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Article

Synthetic and Structural Investigations of Monomeric Dilithium Boraamidinates and Bidentate NBNCN Ligands with Bulky N-Bonded Groups

T. Chivers,* C. Fedorchuk, and M. Parvez

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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The dilithiated boraamidinate complexes $[Li_2\{PhB(NDipp)_2\}(THF)_3]$ (**7a**) (Dipp = 2,6-diisopropylphenyl) and $[Li_2\{PhB(NDipp)(N^tBu)\}(OEt_2)_2]$ (**7b**), prepared by reaction of PhB[N(H)Dipp][N(H)R′] (**6a**, R′ = Dipp; **6b**, R′ = ^{t}Bu) with 2 equiv of ^{n}BuLi, are shown by X-ray crystallography to have monomeric structures with two terminal and one bridging THF ligands (**7a**) or two terminal OEt_2 ligands (**7b**). The derivative **7a** is used to prepare the spirocyclic group 13 derivative $[Li(OEt_2)_4][In\{PhB(NDipp)_2\}_2]$ (**8a**) that is shown by an X-ray structural analysis to be a solvent-separated ion pair. The monoamino derivative PhBCl[N(H)Dipp] (**9a**), obtained by the reaction of $PhBCl_2$ with 2 equiv of $DippNH_2$, serves as a precursor for the synthesis of the four-membered BNCN ring {[R‴N(H)](Ph)-B(μ-N^{t}Bu)$_2$C^{n}Bu} (**10a**, R‴ = Dipp). The X-ray structures of **6a**, **9a**, and **10a** have been determined. The related derivative **10b** (R‴ = ^{t}Bu) was synthesized by the reaction of {Cl(Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} with Li[N(H)^{t}Bu] and characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectra. In contrast to **10a** and **10b**, NMR spectroscopic data indicate that the derivatives {[DippN(H)](Ph)B(NR′)$_2$CR(NR′)} (**11a**: R = ^{t}Bu, R′ = Cy; **11b**: R = ^{n}Bu, R′ = Dipp) adopt acyclic structures with three-coordinate boron atoms. Monolithiation of **10a** produces the novel hybrid boraamidinate/amidinate (bamam) ligand {Li[DippN]PhB(N^{t}Bu)C^{n}Bu(N^{t}Bu)} (**12a**).

Introduction

Amidinate complexes $[RC(NR')_2]^-$ have been thoroughly investigated for p- and d-block metals.[1] Recent studies have focused on the application of aluminum[2] and early transition metal[3] complexes as catalysts for olefin polymerization. By contrast, the isoelectronic boraamidinate dianions $[RB(NR')_2]^{2-}$ (**1**) have received little attention. Although the first examples of boraamidinate compounds were prepared more than 10 years ago, the emphasis of this earlier work was limited to coordination complexes of groups 4, 14, or 16 elements,[4] and the prevalent boraamidinate ligand was $[PhB(N^tBu)_2]^{2-}$. More recently, derivatives of this ligand with group 13 metals and with phosphorus(III) centers have been reported[5] and the first group 5 complexes were described.[6]

Although a variety of methods have been employed for the synthesis of boraamidinate complexes, the most straightforward synthesis involves metathesis between an element halide and the reagents $\{Li_2[PhB(NR')_2]\}_x$, prepared by dilithiation of bis(organoamino)boranes with *n*-butyllithium.[7] An alternative approach involves the reaction of a tris(amino)borane $B[N(H)R']_3$ with 3 equiv of an organo-lithium reagent (eq 1).[8] The application of this method led to the first X-ray structural determinations of dilithio boraamidinates. It was shown that the extent of aggregation is influenced by the substituent (R) on boron.[8] Although dimeric structures are most common for unsolvated clusters, a trimer was obtained for R = Me.[5b,8]

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* Author to whom correspondence should be addressed. E-mail: chivers@ucalgary.ca. Telephone: (403) 220-5741. Fax: (403) 289-9488.

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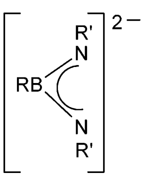
$$3\mathrm{LiR} + \mathrm{B[N(H)R']_3} \rightarrow {}^{1}/_{x}\{\mathrm{Li_2[RB(NR')_2]}\}_x + \mathrm{LiN(H)R'} + 2\mathrm{RH} \quad (1)$$

The initial objective of this work was to investigate the influence of a very bulky aryl substituent, 2,6-diisopropylphenyl (Dipp), attached to the nitrogen atoms of a boraamidinate ligand on cluster aggregation. During the course of the investigation, the amino(chloro)phenylborane PhBCl[N(H)Dipp] was obtained and structurally characterized. The availability of this reagent stimulated attempts to generate hybrid boraamidinate/amidinate (bamam) ligands **2** that are formally isoelectronic with the extensively studied β-diketiminate (nacnac) ligands **3**.[9] There have been several recent reports of the synthesis and structures of alkali metal and alkaline earth complexes of β-ketiminate ligands with Dipp substituents on the two nitrogen atoms.[10−13] It was of interest to assess the influence of the replacement of an R′CCR″ unit in **3** by the polar, isoelectronic R′NBR″ unit in **2** in these sterically encumbered ligands.



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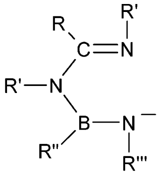

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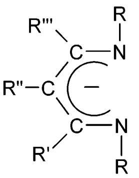

