 18 h, and then the resulting cloudy, yellow solution was filtered to remove LiCl. Concentration (ca. 80 mL) by removal of solvent in vacuo and subsequent cooling (0 °C for 18 h) of the resulting yellow solution yielded colorless crystals of **3b** (0.42 g, 0.73 mmol, 32%). Anal. Calcd for $C_{32}H_{56}B_2InLiN_4O$: C, 58.57; H, 8.60; N, 8.54. Found: C, 58.24; H, 8.96; N, 8.62. ^{1}H NMR (C_6D_6, 23 °C): δ 7.32 (m, 10 H, C_6H_5,), 3.17 (q, 4 H, OCH_2CH_3), 1.31 (s, 36 H, C_4H_9,), 0.89 (t, 6 H, OCH_2CH_3). ^{11}B NMR (C_6D_6, 23 °C): δ 36.0 (br s). ^{7}Li NMR (C_6D_6, 23 °C): δ 0.71 (s).

Preparation of [μ-LiCl(thf)$_2$][PhB(μ-N^{t}Bu)$_2$InCl]$_2$ (4). The addition of a solution of $Li_2[PhB(N^tBu)_2]$ (0.50 g, 2.05 mmol) in thf (50 mL) to solid $InCl_3$ (0.45 g, 2.05 mmol) at −78 °C produced a cloudy, bright pink solution. The reaction mixture was allowed to stir for 3 h at 23 °C, whereupon the solvent was removed in vacuo to give a pale gray residue. This residue was redissolved in Et_2O, and after filtration, a clear yellow filtrate was obtained. Concentration (ca. 30 mL) by removal of solvent in vacuo and subsequent cooling (0 °C for 18 h) of the resulting yellow solution yielded colorless crystals of **4** (1.26 g, 1.40 mmol, 68%). ^{1}H NMR (C_6D_6, 23 °C, δ): 7.51−7.20 (m, 10 H, C_6H_5), 3.55 (m, 8 H, OCH_2CH_2), 1.39 (m, 8 H, OCH_2CH_2), 1.34 (s, 36 H, C_4H_9). ^{13}C NMR (C_6D_6, 23 °C, δ): 132.7, 127.8 (C_6H_5), 67.8 (OCH_2CH_2), 54.75 (br, CMe_3), 35.29 (CMe_3), 25.42 (OCH_2CH_2). ^{11}B NMR (C_6D_6, 23 °C, δ): 35.7. ^{7}Li NMR (C_6D_6, 23 °C, δ): 0.25. Several attempts to obtain CHN analyses gave inconsistent results owing to loss of thf from the complex.

Preparation of {PhB(μ-N^{t}Bu)$_2$GaCl[^{t}BuN(H)]GaCl$_2$} (5). The addition of a solution of $Li_2[PhB(N^tBu)_2]$ (0.500 g, 2.049 mmol) in toluene (10 mL) to a solution of $GaCl_3$ (0.361 g, 2.049 mmol) in toluene (10 mL) at −78 °C produced a colorless solution with small amounts of a white precipitate (LiCl). The reaction mixture was allowed to reach 23 °C very slowly and then heated to 55 °C for 18 h. The completeness of the reaction was monitored by ^{1}H NMR spectroscopy. LiCl was separated by filtration through an Acrodisc syringe filter, and removal of solvent under vacuum produced a sticky white solid. Recrystallization from Et_2O at −19 °C gave **5** (0.392 g, 0.715 mmol, 70% based on $GaCl_3$) as a white solid. ^{1}H NMR (C_4D_8O, 23 °C, δ): 7.86−7.16 (m, 5 H, C_6H_5), 2.29 (s, 1 H, NH), 1.30 (s, 27 H, C_4H_9). ^{13}C NMR (C_4D_8O, 23 °C, δ): 133.6, 133.1, 126.9 (C_6H_5), 56.1 (br) (CMe_3), 35.7 (CMe_3). ^{11}B NMR (C_4D_8O, 23 °C, δ): 37.4. ^{71}Ga NMR (in C_4D_8O, 23 °C, δ): 248.8 ($\Delta\nu_{1/2} = 49$ Hz). Anal. Calcd for $C_{18}H_{33}BCl_3Ga_2N_3$: C, 39.44; H, 6.07; N, 7.67. Found: C, 38.00; H, 6.05; N, 7.07.

Preparation of {[PhB(μ-N^{t}Bu)$_2$InCl][^{t}BuN(H)InCl$_2$][μ-LiCl(OEt$_2$)$_2$]} (6). The addition of a solution of $Li_2[PhB(N^tBu)_2]$ (0.16 g, 0.66 mmol) in Et_2O (15 mL) to a stirred solution of $InCl_3$ (0.15 g, 0.66 mmol) in Et_2O (15 mL) at 23 °C produced a cloudy, pale pink solution. The reaction mixture was allowed to stir for 18 h at 23 °C, whereupon the resulting cloudy, yellow solution was filtered to remove LiCl. Concentration (ca. 15 mL) by removal of solvent in vacuo and subsequent cooling (0 °C for 18 h) of the resulting yellow solution yielded colorless crystals of **6** (0.26 g, 0.31 mmol, 48%). Anal. Calcd for $BC_{26}Cl_4H_{53}In_2LiN_3O_2$: C, 37.67; H, 6.45; N, 5.07. Found: C, 36.68; H, 6.32; N, 5.03. A 1 mL aliquot of the initial Et_2O reaction mixture was pumped to dryness in vacuo and taken up in C_6D_6. ^{1}H NMR (C_6D_6, 23 °C): δ 7.60−7.21 (m, C_6H_5, 5 H), 2.28 (br s, NH), 1.54 (s, C_4H_9), 1.47 (s, C_4H_9), 1.35 (s, C_4H_9). ^{11}B NMR (C_6D_6, 23 °C): δ 31.7 (s). ^{7}Li NMR (C_6D_6, 23 °C): δ −1.48 (s). IR (cm^{-1}): 3217 [ν(N−H)].

Preparation of Cl$_2$Ga[N(H)^{t}Bu]$_2$GaCl$_2$ (7a). A slurry of $Li[N(H)^tBu]$ (0.288 g, 3.640 mmol) in diethyl ether (20 mL) was added to a solution of gallium trichloride (0.641 g, 3.640 mmol) in diethyl ether (30 mL) at −78 °C. The reaction mixture was allowed to reach room temperature, whereupon a white precipitate formed. After 20 h LiCl was removed by filtration through a PTFE syringe filter disk (pore size 0.45 μm). Solvent was removed under vacuum to give **7a** as a white solid (0.678 g, 1.593 mmol, 88%). Anal. Calcd for $C_4H_{10}Cl_2GaN$: C, 22.58; H, 4.74; N, 6.58. Found: C, 22.33; H, 4.78; N, 6.23. NMR data indicated the presence of two isomers (*cis* and *trans*). ^{1}H NMR (C_7D_8, 23 °C): δ 2.46 (s, NH), 2.23 (s, NH), 1.07 (s, C_4H_9), 1.06 (s, C_4H_9). ^{13}C NMR (C_7D_8, 23 °C): 56.8 [s, $C(CH_3)_3$], 56.6 [s, $C(CH_3)_3$], 31.1 [s, $C(CH_3)_3$], 30.7 [s, $C(CH_3)_3$]. IR (cm^{-1}): 3245, 3192 [ν(N−H)]. Recrystallization of the product from diethyl ether at −20 °C gave X-ray-quality crystals of the *trans* isomer.