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Experimental Section

Reagents and General Procedures. The compounds $PhBCl_2$ (97%), $GaCl_3$ (99.99%), $InCl_3$ (99.999%), 1,3-di-*tert*-butylcarbodiimide (99%), $^{t}BuNH_2$ (98%), and $^{n}BuLi$ (1.6 or 2.5 M solution in hexanes) were commercial samples (Aldrich) and used as received. The reagent 2,6-diisopropylaniline (Dippa) [97%, Aldrich] was purified by distillation (110 °C, 10^{-2} Torr). $Li[N(H)^{t}Bu]$ was prepared by the addition of $^{n}BuLi$ (2.5 M, 200 mL, 0.5 mol) to a solution of anhydrous $^{t}BuNH_2$ (65 mL, 0.61 mol) in *n*-hexane (170 mL) at −10 °C, and its purity was checked by ^{1}H NMR spectroscopy [δ in C_7D_8: 1.37 ($-C(CH_3)_3$) and in D_8-thf: 1.07 ($-C(CH_3)_3$), −1.55 (NH)]. Li[N(H)Dipp] was prepared by the addition of $^{n}BuLi$ (1.6 M, 16.6 mL, 0.03 mol) to a solution of anhydrous $DippNH_2$ (5 mL, 0.03 mol) in Et_2O (80 mL) at 0 °C, and its purity was checked by ^{1}H NMR spectroscopy [δ in D_8-thf: 6.69 (m, 2 H, aryl of Dipp), 6.07 (m, 1 H, aryl of Dipp), 3.24 (septet, 2 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz), 2.67 (br s, 1 H, NH), 1.22 (d, 12 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz)] and by ^{7}Li NMR spectroscopy [δ in D_8-thf: 1.16 (s)]. Lithiated carbodiimides $Li\{^{n}BuC(N^{t}Bu)_2\}$ (**4a**), $Li\{^{t}BuC(NCy)_2\}$ (**4b**) (Cy = cyclohexyl), and $Li\{^{n}BuC(NDipp)_2\}$ (**4c**) were prepared (97, 98, 70% yields, respectively) by modification of literature procedures.[14a−c] The compound $\{Cl(Ph)B(\mu\text{-}N^{t}Bu)_2C^{n}Bu\}$ (**5**) was obtained in 82% yield by the literature method.[15] Filtrations were performed using either a PTFE filter disk (Acrodisc syringe filter; diameter: 25 mm; pore size: 0.45 μm) or a glass-sintered frit (8 μm). Solvents were dried with appropriate drying agents and distilled onto molecular sieves before use. All reactions and the manipulation of moisture- and/or air-sensitive products were carried out under an atmosphere of argon or under vacuum. All glassware was carefully dried prior to use.

Instrumentation. ^{1}H NMR spectra were recorded on Bruker AC 200 and DRX 400 spectrometers, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{11}B,^{13}C, ^{71}Ga, and ^{7}Li NMR spectra were measured at 25 °C in C_6D_6 or D_8-thf on a Bruker DRX 400 spectrometer using a 5-mm broadband probe (BBO probe) operating at 128.336, 100.594, 122.014, and 155.459 MHz, respectively. Chemical shifts are reported relative to those of $BF_3\cdot OEt_2$ in C_6D_6, Me_4Si in $CDCl_3$, $Ga(NO_3)_3$ in D_2O, and 1.0 M LiCl in D_2O, respectively. Line-broadening parameters, used in the exponential multiplication of the free induction decays, were 50−0.5 Hz. Chemical shifts with a positive sign are correlated with shifts to high frequencies (downfield) of the reference compound. Infrared spectra were obtained as Nujol mulls between KBr plates on a Nicolet Nexus 470 FT-IR spectrometer in the range 4000−350 cm^{-1}. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

Preparation of $PhB[N(H)Dipp]_2$ (6a). A solution of $PhBCl_2$ (0.20 mL, 1.54 mmol) in *n*-hexane (50 mL) was added slowly to a stirred slurry of Li[N(H)Dipp] (1.13 g, 6.17 mmol) in *n*-hexane (50 mL) at −20 °C. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 18 h. After filtration to remove LiCl and excess Li[N(H)Dipp], and removal of solvent in vacuo, $PhB[N(H)Dipp]_2$ (**6a**) was isolated as a thick yellow oil (0.62 g, 1.41 mmol, 91%). Anal. Calcd for $C_{30}H_{41}BN_2$: C, 81.80; H, 9.38; N, 6.36. Found: C, 81.27; H, 9.31; N, 6.33. ^{1}H NMR (D_8-thf, 25 °C): δ 7.29−6.54 (m, 11 H, Ph and aryl of Dipp), 4.13 (br s, 2 H, NH), 2.97 [septet, 4 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz], 1.23 [d, 24 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz]. ^{11}B NMR (D_8-thf, 25 °C): δ 29 (br s). IR (cm^{-1}): 3393 [ν(N−H)]. Dissolution of $PhB[N(H)Dipp]_2$ in Et_2O followed by cooling (0 °C, 1 week) gave colorless crystals of **6a**.

Preparation of $PhB[N(H)Dipp][N(H)^{t}Bu]$ (6b). A solution of PhBCl[N(H)Dipp] (**9a**) (1.49 g, 4.97 mmol) in *n*-hexane (50 mL) was added slowly to a stirred slurry of $Li[N(H)^{t}Bu]$ (1.57 g, 19.89 mmol) in *n*-hexane (50 mL) at −20 °C. The reaction mixture was allowed to warm slowly to room temperature, and the resulting yellow slurry was stirred for 18 h. The slurry was then filtered, first by using a glass-sintered frit and then by using an Acrodisc syringe filter to remove LiCl and excess $Li[N(H)^{t}Bu]$. The filtrate was then concentrated (ca. 85 mL) by removal of solvent in vacuo and then cooled to −78 °C to precipitate unreacted $Li[N(H)^{t}Bu]$. Finally, the mixture was filtered a third time. The volatile materials from the filtrate were removed under vacuum to give **6b** as an off-white powder (0.98 g, 2.91 mmol, 59%). Anal. Calcd for $C_{22}H_{33}BN_2$: C, 78.57; H, 9.89; N, 8.33. Found: C, 78.35; H, 9.73; N, 8.10. ^{1}H NMR (D_8-thf, 25 °C): δ 7.60−6.48 (m, 8 H, Ph and aryl of Dipp), 3.91 [septet, 2 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz], 1.91 (br s, 1 H, NH), 1.26 [d, 6 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz], 1.14 (br s, 1 H, NH), 1.09 [d, 6 H, $-CH(CH_3)_2$, $^{3}J(^{1}H-^{1}H) = 7$ Hz], 0.83 [s, 9 H, $-C(CH_3)_3$]. ^{11}B NMR (D_8-thf, 25 °C): δ 27

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(br s). ^{13}C NMR (C_6D_6, 25 °C): δ seven resonances in the range 157.15−115.76 (Ph & aryl of Dipp), 47.50 [$-C(CH_3)_3$], 33.60 [$-CH(CH_3)_2$], 26.67 [$-CH(CH_3)_2$], 24.86 [$-CH(CH_3)_2$], 23.50 [$-C(CH_3)_3$]. IR (cm^{-1}): 3386 [ν(N−H)], 3349 [ν(N−H)].