X-ray Structure Determinations. Single crystals of **1**, **2**, **3a**, **3b**, **4**, **5**, **6**, and **7a** were coated with Paratone 8277 oil (Exxon), mounted onto thin glass fibers or inside a mounted CryoLoop (Hampton Research, diameter of the nylon fiber 20 and 10 μm), and quickly frozen in the cold nitrogen stream of the goniometer. Measurements for **2**, **3a**, **3b**, and **4** were made on a Nonius CCD four-circle Kappa FR540C diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were measured using ϕ and ω scans. Data reduction was performed by using the HKL DENZO and SCALEPACK software.[17] A multiscan absorption correction was applied to the data (SCALEPACK).[17] The X-ray data for **1**, **5**, and **6** were collected on a Bruker AXS Platform/Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). In each case three series of frames were collected at a fixed χ angle of 54.79° and at values for ϕ equal to 0°, 90°, and 180°, respectively. Data reduction was performed by using the SAINT software.[18] An empirical absorption correction was applied (SADABS).[19]

Relevant parameters for the data collections and crystallographic data for **1**, **2**, **3a**, **3b**, **4**, **5**, **6**, and **7a** are summarized in Tables 1 and 2. The structures were solved by direct methods (**2**, **3b**, SIR-92;[20a] **1**, **3a**, **4**, **5**, **6**, **7a**, SIR-97[20b]) and refined by a full-matrix

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(20) (a) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. SIR-92, A package for crystal structure solution by direct methods and refinement. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. *SIR 97, A package for crystal structure solution by direct methods and refinement*; Italy, 1997.

Table 1. Crystallographic Data for **1**, **2**, **3a**, and **3b**

	1	**2**	**3a**	**3b**
empirical formula	$C_{30}H_{55}BCl_5Ga_2LiN_2O_4$	$C_{28}H_{46}B_2Cl_2Ga_2N_4$	$C_{32}H_{56}B_2GaLiN_4O$	$C_{32}H_{56}B_2InLiN_4O$
fw	842.20	670.65	611.09	656.19
space group	$P2_1/c$	$P2_1/c$	Pbcn	$C2/c$
a, Å	13.9213(13)	10.0624(2)	15.7660(5)	11.1322(2)
b, Å	11.6036(11)	13.6143(3)	11.9720(9)	16.7074(3)
c, Å	25.361(2)	12.1416(3)	18.6330(9)	20.3868(4)
β, deg	99.0474(19)	104.3800(10)	90[a]	103.3140(10)
V, Å^3	4045.7(7)	1611.20(6)	3517.0(3)	3689.83(12)
Z	4	2	4	4
T (°C)	−80(2)	−100(2)	−100(2)	−100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.383	1.382	1.154	1.181
μ, cm^{-1}	16.95	18.62	8.11	6.7
R[b]	0.0413	0.0345	0.0549	0.04
R_w[c]	0.1005	0.0912	0.1293	0.115

[a] $\alpha = \beta = \gamma = 90°$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [$I \geq 2.00\sigma(I)$]. [c] $R_w = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

Table 2. Crystallographic Data for **4**, **5**, **6**, and **7a**

	4	**5**	**6**	**7a**
empirical formula	$C_{36}H_{62}B_2Cl_3In_2LiN_4O_2$	$C_{18}H_{33}BCl_3Ga_2N_3$	$C_{26}H_{53}BCl_4In_2LiN_3O_2$	$C_8H_{20}Cl_4Ga_2N_2$
fw	947.45	548.07	828.90	425.50
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	13.5690(2)	13.8474(12)	18.1901(14)	6.4670(2)
b, Å	20.2680(2)	12.4157(11)	10.4585(8)	11.8600(5)
c, Å	20.4090(2)	14.2062(11)	20.3996(15)	10.7420(5)
β, deg	127.7511(5)	91.0080(18)	106.2219(13)	97.3790(14)
V, Å^3	4437.92(9)	2449.0(4)	3726.6(5)	818.80(6)
Z	4	4	4	2
T (°C)	−100(2)	−80(2)	−80(2)	−100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.418	1.491	1.478	1.726
μ, cm^{-1}	12.53	25.43	15.50	39.22
R[a]	0.0482	0.0333	0.0295	0.0392
R_w[b]	0.1249	0.0825	0.0666	0.0976

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [$I \geq 2.00\sigma(I)$]. [b] $R_w = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

least-squares method based on F^2 using SHELXL-97.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C−H bond distances 0.95 Å) and were not refined. The NH protons in **5**, **6**, and **7a** were initially located in the difference Fourier map and then included at geometrically idealized positions (N−H bond distances 0.95 Å) and were not refined. The isotopic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon or nitrogen atom.

Two carbon atoms [labeled as C(73), C(74), C(73′), and C(74′)] in one of the four coordinating thf molecules in **1** were disordered over two sites. The disorder was modeled using the split-atom model, and the carbon atoms were refined using the SAME and SIMU contraints. The partial occupancy factors for these atoms were refined to 0.658(19) and 0.342(19), respectively. From a second crystallization colorless thin-plate crystals of (thf)$_3$-(Et_2O){Li[PhB(μ-N^{t}Bu)$_2$GaCl$_2$(GaCl$_3$)]}, which belong to the space group $P2_1/c$, were obtained. The cell dimensions are $a = 17.1100(4)$ Å, $b = 13.8690(4)$ Å, $c = 13.0020(6)$ Å, $\beta = 113.7170(14)°$, $V = 4128.3(2)$ Å^3, and $Z = 4$. The coordinated thf and Et_2O molecules show severe disorder. The bond distances and bond angles for the [PhB(μ-N^{t}Bu)$_2$GaCl$_2$(GaCl$_3$)]}$^-$ anion are essentially identical to those obtained for the anion in **1**. Therefore, structural data for (thf)$_3$-(Et_2O){Li[PhB(μ-N^{t}Bu)$_2$GaCl$_2$(GaCl$_3$)]} will not be discussed further.

The carbon atoms [labeled as C(31), C(32), C(31′), and C(32′)] of the Et_2O molecule in **3a** were disordered around a 2-fold screw axis with partial occupancy factors of 0.582(15) and 0.418(15), respectively. The SAME and SIMU constraints were used to refine these atoms. A disordered Et_2O molecule was also located on a special position in **3b** with a partial occupancy factor of 0.50. The carbon atoms of this Et_2O molecule could only be refined isotropically, and the isotropic displacement parameters were constrained to be equal for the two CH_3 and two CH_2 carbon atoms, respectively. The O−C and C−C bond distances were restrained to 1.480(5) and 1.500(5) Å. In **4** one of the carbon atoms [C(84), C(84′)] of one of the coordinated thf molecules was disordered over two positions with partial occupancy factors of 0.56(4) and 0.44(4), respectively. The SAME and SIMU constraints were used to refine this atom. The atoms of one of the two Et_2O molecules in **6** were disordered over two sites [labeled as O(2A), C(61A), C(62A), C(63A), C(64A), O(2B), C(61B), C(62B), C(63B), and C(64B)]. The occupancy factors of these atoms were refined initially and then set to 0.60 and 0.40, respectively.