Preparation of [Li_2\{PhB(NDipp)$_2$\}(THF)$_3$] (7a). A 2.5 M solution of ^{n}BuLi in hexanes (1.13 mL, 2.82 mmol) was added slowly to a stirred solution of PhB[N(H)Dipp]$_2$ (**6a**) (0.62 g, 1.41 mmol) in *n*-hexane (200 mL) at −10 °C, producing a clear pale yellow solution. The resulting reaction mixture was allowed to warm slowly to room temperature (approximately 30 min), whereupon the solution became cloudy. The reaction mixture was then set to reflux for 18 h, and the resulting cloudy solution was bright yellow. Removal of solvent in vacuo (−20 °C) and several washings with *n*-hexane gave pale yellow amorphous [Li_2\{PhB(NDipp)$_2$\}] (0.50 g, 1.11 mmol, 79%); mp 140−142 °C (dec). Dissolution of [Li_2\{PhB(NDipp)$_2$\}] in THF followed by cooling (0 °C, 24 h) gave colorless crystals of **7a**. Anal. Calcd for $C_{34}H_{47}BLi_2N_2O$ (loss of 2 THF): C, 77.86; H, 9.03; N, 5.34. Found: C, 77.34; H, 9.04; N, 5.86. ^{1}H NMR (D_8-thf, 25 °C): δ 7.29−6.33 (m, 11 H, Ph and aryl of Dipp), 3.66 [septet, 4 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 3.62 [m, 12 H, $O(CH_2)_2(CH_2)_2$], 1.77 [m, 12 H, $O(CH_2)_2(CH_2)_2$], 1.11 [d, 24 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz]. ^{11}B NMR (D_8-thf, 25 °C): δ 29 (br s). ^{7}Li NMR (D_8-thf, 25 °C): δ 0.24 (s). ^{13}C NMR (D_8-thf, 25 °C): δ 158.06 (C_1 aryl of Dipp), 140.00 (C_2 and C_6 aryl of Dipp), 134.90 (C_3 and C_5 aryl of Dipp), 122.75 (C_4 aryl of Dipp), four resonances in the range 126.94−115.30 (Ph), 68.28 [$O(CH_2)_2(CH_2)_2$], 28.33 [$-CH(CH_3)_2$], 26.43 [$O(CH_2)_2(CH_2)_2$], 14.11 [$-CH(CH_3)_2$]. IR (cm^{-1}): No N−H stretch.

Preparation of [Li_2\{PhB(NDipp)(N^{t}Bu)\}(OEt$_2$)$_2$] (7b). A 2.5 M solution of ^{n}BuLi in hexanes (2.33 mL, 5.83 mmol) was added slowly to a stirred solution of **6b** (0.98 g, 2.91 mmol) in *n*-hexane (150 mL) at −10 °C, producing a clear yellow solution. The resulting reaction mixture was allowed to warm slowly to room temperature (approximately 30 min) and then set to reflux for 18 h. The clear yellow solution was cooled to −20 °C and then concentrated (ca. 140 mL) by removal of solvent in vacuo. The resulting solution was further cooled to −78 °C, at which point a white solid was deposited. Removal of the clear yellow supernatant via decantation and several washings with *n*-hexane gave off-white amorphous [Li_2\{PhB(NDipp)(N^{t}Bu)\}] (0.76 g, 2.18 mmol, 75%). Dissolution of [Li_2\{PhB(NDipp)(N^{t}Bu)\}] in Et_2O followed by cooling (0 °C, 0.5 h) gave colorless crystals of **7b**. Several attempts to obtain CHN analyses gave inconsistent results, owing to the loss of Et_2O from the complex. ^{1}H NMR (C_6D_6, 25 °C): δ 7.29−6.63 (m, 8 H, Ph and aryl of Dipp), 3.54 [septet, 1 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 3.26 [q, 8 H, $(CH_3CH_2)_2O$], 2.99 [septet, 1 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.40 [d, 3 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.37 [d, 3 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.31 [s, 9 H, $-C(CH_3)_3$], 1.10 [t, 12 H, $(CH_3CH_2)_2O$], 0.99 [d, 3 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 0.34 [d, 3 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz]. ^{11}B NMR (C_6D_6, 25 °C): δ 35 (br s). ^{7}Li NMR (C_6D_6, 25 °C): δ 2.33 (s). ^{13}C NMR (C_6D_6, 25 °C): δ eight resonances in the range 150.43−119.65 (Ph and aryl of Dipp), 67.20 [$(CH_3CH_2)_2O$], 51.46 [$-C(CH_3)_3$], 37.57 [$-CH(CH_3)_2$], 35.78 [$-CH(CH_3)_2$], 28.97 [$-CH(CH_3)_2$], 27.40 [$-CH(CH_3)_2$], 24.03 [$-CH(CH_3)_2$], 23.24 [$-CH(CH_3)_2$], 22.47 [$-C(CH_3)_3$], 14.20 [$(CH_3CH_2)_2O$]. IR (cm^{-1}): No N−H stretch.

Preparation of [Li(OEt$_2$)$_4$][In\{PhB(NDipp)$_2$\}$_2$] (8a). A slurry of **7a** (0.51 g, 1.13 mmol) in Et_2O (150 mL) was added to solid $InCl_3$ (0.12 g, 0.56 mmol) at −78 °C, producing a yellow slurry with a pink tinge. The stirred reaction mixture was allowed to warm slowly to room temperature, at which point it became a paler yellow slurry. After 18 h, the reaction mixture was allowed to settle and then filtered to remove LiCl. After removal of solvent in vacuo from the clear golden yellow filtrate, the residue was redissolved in *n*-pentane, forming two phases. The yellow supernatant was discarded and a light yellow powder was isolated and washed twice with *n*-pentane (0.37 g, 0.29 mmol, 51%). ^{1}H NMR (C_6D_6, 25 °C): δ 7.29−6.74 (m, 22 H, Ph and aryl of Dipp), 4.49 [septet, 4 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 3.81 [septet, 4 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 2.93 [q, 16 H, $(CH_3CH_2)_2O$], 1.74 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.64 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 0.82 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 0.77 [t, 24 H, $(CH_3CH_2)_2O$], 0.65 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz]. ^{11}B NMR (C_6D_6, 25 °C): δ 30 (br s). ^{7}Li NMR (C_6D_6, 25 °C): δ −7.06 (s). ^{13}C NMR (C_6D_6, 25 °C): δ eight resonances in the range 149.38−120.81 (Ph and aryl of Dipp), 65.51 [$(CH_3CH_2)_2O$], 29.06 [$-CH(CH_3)_2$], 28.30 [$-CH(CH_3)_2$], 24.33 [$-CH(CH_3)_2$], 24.03 [$-CH(CH_3)_2$], 23.37 [$-CH(CH_3)_2$], 22.93 [$-CH(CH_3)_2$], 14.68 [$(CH_3CH_2)_2O$]. Dissolution of **8a** in Et_2O followed by cooling (0 °C, 48 h) gave colorless X-ray quality crystals. Several attempts to obtain CHN analyses gave inconsistent results, owing to the loss of Et_2O from the complex.

Preparation of [Li(OEt$_2$)$_x$][Ga\{PhB(NDipp)$_2$\}$_2$] (8b). Complex **8b** (0.47 g, 0.38 mmol, 51%) was obtained as a golden yellow powder using the procedure described for **8a** [**7a**: 0.67 g, 1.47 mmol; $GaCl_3$: 0.13 g, 0.74 mmol]. ^{1}H NMR (C_6D_6, 25 °C): δ 7.73−6.96 (m, 22 H, Ph and aryl of Dipp), 4.02 [septet, 4 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 3.62 [septet, 4 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 2.97 [q, 16 H, $(CH_3CH_2)_2O$], 1.59 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.30 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.17 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.05 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 0.79 [t, 24 H, $(CH_3CH_2)_2O$]. ^{11}B NMR (C_6D_6, 25 °C): δ 28 (br s). ^{71}Ga NMR (C_6D_6, 25 °C): δ 430.9 (s). ^{7}Li NMR (C_6D_6, 25 °C): δ −0.72 (s). ^{13}C NMR (C_6D_6, 25 °C): δ eight resonances in the range 147.52−118.26 (Ph and aryl of Dipp), 65.71 [$(CH_3CH_2)_2O$], 28.78 [$-CH(CH_3)_2$], 28.52 [$-CH(CH_3)_2$], 25.45 [$-CH(CH_3)_2$], 25.03 [$-CH(CH_3)_2$], 24.89 [$-CH(CH_3)_2$], 24.59 [$-CH(CH_3)_2$], 15.02 [$(CH_3CH_2)_2O$]. Several attempts to obtain CHN analyses gave inconsistent results, owing to the loss of Et_2O from the complex.

Preparation of PhBCl[N(H)Dipp] (9a). A solution of DippNH$_2$ (0.58 mL, 3.08 mmol) in Et_2O (20 mL) was added to a stirred solution of $PhBCl_2$ (0.20 mL, 1.54 mmol) in Et_2O (50 mL) at −40 °C, instantly producing a white slurry. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 2 h. A clear colorless filtrate was isolated after filtration. The volatile materials were removed under vacuum to give **9a** as a white crystalline solid (0.43 g, 1.44 mmol, 93%). Anal. Calcd for $C_{18}H_{23}BClN$: C, 72.15; H, 7.74; N, 4.67. Found: C, 71.92; H, 7.93; N, 4.60. ^{1}H NMR (C_6D_6, 25 °C): δ 7.74−6.93 (m, 8 H, Ph and aryl of Dipp), 5.71 (br s, 1 H, NH), 3.23 [septet, 2 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz], 1.16 [d, 12 H, $-CH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz]. ^{11}B NMR (C_6D_6, 25 °C): δ 40 (br s). ^{13}C NMR (C_6D_6, 25 °C): δ 145.31 (C_1 aryl of Dipp), 135.72 (C_2 and C_6 aryl of Dipp), 135.51 (C_3 and C_5 aryl of Dipp), 135.19 (C_4 aryl of Dipp), four resonances in the range 133.38−123.47 (Ph), 28.67 [$-CH(CH_3)_2$], 24.15 [$-CH(CH_3)_2$].

Preparation of PhBCl[N(H)^{t}Bu] (9b). A solution of ^{t}BuNH$_2$ (0.82 mL, 7.71 mmol) in Et_2O (20 mL) was added to a stirred solution of $PhBCl_2$ (0.50 mL, 3.85 mmol) in Et_2O (50 mL) at −40 °C, instantly producing a white slurry. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 2 h. The slurry was then filtered and the volatile materials were removed from the filtrate under vacuum to give a viscous oil. Pure PhBCl[N(H)^{t}Bu] (0.70 g, 3.58 mmol, 93%) was obtained as a clear colorless liquid by distillation (80 °C, 10^{-2} Torr). Anal. Calcd for $C_{10}H_{15}BClN$: C, 61.44; H, 7.73; N, 7.16. Found: C, 61.29; H, 7.79; N, 6.72. ^{1}H NMR (C_6D_6, 25 °C): δ 7.67−7.15 (m, 5 H, Ph), 4.66 (br s, 1 H, NH), 1.23 [s, 9 H, (−C(C*H*$_3$)$_3$]. ^{11}B NMR (C_6D_6, 25 °C): δ 36 (s). ^{13}C NMR (C_6D_6, 25 °C): δ four resonances in the range 132.7−127.9 (Ph), 50.96 [−*C*(CH$_3$)$_3$], 31.3 [−C(*C*H$_3$)$_3$].