Results and Discussion

Formation and X-ray Structures of Gallium Boraamidinates. The reaction of Li$_2$[PhB(N^{t}Bu)$_2$] with GaCl$_3$ was carried out under a variety of conditions with variations in stoichiometry, solvent, and reaction time. All products were characterized by X-ray crystal structures in addition to their multinuclear (^{1}H, ^{13}C, ^{11}B, and, where appropriate, ^{7}Li and ^{71}Ga) NMR spectra. An interesting feature of these reactions is the formation of intensely colored solutions when the boraamidinate reagent is added to the group 13 metal halide.

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[21] Sheldrick, G. M. *SHELXL97-2*: *Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

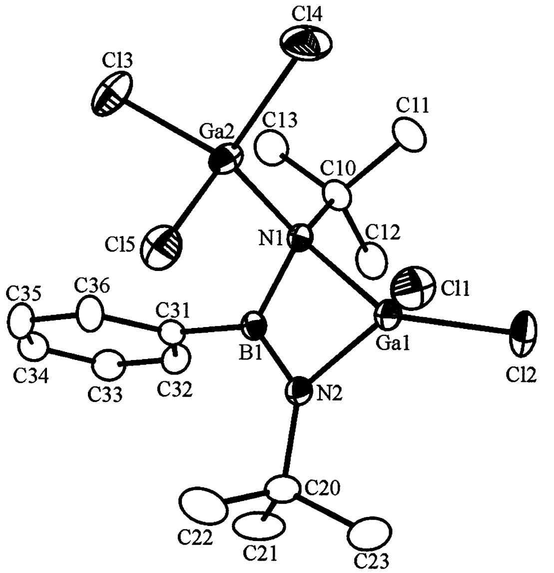
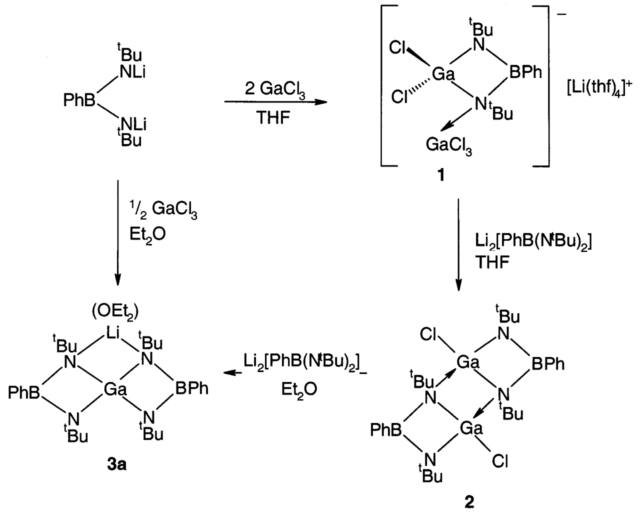


Figure 1. Molecular structure of the anion $[PhB(\mu\text{-}N^tBu)_2GaCl_2\cdot GaCl_3]^-$ in **1**. The cation $[Li(thf)_4]^+$ is not shown.

Scheme 1



The colors, which are more intense in the reaction with $GaCl_3$ (purple) than that with $InCl_3$ (pink), are tentatively attributed to the formation of radicals.[22]

When the reaction of $Li_2[PhB(N^tBu)_2]$ with $GaCl_3$ is carried out in a 1:2 molar ratio in thf, the ion-separated complex $[Li(thf)_4][PhB(\mu\text{-}N^tBu)_2GaCl_2\cdot GaCl_3]$ (**1**) is obtained in 82% yield (Scheme 1). The coordination of the gallate anion $[PhB(\mu\text{-}N^tBu)_2GaCl_2]^-$ to a neutral $GaCl_3$ molecule was established by an X-ray crystal structure of **1** (Figure 1). The ^1H NMR spectrum of **1** in d_8-thf shows resonances corresponding to the Ph and N^tBu groups, as well as the coordinated thf ligands, with the appropriate relative intensities. A singlet is observed at δ -0.71 in the ^7Li NMR spectrum. Surprisingly, only one resonance is observed in the ^{71}Ga NMR spectrum. This observation may indicate dissociation into $[Li(thf)_4][PhB(\mu\text{-}N^tBu)_2GaCl_2]$ and $GaCl_3\cdot$thf in thf solution. The lack of a ^{71}Ga resonance for $GaCl_3\cdot$thf has been attributed to quadrupole broadening.[23] This suggestion is consistent with the equivalence of the two N^tBu environments revealed in the ^1H and ^{13}C NMR spectra.

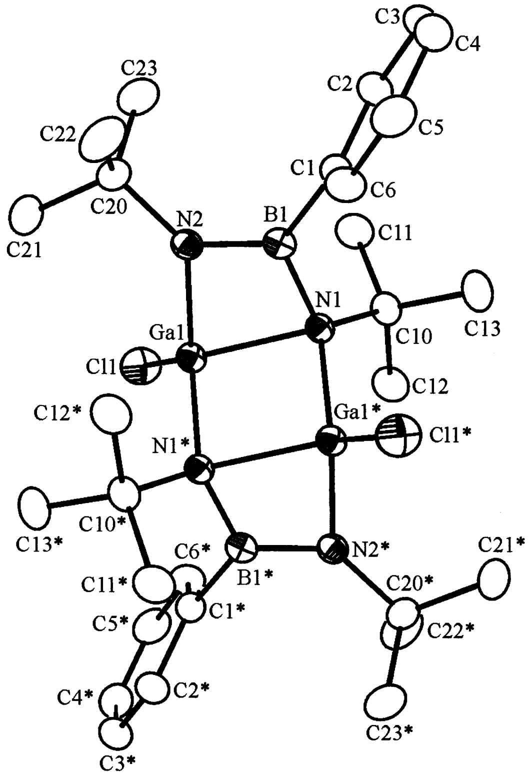


Figure 2. Molecular structure of **2**.

The reaction of $GaCl_3$ with an equimolar amount of $Li_2[PhB(N^tBu)_2]$ in thf produces a mixture of $[PhB(\mu\text{-}N^tBu)_2GaCl]_2$ (**2**) and the spirocyclic complex $[Li\{PhB(\mu\text{-}N^tBu)_2\}_2Ga]$ (vide infra). As a result of the similar solubilities of these two products it was not possible to isolate a pure sample of **2** from this route. Crystals of **2** suitable for X-ray analysis were obtained, however, from the reaction of **1** with $Li_2[PhB(N^tBu)_2]$. The dimeric structure of **2** (Figure 2) is comparable to those of the previously reported tin(II)[10] and lead(II)[5a] boraamidinates.