Preparation of {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} (10a). A solution of **9a** (1.02 g, 3.40 mmol) in *n*-hexane (50 mL) was added to a stirred mixture of Li{^{n}BuC(N^{t}Bu)$_2$} (**4a**) (0.74 g, 3.40 mmol) in *n*-hexane (50 mL) at −78 °C. The reaction mixture was allowed to slowly warm to room temperature (white cloudy solution), stirred for 18 h, and then filtered to remove LiCl. The solvent was removed in vacuo from the clear colorless filtrate to give a white powder {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} (**10a**) (1.42 g, 2.99 mmol, 88%). X-ray quality crystals were isolated from a concentrated solution of **10a** in toluene (−10 °C, 2 d). Anal. Calcd for $C_{31}H_{50}BN_3$: C, 78.29; H, 10.60; N, 8.84. Found: C, 78.18; H, 10.85; N, 8.88. ^{1}H NMR (C_6D_6, 25 °C): δ 7.80−7.04 (m, 8 H, Ph and aryl of Dipp), 4.13 (br s, 1 H, NH), 3.70 [septet, 2 H, −C*H*(CH$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 2.36 (m, 2 H, −C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.71 (m, 2H, −CH$_2$C*H*$_2$-CH$_2$CH$_3$), 1.40 (m, 2 H, −CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.27 [d, 12 H, −CH-(C*H*$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 1.03 [s, 18 H, −C(C*H*$_3$)$_3$], 0.78 (t, 3 H, −CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{11}B NMR (C_6D_6, 25 °C): δ 5.32 (s). ^{13}C NMR (C_6D_6, 25 °C): δ 169.8 (−*C*^{n}Bu), 153.3−117.7 (Ph and aryl of Dipp), 51.8 [−*C*(CH$_3$)$_3$], 31.5 [−C(*C*H$_3$)$_3$], 30.4 (−*C*H$_2$CH$_2$-CH$_2$CH$_3$), 28.9 (−CH$_2$*C*H$_2$CH$_2$CH$_3$), 27.6 [−CH(*C*H$_3$)$_2$], 27.1 [−*C*H(CH$_3$)$_2$], 22.9 (−CH$_2$CH$_2$*C*H$_2$CH$_3$), 12.6 (−CH$_2$CH$_2$CH$_2$*C*H$_3$). IR (cm^{-1}): 3420 [ν(N−H)].

Preparation of {[^{t}BuN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} (10b). A solution of **5** (0.07 g, 0.21 mmol) in THF (15 mL) was added to a stirred mixture of Li[N(H)^{t}Bu] (0.03 g, 0.42 mmol) in THF (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 48 h. Solvent was removed in vacuo and the residue was taken up in *n*-hexane. After filtration and removal of solvent in vacuo, {[^{t}BuN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} (**10b**) was isolated as an off-white crystalline solid (0.04 g, 0.11 mmol, 51%). Anal. Calcd for $C_{23}H_{42}BN_3$: C, 74.38; H, 11.40; N, 11.31. Found: C, 73.95; H, 10.99; N, 11.24. ^{1}H NMR (C_6D_6, 25 °C): δ 7.70−7.24 (m, 5 H, Ph), 2.31 (m, 2 H, −C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.68 (m, 2 H, −CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.43 [s, 9 H, *exo*-C(C*H*$_3$)$_3$], 1.21 [s, 18 H, *endo*-C(C*H*$_3$)$_3$], 1.17 (m, 2 H, −CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.11 (br s, 1 H, NH), 0.80 (t, 3 H, −CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{11}B NMR (C_6D_6, 25 °C): δ 5.1 (s). ^{13}C NMR (C_6D_6, 25 °C): δ 171.03 (−*C*CH$_2$CH$_2$CH$_2$-CH$_3$), 132.60 (Ph), 127.61 (Ph), 127.06 (Ph), 125.98 (Ph), 52.09 [*endo*-*C*(CH$_3$)$_3$], 49.52 [*exo*-*C*(CH$_3$)$_3$], 33.25 [*exo*-C(*C*H$_3$)$_3$], 30.70 [*endo*-C(*C*H$_3$)$_3$], 29.12 (−*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.99 (−CH$_2$*C*H$_2$CH$_2$-CH$_3$), 23.31 (−CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.31 (−CH$_2$CH$_2$CH$_2$*C*H$_3$).

Preparation of {[DippN(H)]PhB(NCy)C^{t}Bu(NCy)} (11a). A solution of **9a** (1.05 g, 3.50 mmol) in *n*-hexane (50 mL) was added to a stirred solution of **4b** (0.95 g, 3.50 mmol) in *n*-hexane (50 mL) at −78 °C. The reaction mixture was allowed to slowly warm to room temperature (white cloudy solution), stirred for an additional 18 h, and then filtered to remove LiCl. The solvent was removed in vacuo from the filtrate to give a very viscous yellow oil. The oil was redissolved in a minimal amount of Et$_2$O and then the solvent was removed in vacuo. This process was repeated twice to give **11a** as a yellow sticky residue (1.64 g, 3.11 mmol, 89%). Anal. Calcd for $C_{35}H_{54}BN_3$: C, 79.67; H, 10.32; N, 7.96. Found: C, 79.11; H, 10.70; N, 7.88. ^{11}B NMR (C_6D_6, 25 °C): δ 30 (br s). A sharp very minor resonance was also observed at δ 1.55. The ^{1}H NMR spectrum was uninformative, owing to the complex resonances of the inequivalent cyclohexyl groups.

Preparation of {[DippN(H)]PhB(NDipp)C^{n}Bu(NDipp)} (11b). A solution of **9a** (0.58 g, 1.94 mmol) in *n*-hexane (50 mL) was added to a stirred solution of **4c** (0.83 g, 1.94 mmol) in *n*-hexane (50 mL) at −78 °C. The reaction mixture was allowed to slowly warm to room temperature (pale yellow cloudy solution) and then stirred for 18 h. The reaction mixture was then filtered, and the solvent was removed in vacuo from the clear yellow filtrate to give a very viscous yellow oil (1.01 g, 1.48 mmol, 76%). Anal. Calcd for $C_{47}H_{66}BN_3$: C, 82.55; H, 9.73; N, 6.14. Found: C, 82.07; H, 9.98; N, 6.11. ^{11}B NMR (C_6D_6, 25 °C): δ 32 (br s).

Preparation of {Li[DippN]PhB(N^{t}Bu)C^{n}Bu(N^{t}Bu)} (12a). A 2.5 M solution of ^{n}BuLi in hexanes (1 mL, 2.50 mmol) was added slowly to a stirred solution of **10a** (1.00 g, 2.10 mmol) in *n*-hexane (100 mL) at room temperature, producing a clear very pale yellow solution. A white slurry is formed approximately 30 s after complete addition. The resulting reaction mixture was stirred for an additional 2 h, and the precipitate was isolated by filtration using a glass-sintered frit. The product was then washed with cold *n*-hexane three times to give {Li[DippN](Ph)B(N^{t}Bu)C^{n}Bu(N^{t}Bu)} (**12a**) (0.63 g, 1.31 mmol, 62%). Anal. Calcd for $C_{31}H_{49}BN_3Li$: C, 77.33; H, 10.26; N, 8.73. Found: C, 76.75; H, 10.50; N, 8.45. ^{1}H NMR (C_6D_6, 25 °C): δ 7.89−7.10 (m, 8 H, Ph and aryl of Dipp), 3.79 [septet, 1 H, −C*H*(CH$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 3.20 [septet, 1 H, −C*H*(CH$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 2.21 (m, 2 H, −C*H*$_2$CH$_2$CH$_2$-CH$_3$), 2.07 (m, 2H, −CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.53 (m, 2 H, −CH$_2$-CH$_2$C*H*$_2$CH$_3$), 1.44 [d, 3 H, −CH(C*H*$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 1.40 [s, 9 H, −C(C*H*$_3$)$_3$], 1.38 [d, 3 H, −CH(C*H*$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 1.28 [d, 3 H, −CH(C*H*$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 1.08 [d, 3 H, −CH(C*H*$_3$)$_2$, $^3J(^1H-^1H) = 7$ Hz], 0.99 [s, 9 H, −C(C*H*$_3$)$_3$], 0.81 (t, 3 H, −CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{11}B NMR (C_6D_6, 25 °C): δ 29 (br s). ^{7}Li NMR (C_6D_6, 25 °C): δ 0.13 (s). ^{13}C NMR (C_6D_6, 25 °C): δ eight resonances in the range 152.90−118.72 (Ph and aryl of Dipp), 54.95 [−*C*(CH$_3$)$_3$], 52.85 [−*C*(CH$_3$)$_3$], 36.94 (−*C*CH$_2$CH$_2$CH$_2$CH$_3$), 31.24 [−C(*C*H$_3$)$_3$], 30.23 [−C(*C*H$_3$)$_3$], 28.41 [−*C*H(CH$_3$)$_2$], 28.14 [−*C*H(CH$_3$)$_2$], 27.62 [−CH(*C*H$_3$)$_2$], 24.72 [−CH(*C*H$_3$)$_2$], 24.51 [−CH(*C*H$_3$)$_2$], 24.14 [−CH(*C*H$_3$)$_2$], 23.75 (−*C*H$_2$CH$_2$CH$_2$CH$_3$), 23.47 (−CH$_2$*C*H$_2$CH$_2$CH$_3$), 23.10 (−CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.59 (−CH$_2$CH$_2$CH$_2$*C*H$_3$). IR (cm^{-1}): No N−H stretch.

X-ray Analyses. Single crystals of **6a**, **7a**, **8a**, and **7b** (colorless block), **10a** (colorless prismatic crystal), and **9a** (colorless plate) 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 **6a**, **7a**, **8a**, **9a**, **7b**, and **10a** were made on a Nonius CCD four-circle Kappa FR540C diffractometer using graphite-monochromated Mo Kα radiation (**6a**, **7a**, **8a**, **7b**, **10a**: $\lambda = 0.71073$ Å; **9a**: $\lambda = 0.71069$ Å). Data were measured using ϕ and ω scans. Data reduction was performed by using the HKL DENZO and SCALEPACK software.[16] A multiscan absorption correction was applied to the data (SCALEPACK).[16]

Relevant parameters for the data collections and crystallographic data for **6a**, **7a**, **8a**, **9a**, **7b**, and **10a** are summarized in Table 1. The structures were solved by direct methods (SIR-92[17]) and refined by a full-matrix least-squares method based on F^2 using SHELXL-97.[18] The non-hydrogen atoms were refined anisotropically (unless

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(16) HKL DENZO and SCALEPACK vl.96: Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A.; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: San Diego, CA, 1997; pp 307−326.

(17) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardid, A. SIR-92, A package for crystal structure solution by direct methods and refinement. *J. Appl. Crystallogr.* **1993**, *26*, 343.

Table 1. Selected Crystal Data and Data Collection Parameters for PhB[N(H)Dipp]$_2$·$(C_4H_{10}O)_{0.25}$ (**6a**), [Li$_2${PhB(NDipp)$_2$}(THF)$_3$] (**7a**), [Li(OEt$_2$)$_4$][In{PhB(NDipp)$_2$}$_2$]·$(C_7H_8)_2$ (**8a**), PhBCl[N(H)Dipp] (**9a**), [Li$_2${PhB(NDipp)(N^{t}Bu)}(OEt$_2$)$_2$] (**7b**), and {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} (**10a**)

	6a	**7a**	**8a**	**9a**	**7b**	**10a**
formula	$C_{30}H_{41}BN_2{\cdot}CH_{2.5}O_{0.25}$	$C_{42}H_{63}BLi_2N_2O_3$	$C_{60}H_{78}B_2InN_4{\cdot}C_{16}H_{40}LiO_4{\cdot}C_{14}H_{16}$	$C_{18}H_{23}BClN$	$C_{30}H_{51}BLi_2N_2O_2$	$C_{31}H_{50}BN_3$
fw	458.99	668.63	1479.39	299.63	496.42	475.55
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/a$	$P2_1/n$	$P2_1$
a, Å	11.092(2)	10.5766(4)	12.580(2)	11.7907(5)	19.019(3)	10.634(7)
b, Å	15.078(2)	20.9002(8)	18.196(2)	13.1664(5)	18.461(3)	9.724(7)
c, Å	19.185(3)	18.2412(10)	19.164(3)	11.9232(6)	20.330(4)	14.733(13)
α, deg	67.634(6)	90	99.140(8)	90	90	90
β, deg	88.134(6)	93.037(2)	104.177(6)	113.866(2)	117.523(9)	99.06(3)
γ, deg	82.276(9)	90	95.163(6)	90	90	90
V, Å^3	2939.7(8)	4026.6(3)	4160.9(10)	1692.70(13)	6330.2(19)	1504(2)
Z	4	4	2	4	8	2
T, K	173(2)	123(2)	173(2)	173(2)	123(2)	173(2)
λ, Å	0.71073	0.71073	0.71073	0.71069	0.71073	0.71073
d_{calcd}, g cm^{-3}	1.037	1.103	1.181	1.176	1.042	1.050
μ, mm^{-1}	0.060	0.067	0.34	0.22	0.062	0.060
F(000)	1002	1456	1592	640	2176	522
R^a	0.063	0.077	0.066	0.042	0.062	0.061
$R_w{}^b$	0.163	0.171	0.179	0.109	0.148	0.159

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

otherwise stated). Hydrogen atoms were included at geometrically idealized positions (C−H bond distances 0.95 Å) and were not refined. The NH protons in **6a**, **9a**, and **10a** 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 isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon or nitrogen atom.