When the stoichiometry of the reaction of $Li_2[PhB(N^tBu)_2]$ with $GaCl_3$ is changed to 2:1, the spirocyclic compound $[Li(OEt_2)\{PhB(\mu\text{-}N^tBu)_2\}_2Ga]$ (**3a**) is obtained in 20% yield. The X-ray structural analysis of **3a** (Figure 3) showed that the spirocyclic anion $[\{PhB(\mu\text{-}N^tBu)_2\}_2Ga]^-$ is *N*,*N*′-chelated to a monosolvated lithium cation.[24] This anion and the indium analogue in **3b** are isoelectronic with the corresponding neutral spirocyclic Ge(IV) and Sn(IV) derivatives, respectively.[5b] Since **3a** and **3b** are isostructural, only the molecular structure of **3a** is shown in Figure 3. The ^1H NMR spectra of **3a** and **3b** in d_8-thf show resonances for the Ph and N^tBu groups, in addition to the coordinated OEt_2 ligand, with the

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[22] Detailed EPR investigations of the radicals formed from $\{Li_2[PhB(N^tBu)_2]\}_2$ upon air oxidation and in reactions with main group element halides are in progress. Boeré, R. T.; Chivers, T.; Fedorchuk, C.; Schatte, G. Unpublished observations.

[23] The ^{71}Ga resonance for a thf solution of $GaCl_3$ has a half-width of 19000 Hz. Böck, S.; Nöth, H.; Wietelmann, A. *Z. Naturforsch.* **1990**, *45b*, 979.

[24] The first spirogallane $[Li(thf)\cdot 12\text{-crown-}4][PhC{=}\overline{CPhPhC}{=}CPh]_2$. It is a solvent-separated ion pair with Ga−C bonds. Su, J.; Goodwin, S. D.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 12994.

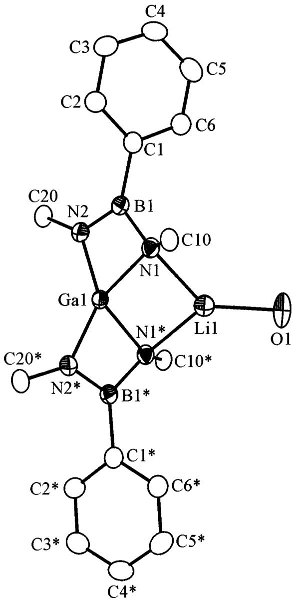


Figure 3. Molecular structure of **3a**. For clarity, only the α-carbon atoms of ^{t}Bu groups and the O atoms of Et_2O ligands are shown.

appropriate relative intensities. The equivalence of all four N^{t}Bu environments in **3a** and **3b** indicated by the ^{1}H and ^{13}C NMR spectra at 23 °C suggest the occurrence of an exchange process in which the chelation of Li^+ changes rapidly from N(1)/N(1)* to N(2)/N(2)*. Such fluxional processes in lithium derivatives of polyimido anions of p-block elements have low activation energies.[25] Singlets are observed in the ^{7}Li NMR spectra of **3a** and **3b** at δ 0.40 and 0.71, respectively.

In summary, a series of gallium boraamidinates in which each of the three chlorides attached to gallium is replaced successively by the dianionic $[PhB(N^tBu)_2]^{2-}$ ligand may be prepared by varying the stoichiometry of the reaction of $Li_2[PhB(N^tBu)_2]$ and $GaCl_3$.

Formation and X-ray Structures of Indium Boraamidinates. As indicated in Scheme 2, indium analogues of **2** and **3a** are obtained from the reaction of $Li_2[PhB(N^tBu)]_2$ and $InCl_3$. When equimolar amounts of these two reagents are allowed to react in thf, the complex $[\mu\text{-}LiCl(thf)_2][PhB(\mu\text{-}N^tBu)_2InCl]_2$ (**4**) is isolated in 68% yield. Complex **4** can be viewed as the indium analogue of the dimeric gallium system **2** with the incorporation of a bissolvated lithium chloride molecule in the indium complex (Figure 4). The ^{1}H NMR spectra of **3** in d_6-benzene show resonances for the Ph and N^{t}Bu groups, in addition to the coordinated thf ligand, with the expected intensities. As in the case of **2** the apparent equivalence of the N^{t}Bu environments may indicate the formation of a solvated monomer in thf solution. A singlet is observed in the ^{7}Li NMR spectrum at δ 0.25.

When the reaction of $Li_2[PhB(N^tBu)_2]$ and $InCl_3$ is carried out in a 2:1 molar ratio in boiling diethyl ether, the spirocyclic complex **3b**, the indium analogue of **3a**, is isolated in 32% yield.

Formation of the Bicyclic Complexes 5 and 6. The bicyclic complexes $[PhB(\mu\text{-}N^tBu)_2GaCl][{}^tBuN(H)GaCl_2]$ (**5**)

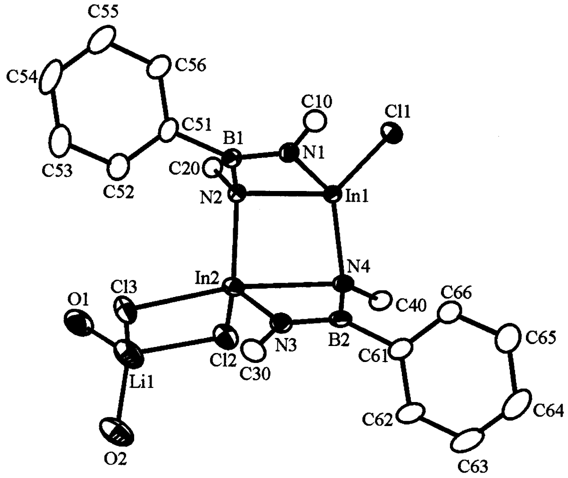
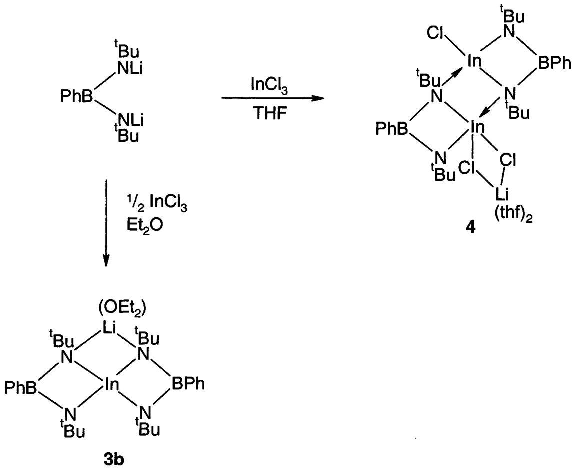


Figure 4. Molecular structure of **4**. For clarity, only the α-carbon atoms of ^{t}Bu groups and the O atoms of thf ligands are shown.