The asymmetric unit of **6a** is composed of two independent molecules of $C_{30}H_{41}BN_2$ [since data are very similar for both molecules, only selected bond lengths and angles are included for one of the molecules (Table 2) and only one molecule is depicted in the thermal ellipsoid plot (Figure 1)] and a half molecule of diethyl ether lying close to an inversion center that is disordered. The disordered solvent molecule was refined with isotropic thermal parameters. The H-atoms of the disordered solvate molecule were ignored. Two carbon atoms [labeled as C(36), C(37), C(36′), and C(37′)] in one of the three coordinating THF molecules in **7a** were disordered over two sites with refined site occupancy factors of 0.496(2) and 0.504(2), respectively. For **8a**, the non-hydrogen atoms of the In-complex were refined anisotropically, while the other atoms were allowed isotropic thermal parameters. The structure contained one ordered and two disordered half molecules of toluene solvate and four disordered molecules of diethyl ether coordinated to Li. Two of the ether molecules had full occupancy factors while the other two molecules were located over three sites with partial site occupancy factors. Two H-atoms of the disordered toluene molecules were ignored. For **7b**, there are two molecules of $C_{30}H_{51}BLi_2N_2O_2$ in an asymmetric unit; since data are very similar for both molecules, only selected bond lengths and angles are included for one of the molecules (Table 6) and only one molecule is depicted in the thermal ellipsoid plot (Figure 5). A diethyl ether molecule [labeled as O(3), C(53), C(54), C(55), and C(56)] was disordered; the smaller fraction of C-atoms of this molecule were refined with isotropic thermal parameters.

Thermal ellipsoid plots for the crystal structures were generated using the programs CAMERON[19] and XP (part of the SHELXTL-NT 5.1[20] program library) and then imported into CorelDRAW 9.[21] Thermal ellipsoids are shown at the 30% probability level and only selected carbon atoms are labeled.

Results and Discussion

Syntheses and X-ray Structures of PhB[N(H)Dipp]$_2$ (6a) and [Li$_2${PhB(NDipp)$_2$}(THF)$_3$] (7a). The usual route to the synthesis of dilithio boraamidinate complexes {Li$_2$[RB(NR′)$_2$]}$_x$ is the dilithiation of the phenylbis(organoamino)boranes PhB[N(H)R′]$_2$ with *n*-butyllithium.[5b] The bis-amino derivative PhB[N(H)Dipp]$_2$ (**6a**) can be prepared by reaction of Li[N(H)Dipp] with PhBCl$_2$ over a period of 18 h at room temperature (eq 2). An excess (4 equiv) of the former reagent was necessary in order to drive this reaction to completion. The structure of **6a** was determined by a single-crystal X-ray analysis, and the molecular geometry and atomic numbering scheme are shown in Figure 1, while pertinent structural parameters are summarized in Table 2. Typically, organobis(organoamino)borane species exist as oils;[22a] the only structurally characterized example is MeB[N(H)Me]$_2$.[22b] As expected, the boron atom in **6a** adopts a trigonal planar geometry (Σ∠B = 360.0°). The mean B−N bond length is 1.417 Å (cf. 1.414 Å in MeB[N(H)Me]$_2$).[22b] The orientation of the bulky Dipp substituents is similar to that of the N−Me groups in MeB[N(H)Me]$_2$ and the phenyl rings are rotated with respect to each other to minimize steric interactions. The intermolecular N···H bridges observed in MeB[N(H)Me]$_2$[22b] are not observed in **6a**. In the ^{1}H NMR spectrum of **6a**, only one resonance is observed for both the CH and CH$_3$ groups of the Dipp substituents. These signals

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(22) (a) For an example, see: Burch, J. E.; Gerrard, W.; Mooney, E. F. *J. Chem. Soc*. **1962**, 2200. (b) Niederpruem, N.; Boese, R.; Schmid, G. *Z. Naturforsch., Teil B* **1991**, *46*, 84.

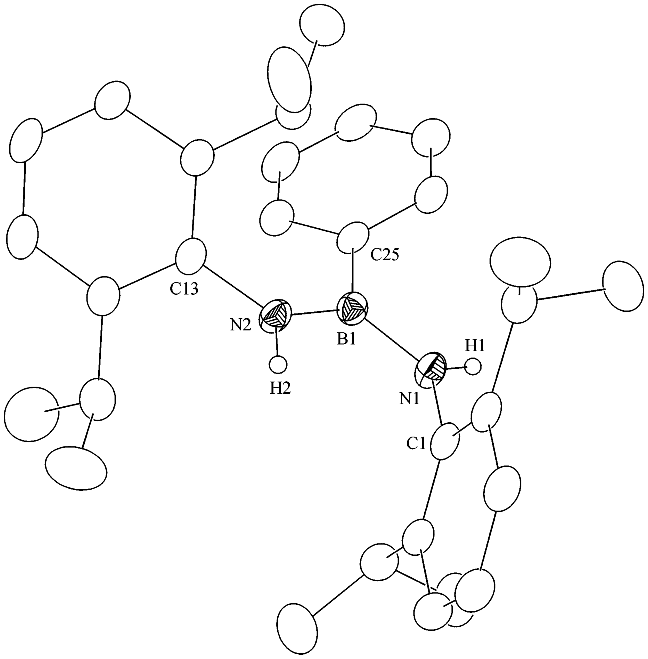


Figure 1. Thermal ellipsoid plot of PhB[N(H)Dipp]$_2$ (**6a**). For clarity, H atoms are omitted except H1 on N1 and H2 on N2.