Scheme 2



and $\{[PhB(\mu\text{-}N^tBu)_2InCl][{}^tBuN(H)InCl_2][\mu\text{-}LiCl(OEt_2)_2]$ (**6**) were obtained from the reaction of $Li_2[PhB(N^tBu)_2]$ (prepared from $B(NH^tBu)_3$ and PhLi) with $GaCl_3$ or $InCl_3$ in a 1:1 molar ratio when long reaction times (ca. 18 h) were employed. Apart from the incorporation of the bissolvated LiCl molecule in **6**, these two complexes have the same bicyclic framework, which is formally comprised of a ${}^{t}BuN(H)ECl_2$ (E = Ga, In) monomer coordinated to the four-membered rings $PhB(\mu\text{-}N^tBu)_2ECl$ as depicted in Figures 5 and 6. *tert*-Butylamidolithium is a byproduct in the preparation of $Li_2[PhB(N^tBu)_2]$ from $B(NH^tBu)_3$ and 3 equiv of PhLi.[7] Thus, it is conceivable that $[{}^tBuN(H)ECl_2]_n$ could be generated in situ from the reaction of ECl_3 with $LiN(H)^tBu$ impurity present in the boraamidinate reagent. The subsequent reaction of $[{}^tBuN(H)ECl_2]_n$ (E = Ga, In) with **2** or **4** may generate **5** or **6**, respectively.

We have prepared $Cl_2Ga[N(H)R]_2GaCl_2$ (**7a**, R = ^{t}Bu) by the reaction of $GaCl_3$ with $LiN(H)^tBu$ in thf. However, attempts to make the indium analogue of **7a** by a similar method gave a mixture of products that could not be separated. The dimeric trimethylsilylamido derivative **7b** (R = $SiMe_3$) has been structurally characterized as the *trans* isomer.[25] In C_7D_8 solution, however, ^{1}H NMR spectra revealed that **7b** consists of a mixture of *cis* and *trans* dimers

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(25) Brask, J. K.; Chivers, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3960.

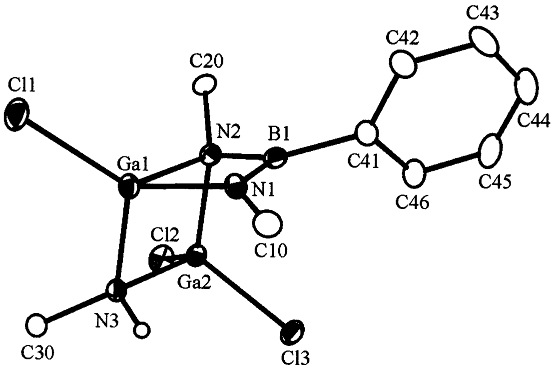


Figure 5. Molecular structure of **5**. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

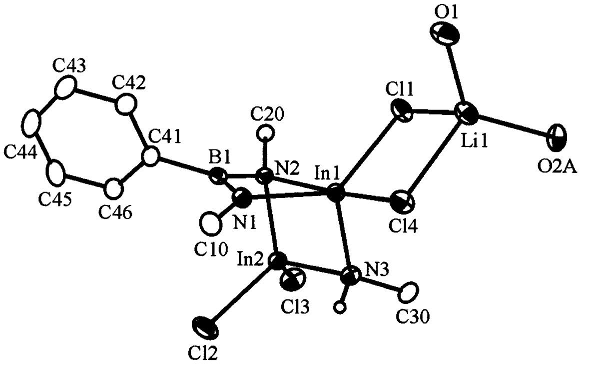


Figure 6. Molecular structure of **6**. For clarity, only the α-carbon atoms of ^{t}Bu groups and the O atoms of OEt_2 ligands are shown.

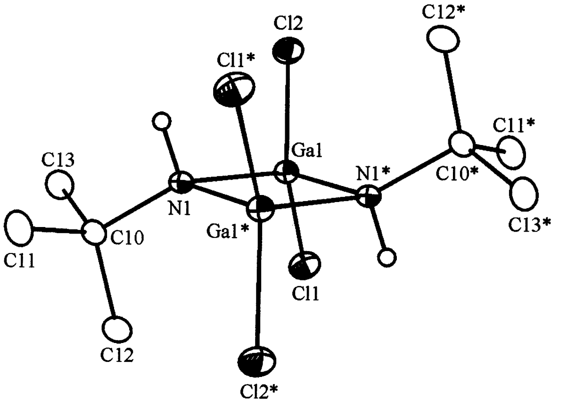


Figure 7. Molecular structure of **7a**.

in equilibrium with a trimer.[26] By contrast, the ^{1}H and ^{13}C NMR of **7a** indicate a mixture of *cis* and *trans* isomers in C_7D_8, but no resonances for the corresponding trimer are observed. Recrystallization of **7a** from toluene or diethyl ether produced the pure *trans* isomer as established by an X-ray structure (Figure 7). The bond lengths and bond angles for **7a** and **7b** are compared in Table 8.

In view of the close similarity of the structural parameters for these two derivatives, further discussion is not warranted. It is noted, however, that the mean Ga−N and Ga−Cl distances in the mesityl derivative **7c** (R = Mes) are ca. 0.03 and 0.08 Å longer than those in **7a** and **7b**,[27] presumably as a result of a combination of steric and electronic factors.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

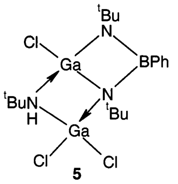
Ga(1)−N(2)	1.880(2)	N(1)−B(1)	1.565(4)
Ga(1)−N(1)	2.048(2)	N(2)−B(1)	1.377(4)
Ga(1)−Cl(1)	2.1718(10)	C(31)−B(1)	1.592(4)
Ga(1)−Cl(2)	2.1834(9)	O(1)−Li(1)	1.911(7)
Ga(2)−N(1)	1.966(2)	O(2)−Li(1)	1.923(6)
Ga(2)−Cl(4)	2.1792(10)	O(3)−Li(1)	1.913(6)
Ga(2)−Cl(3)	2.1875(9)	O(4)−Li(1)	1.921(7)
Ga(2)−Cl(5)	2.1876(10)		
N(2)−Ga(1)−N(1)	74.13(9)	C(10)−N(1)−B(1)	115.8(2)
N(2)−Ga(1)−Cl(1)	122.77(8)	C(10)−N(1)−Ga(2)	116.00(17)
N(1)−Ga(1)−Cl(1)	118.51(7)	B(1)−N(1)−Ga(2)	110.75(17)
N(2)−Ga(1)−Cl(2)	117.48(8)	C(10)−N(1)−Ga(1)	116.23(17)
N(1)−Ga(1)−Cl(2)	120.70(7)	B(1)−N(1)−Ga(1)	83.37(15)
Cl(1)−Ga(1)−Cl(2)	102.82(4)	Ga(2)−N(1)−Ga(1)	110.37(11)
N(1)−Ga(2)−Cl(4)	112.88(7)	B(1)−N(2)−C(20)	133.5(2)
N(1)−Ga(2)−Cl(3)	118.45(7)	B(1)−N(2)−Ga(1)	95.23(18)
Cl(4)−Ga(2)−Cl(3)	105.27(4)	C(20)−N(2)−Ga(1)	130.97(19)
N(1)−Ga(2)−Cl(5)	106.65(7)	N(2)−B(1)−N(1)	107.2(2)
Cl(4)−Ga(2)−Cl(5)	108.79(4)	N(2)−B(1)−C(31)	129.1(3)
Cl(3)−Ga(2)−Cl(5)	104.20(4)	N(1)−B(1)−C(31)	123.6(2)

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**

Ga(1)−N(2)	1.8967(19)	N(1)−B(1)	1.552(3)
Ga(1)−N(1)[a]	1.9657(18)	N(2)−B(1)	1.394(3)
Ga(1)−N(1)	2.0421(18)		
Ga(1)−Cl(1)	2.1554(7)		
N(2)−Ga(1)−N(1)[a]	118.73(8)	B(1)−N(2)−C(20)	131.9(2)
N(2)−Ga(1)−N(1)	74.11(8)	B(1)−N(2)−Ga(1)	94.10(15)
N(1)[a]−Ga(1)−N(1)	89.92(7)	C(20)−N(2)−Ga(1)	133.81(15)
N(2)−Ga(1)−Cl(1)	118.99(6)	N(1)−B(1)−C(1)	125.1(2)
N(1)[a]−Ga(1)−Cl(1)	117.89(6)	N(2)−B(1)−C(1)	127.3(2)
N(1)−Ga(1)−Cl(1)	126.29(6)	N(2)−B(1)−N(1)	107.42(19)
C(10)−N(1)−B(1)	115.72(18)		
C(10)−N(1)−Ga(1)	123.54(14)		
B(1)−N(1)−Ga(1)	84.03(13)		
Ga(1)[a]−N(1)−Ga(1)	90.08(7)		

[a] Symmetry transformations used to generate equivalent atoms: $*-x$, $-y + 1$, $-z$.

In view of the difficulties of obtaining pure **2** (vide supra), we were unable to determine whether the reaction of **2** with **7a** is a viable source of **5**. As an alternative, we carried out the reaction of an equimolar mixture of Li[N(H)^{t}Bu] and $Li_2[PhB(N^{t}Bu)_2]$ with 2 equiv of $GaCl_3$. Fractional crystallization of the mixture of products from diethyl ether at −20 °C led to the isolation of colorless crystals of **2** after 2 d. Complex **2** was identified by determination of unit cell constants. After an additional 20 d, blocklike crystals were obtained and identified as pure **5** by XRD (cell constants) and by ^{1}H and ^{13}C NMR spectra.



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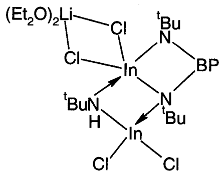

6

Structural Trends for Boraamidinate Complexes of Gallium and Indium. Selected bond lengths and bond angles for the individual boraamidinate complexes **1**, **2**, **3a**, **3b**, **4**, **5**, and **6** are summarized in Tables 3−7. In the discussion of these structures the focus will be on general trends within

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(26) Nult, W. R.; Anderson, J. A.; Odom, J. D.; Williamson, M. M.; Rubin, B. H. *Inorg. Chem.* **1985**, *24*, 159.

(27) Kopp, M. R.; Kräuter, T.; Dashti-Mommertz, A.; Neumüller, B. *Z. Naturforsch.* **1999**, *54b*, 627.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **3a** and **3b**

	3a (M = Ga)	**3b** (M = In)		**3a** (M = Ga)	**3b** (M = In)
M(1)−N(1)	1.974(3)	2.195(2)	Li(1)−N(1)	2.101(7)	2.109(4)
M(1)−N(2)	1.887(3)	2.069(2)	Li(1)−O(1)	1.926(10)	1.885(8)
B(1)−N(1)	1.491(5)	1.472(3)			
B(1)−N(2)	1.423(5)	1.424(4)			
N(2)[a]−M(1)−N(2)	140.92(19)	157.51(13)	B(1)−N(2)−C(20)	135.1(4)	135.0(2)
N(2)[a]−M(1)−N(1)	131.31(14)	128.70(8)	B(1)−N(2)−M(1)	91.3(2)	93.20(15)
N(2)−M(1)−N(1)	75.07(13)	68.28(8)	C(20)−N(2)−M(1)	133.4(3)	131.56(18)
N(1)−M(1)−N(1)[a]	106.01(18)	98.31(10)	N(2)−B(1)−N(1)	107.7(4)	111.6(2)
C(10)−N(1)−B(1)	122.5(3)	121.8(2)	N(2)−B(1)−C(1)	125.9(4)	125.3(2)
C(10)−N(1)−M(1)	131.5(3)	127.52(18)	N(1)−B(1)−C(1)	126.4(4)	123.3(2)
B(1)−N(1)−M(1)	86.0(2)	86.93(14)	O(1)−Li(1)−N(1)	131.4(2)	128.09(15)
C(10)−N(1)−Li(1)	104.2(3)	107.15(17)	N(1)[a]−Li(1)−N(1)	97.3(4)	103.8(3)
B(1)−N(1)−Li(1)	128.0(3)	126.58(17)			
M(1)−N(1)−Li(1)	78.4(2)	78.93(15)			

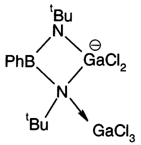
[a] Symmetry transformations used to generate equivalent atoms: $*-x+1, y, -z+{}^1/_2$ (**3a**); $-x+1, y, -z+{}^3/_2$ (**3b**).

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

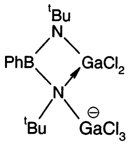
In(1)−N(1)	2.105(3)	N(1)−B(1)	1.393(5)
In(1)−N(2)	2.243(3)	N(2)−B(1)	1.538(5)
In(1)−N(4)	2.114(3)	N(3)−B(2)	1.404(5)
In(1)−Cl(1)	2.3730(10)	N(4)−B(2)	1.497(5)
In(2)−N(2)	2.191(3)	Cl(2)−Li(1)	2.417(11)
In(2)−N(3)	2.099(3)	Cl(3)−Li(1)	2.345(10)
In(2)−N(4)	2.566(3)	O(1)−Li(1)	1.925(13)
In(2)−Cl(2)	2.4550(11)	O(2)−Li(1)	1.913(12)
In(2)−Cl(3)	2.5408(12)		
N(1)−In(1)−N(4)	124.01(2)	B(2)−N(3)−C(30)	131.5(3)
N(1)−In(1)−N(2)	67.07(11)	B(2)−N(3)−In(2)	103.7(2)
N(4)−In(1)−N(2)	96.61(12)	C(30)−N(3)−In(2)	124.8(3)
N(1)−In(1)−Cl(1)	113.28(9)	B(2)−N(4)−C(40)	121.3(3)
N(4)−In(1)−Cl(1)	119.74(9)	B(2)−N(4)−In(1)	112.0(2)
N(2)−In(1)−Cl(1)	122.87(8)	C(40)−N(4)−In(1)	117.4(2)
N(3)−In(2)−N(2)	112.20(12)	B(2)−N(4)−In(2)	82.1(2)
N(3)−In(2)−Cl(2)	121.20(9)	C(40)−N(4)−In(2)	131.0(3)
N(2)−In(2)−Cl(2)	118.88(8)	In(1)−N(4)−In(2)	84.47(10)
N(3)−In(2)−Cl(3)	109.39(9)	N(1)−B(1)−N(2)	110.2(3)
N(2)−In(2)−Cl(3)	104.45(8)	N(1)−B(1)−C(51)	126.7(3)
Cl(2)−In(2)−Cl(3)	84.64(4)	N(2)−B(1)−C(51)	123.1(3)
N(3)−In(2)−N(4)	61.20(11)	N(3)−B(2)−N(4)	112.2(3)
N(2)−In(2)−N(4)	85.94(10)	N(3)−B(2)−C(61)	126.5(4)
Cl(2)−In(2)−N(4)	94.75(7)	N(4)−B(2)−C(61)	121.3(3)
Cl(3)−In(2)−N(4)	168.49(7)	O(2)−Li(1)−O(1)	110.1(5)
Li(1)−Cl(2)−In(2)	92.9(2)	O(2)−Li(1)−Cl(3)	111.3(5)
Li(1)−Cl(3)−In(2)	92.5(3)	O(1)−Li(1)−Cl(3)	112.2(5)
B(1)−N(1)−C(10)	134.5(3)	O(2)−Li(1)−Cl(2)	108.7(6)
B(1)−N(1)−In(1)	96.0(2)	O(1)−Li(1)−Cl(2)	123.0(5)
C(10)−N(1)−In(1)	129.3(2)	Cl(3)−Li(1)−Cl(2)	89.9(3)
C(20)−N(2)−B(1)	117.8(3)		
C(20)−N(2)−In(2)	118.3(2)		
B(1)−N(2)−In(2)	115.1(2)		
C(20)−N(2)−In(1)	121.2(2)		
B(1)−N(2)−In(1)	86.5(2)		
In(2)−N(2)−In(1)	91.02(10)		

this series of closely related group 13 complexes. In addition, the significant features of individual structures will be addressed.

The boron atom in all these boraamidinate complexes adopts a trigonal planar geometry (Σ−B = 360.0 ± 0.2°) with bond angles −N−B−N in the range 106.5−110.2°. Consistently their ^{11}B NMR chemical shifts all fall within a narrow range (δ 32−36). As indicated in Table 9 there is a significant difference in the two B−N bond distances in the planar, four-membered BN_2M (M = Ga, In) rings, ranging from ca. 0.05 to 0.19 Å. This disparity, which is also observed for $[Pb(\mu\text{-N}^tBu)_2BPh]_2$,[5a] can be related to the different coordination numbers of the two nitrogen atoms in these dimeric complexes or, in the case of **1**, to the coordination of one N atom to a $GaCl_3$ molecule. The B−N bonds involving 3-coordinate nitrogen atoms are consistently shorter than those involving 4-coordinate nitrogen atoms. Consistently we note that the B−N bond distances are approximately equal in the monomers $PhB(\mu\text{-N}^tBu)_2TeN^tBu$[16] and $PhB(\mu\text{-N}^tBu)_2PBr$,[7] in which both nitrogen atoms are 3-coordinate. The Ga−Cl bond lengths in **1** fall within the narrow range 2.172(1)−2.188 (1) Å (Table 3). These values are typical for 4-coordinate Ga complexes.[28] Interestingly, the endocyclic Ga−N bond involving the 4-coordinate N(1) atom is ca. 0.07 Å longer than the exocyclic Ga(2)−N(1) bond, suggesting contributions from both resonance forms **1A** and **1B** to the overall structure.



1A



1B

The central Ga_2N_2 ring in the step-shaped dimer **2** (Figure 2 and Table 4) is planar with unequal Ga−N distances of 1.966 and 2.042 Å (cf. 2.001 and 2.054 Å for the related dimer $[Me_2Si(\mu\text{-N}^tBu)_2GaCl]_2$).[29] The Ga−N distance of 1.897 Å involving the 3-coordinate nitrogen atom [N(1)] is significantly shorter than the mean value of 2.004 Å for the Ga−(λ^4)N bonds. The Ga−Cl bond length of 2.155 Å in **2** is similar to the reported literature values for *d*(Ga−Cl) in complexes with 4-coordinate gallium in a N_3Cl environment.[29,30] The distorted tetrahedral geometry at gallium involves bond angles in the range 74.1−126.3° with −N−Ga−N = 74.1° and 89.9° in the four-membered GaN_2B and Ga_2N_2 rings, respectively.

Complex **4** can be viewed as the indium analogue of **2** in which one In−Cl unit has trapped a bissolvated LiCl molecule (Figure 4 and Table 6). As expected the mean In−

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Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) for **5** and **6**

	5 (M = Ga)	**6** (M = In)		**5** (M = Ga)	**6** (M = In)
B(1)−N(1)	1.395(4)	1.401(4)	M(1)−Cl(1)	2.1437(8)	2.4450(8)
B(1)−N(2)	1.563(4)	1.508(4)	M(1)−Cl(4)		2.4973(7)
B(1)−C(41)	1.586(5)	1.599(4)	M(2)−Cl(2)	2.1619(8)	2.3643(9)
M(1)−N(1)	1.879(2)	2.100(2)	M(2)−Cl(3)	2.1776(8)	2.3800(8)
M(1)−N(2)	2.035(2)	2.457(2)	Li(1)−Cl(1)		2.425(5)
M(1)−N(3)	1.978(2)	2.208(2)	Li(1)−Cl(4)		2.389(5)
M(2)−N(2)	1.973(2)	2.137(2)	Li(1)−O(1)		1.929(6)
M(2)−N(3)	1.995(2)	2.179(2)	Li(1)−O(2A)		2.029(10)
N(1)−M(1)−N(3)	108.42(10)	102.88(9)	B(1)−N(1)−C(10)	133.9(2)	132.3(2)
N(1)−M(1)−N(2)	74.49(10)	62.81(8)	B(1)−N(1)−M(1)	94.78(18)	100.77(17)
N(3)−M(1)−N(2)	89.78(9)	83.63(8)	C(10)−N(1)−M(1)	130.37(19)	126.86(18)
N(1)−M(1)−Cl(1)	124.81(8)	133.73(7)	C(20)−N(2)−B(1)	119.5(2)	122.9(2)
N(3)−M(1)−Cl(1)	119.97(7)	115.83(6)	C(20)−N(2)−M(2)	120.00(17)	129.80(16)
N(2)−M(1)−Cl(1)	127.12(7)	96.17(5)	B(1)−N(2)−M(2)	110.69(16)	106.89(17)
N(1)−M(1)−Cl(4)		107.42(6)	C(20)−N(2)−M(1)	125.25(18)	120.80(16)
N(3)−M(1)−Cl(4)		105.02(6)	B(1)−N(2)−M(1)	83.97(16)	106.89(17)
Cl(1)−M(1)−Cl(4)		86.77(2)	M(2)−N(2)−M(1)	89.05(9)	88.30(8)
N(2)−M(2)−N(3)	91.10(9)	83.63(8)	C(30)−N(3)−Ga(1)	123.95(17)	123.63(19)
N(2)−M(2)−Cl(2)	120.59(7)	115.56(6)	C(30)−N(3)−Ga(2)	124.50(17)	121.26(17)
N(3)−M(2)−Cl(2)	116.06(7)	106.07(7)	Ga(1)−N(3)−Ga(2)	90.03(9)	93.97(9)
N(2)−M(2)−Cl(3)	114.46(7)	121.85(6)	N(1)−B(1)−N(2)	106.5(3)	110.7(2)
N(3)−M(2)−Cl(3)	105.72(7)	116.80(6)	N(1)−B(1)−C(41)	128.8(3)	125.0(2)
Cl(2)−M(2)−Cl(3)	107.47(3)	103.52(3)	N(2)−B(1)−C(41)	124.7(2)	124.2(2)

Table 8. Bond Lengths (Å) and Bond Angles (deg) for **7a** and **7b**

	7a	**7b**[a]		**7a**	**7b**[a]
Ga(1)−N(1)	1.976(3)	1.974(4)	Ga(1)−Cl(1)	2.1605(9)	2.150(2)
Ga(1)−N(1)	1.979(3)	1.964(4)	Ga(1)−Cl(2)	2.1439(11)	2.136(2)
N(1)−Ga(1)−N(1)	86.79(12)	89.0(1)			
N(1)−Ga(1)−Cl(2)	110.37(9)	111.7(1)	N(1)−Ga(1)−Cl(1)	109.91(8)	110.8(1)
N(1)−Ga(1)−Cl(2)	118.75(9)	116.0(1)	Cl(2)−Ga(1)−Cl(1)	110.26(5)	111.9(1)
N(1)−Ga(1)−Cl(1)	119.47(8)	115.8(1)	Ga(1)−N(1)−Ga(1)	93.21(12)	91.0(1)

[a] Data taken from ref 25.

Table 9. B−N Bond Lengths (Å) in Complexes of the Boraamidinate Ligand $[PhB(N^tBu)_2]^{2-}$

complex	d(B−N)	Δ[a]	ref
1	1.377, 1.565	0.188	this work
2	1.394, 1.552	0.158	this work
3a	1.423, 1.491	0.068	this work
3b	1.424, 1.472	0.048	this work
4	1.404, 1.538	0.134	this work
5	1.395, 1.563	0.168	this work
6	1.401, 1.508	0.107	this work
$\{Pb[(\mu\text{-}N^tBu)_2BPh]_2\}_2$	1.393(10), 1.498(8)	0.105	5a
$\{Sn[(\mu\text{-}N^tBu)_2BPh]_2\}_2$	1.422(24), 1.484(27)	0.062	10
$Cp_2Ti[(\mu\text{-}N^tBu)_2BPh]$	1.453(9), 1.475(10)	0.022	5b
$BrP[(\mu\text{-}N^tBu)_2BPh]$	1.440(4), 1.440(4)	0	7
$S[(\mu\text{-}N^tBu)_2BPh]$	1.439(2), 1.439(2)	0	11a
$Te[(\mu\text{-}N^tBu)_2BPh]_2$[b]	1.413(8), 1.448(5)	0.035	6
$[Cl_2Te[(\mu\text{-}N^tBu)_2BPh]]_2$[c]	1.447(3), 1.447(3)	0	7

[a] Difference (Å) between short and long B−N bonds. [b] All N atoms are 3-coordinate in this spirocyclic complex with *pseudo*-tbp geometry. The shorter B−N bonds involve the N atoms in the axial positions, i.e., the longer Te−N bonds. [c] This complex dimerizes through weak Te···Cl interactions. All N atoms are 3-coordinate.

Cl bond lengths involving the 5-coordinate indium atom are longer (by ca. 0.13 Å) than that involving the 4-coordinate indium atom (cf. $d(\lambda^5)$In−Cl = 2.405(1) Å in the formamidinate complex $[HC(\mu\text{-}NCy)_2InCl]_2$).[2a] The In−N bonds follow the trend of increasing bond length as the coordination number of N and/or In increases. However, the value of 2.566(3) Å for In(2)−N(4) is exceptionally long, even allowing for the fact that this bond occupies one of the axial positions of a tbp (cf. $|d(\text{In−N})|$ = 2.237 Å for the axial bonds in $[HC(\mu\text{-}NCy)_2InCl]_2$).[2a] The geometry at In(2) is distorted trigonal bipyramidal (tbp) with a bond angle −Cl(3)−In(2)−N(4) = 168.49(7)° and $\sum$−In(2) = 352.3° for the equatorial−equatorial bond angles. The values of the bond angles −N−In−N in the four-membered InN_2B rings are ca. 61.2° and 67.1° for 5-coordinate and 4-coordinate indium, respectively.

In contrast to their neutral, isoelectronic Ge(IV) and Sn(IV) analogues, the spirocyclic structures in **3a** and **3b** are distorted by *N*,*N*′-chelation of the anion to the monosolvated Li^+ counterion (Figure 3). The bond angles at the central group 13 element deviate markedly from tetrahedral [ranges ca. 75−141° (**3a**) and ca. 68−157.5° (**3b**)] (Table 5). As expected, there are significant differences in M−N distances involving the 3- and 4-coordinate nitrogen atom [0.09 Å (M = Ga) and 0.13 Å (M = In)].

The final pair of complexes **5** and **6** have closely related bicyclic structures, which formally involve the entrapment of a monomeric $^tBuN(H)MCl_2$ unit by a BN_2M (M = Ga, In) four-membered ring (Figures 5 and 6). The fold angles between the two four-membered rings in **5** and **6** are 70.36(8)° and 74.11(7)°, respectively. In the indium complex **6** the InCl unit is coordinated to a bissolvated LiCl molecule.[31] This gives rise to a 5-coordinate geometry at In(1) similar to that described for In(2) in **4**. Thus, the bond angle N(20)−In(1)−Cl(1) = 168.6°, and the sum of the bond angles in the trigonal plane is 352.4° (Table 5). The geometry at the 4-coordinate indium atom In(2) is distorted tetrahedral with bond angles in the range 92.4−121.9°. The In−Cl distances for In(2) are ca. 0.07 Å shorter than those involving In(1).

The most significant feature of the structure of **6** is the long transannular In(1)−N(2) bond, 2.457(2) Å. The weakness of this interaction is highlighted by the observation that this bond is 0.25 Å longer than the other bond [In(1)−N(3)] involving 5-coordinate indium and 4-coordinate nitrogen. A similar, but much less pronounced, trend is observed for **5** in which the transannular Ga(2)−N(2) bond is significantly longer than the other Ga−N bonds, 2.035(2) Å vs 1.879(2)−1.995(2) Å. In **5**, however, both gallium atoms are 4-coordinate with bond angles in the ranges 74.5−127° [Ga(1)] and 91−120.6° [Ga(2)] and typical Ga−Cl bond lengths.

Conclusions

The chloride substituents in MCl_3 (M = Ga, In) can be successively replaced by an *N*,*N′*-chelating boraamidinate ligand via metathetical reactions. The complexes with M−Cl functionalities, e.g., **2** and **4**, are suitable precursors for alkyl derivatives with Lewis acidic centers. The Lewis base properties of the BN_2Ga ring toward $GaCl_3$ in **1** may be significant in future studies of the catalytic behavior of group 13 boraamidinates. The oxidation of the spirocyclic anions in **3a** and **3b** to the corresponding neutral radicals is an intriguing possibility that is being pursued.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **2**, **3a**, **3b**, **4**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) For recent examples of the entrapment of LiCl by amidinate complexes, see: Chivers, T.; Downard, A.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 4347.