Table 2. Selected Bond Lengths and Bond Angles for PhB[N(H)Dipp]$_2$·(C$_4$H$_{10}$O)$_{0.25}$ (**6a**)

Bond Distances (Å)			
B(1)−N(1)	1.420(3)	N(2)−C(13)	1.433(3)
N(1)−C(1)	1.441(3)	B(1)−C(25)	1.576(3)
B(1)−N(2)	1.414(3)		
Bond Angles (deg)			
B(1)−N(1)−C(1)	124.6(2)	N(2)−B(1)−C(25)	122.8(2)
B(1)−N(2)−C(13)	128.0(2)	N(1)−B(1)−C(25)	118.7(2)
N(2)−B(1)−N(1)	118.5(2)		

are very broad at ambient temperature, indicating that there is rapid rotation of the N-aryl groups in solution, resulting in the observed equivalence in the spectrum.

Addition of 2 equiv of ^{n}BuLi to a solution of **6a** in *n*-hexane followed by an 18 h reflux provided yellow amorphous Li$_2${PhB(NDipp)$_2$} (**7a**) in a 79% yield (eq 3). Dissolution of **7a** in THF provided colorless crystals, which were characterized by CHN analyses, multinuclear (^{1}H, ^{11}B, ^{7}Li, and ^{13}C) NMR spectroscopy, IR spectroscopy, and a single-crystal X-ray diffraction experiment. The ^{1}H NMR spectrum showed resonances for the Ph and Dipp substituents with intensities indicative of symmetrically equivalent Dipp substituents. Deprotonation was also indicated by the lack of an N−H stretch in the IR spectrum.

$$\mathrm{PhBCl_2 + 2Li[N(H)Dipp] \rightarrow \underset{\textbf{6a}}{PhB[N(H)Dipp]_2} + 2LiCl} \qquad (2)$$

$$\mathrm{\underset{\textbf{6a}}{PhB[N(H)Dipp]_2} + 2\,^{n}BuLi \rightarrow \underset{\textbf{7a}}{Li_2\{PhB(NDipp)_2\}} + 2\,^{n}BuH} \qquad (3)$$

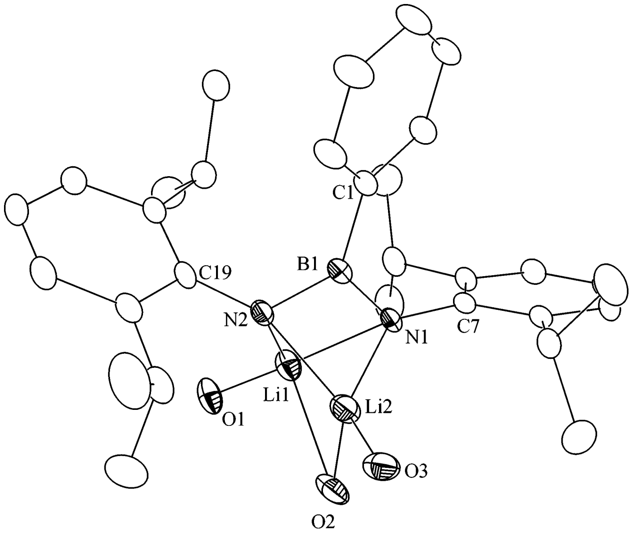
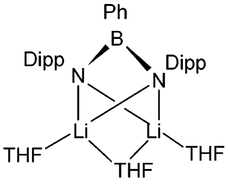


Figure 2. Thermal ellipsoid plot of [Li$_2${PhB(NDipp)$_2$}(THF)$_3$] (**7a**). For clarity, H atoms are omitted and only the oxygen atoms of the THF molecules are shown.

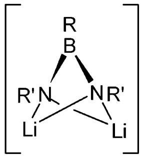
Table 3. Selected Bond Lengths and Bond Angles for [Li$_2${PhB(NDipp)$_2$}(THF)$_3$] (**7a**)

Bond Distances (Å)			
B(1)−N(1)	1.415(5)	N(2)−Li(1)	2.010(6)
B(1)−N(2)	1.446(4)	N(2)−Li(2)	2.049(7)
B(1)−C(1)	1.599(5)	O(1)−Li(1)	1.916(6)
N(1)−C(7)	1.400(4)	O(2)−Li(2)	2.013(6)
N(1)−Li(2)	2.115(6)	O(2)−Li(1)	2.270(7)
N(1)−Li(1)	2.022(6)	O(3)−Li(2)	1.922(7)
N(2)−C(19)	1.390(4)		
Bond Angles (deg)			
N(1)−B(1)−N(2)	111.4(3)	N(2)−B(1)−C(1)	122.9(3)
N(1)−B(1)−C(1)	125.2(3)	N(2)−Li(1)−N(1)	71.8(2)
N(1)−Li(1)−O(2)	87.6(2)	N(2)−Li(2)−N(1)	69.1(2)
B(1)−N(1)−Li(2)	77.5(2)	N(2)−Li(1)−O(2)	101.9(3)
B(1)−N(2)−Li(1)	83.4(2)	Li(1)−N(1)−Li(2)	70.1(2)
B(1)−N(2)−Li(2)	79.2(2)	Li(1)−N(2)−Li(2)	71.7(3)
B(1)−N(1)−Li(1)	83.7(3)	Li(2)−O(2)−Li(1)	67.1(2)
C(7)−N(1)−Li(1)	135.5(3)	O(1)−Li(1)−N(2)	121.7(3)
C(7)−N(1)−Li(2)	135.9(3)	O(1)−Li(1)−N(1)	163.0(4)
C(7)−N(1)−B(1)	130.4(3)	O(1)−Li(1)−O(2)	98.6(3)
C(19)−N(2)−Li(2)	148.1(3)	O(2)−Li(2)−N(1)	92.2(3)
C(19)−N(2)−B(1)	126.4(3)	O(2)−Li(2)−N(2)	110.0(3)
C(19)−N(2)−Li(1)	124.4(3)	O(3)−Li(2)−N(1)	137.3(3)
O(3)−Li(2)−N(2)	127.9(3)		
O(3)−Li(2)−O(2)	111.5(3)		

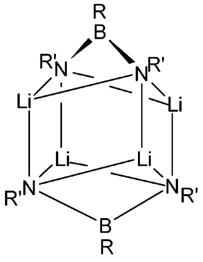
The molecular geometry and atomic numbering scheme for **7a** are shown in Figure 2, and pertinent structural parameters are summarized in Table 3. In all previous structures of dilithio derivatives of boraamidinates, the fundamental building block is the Li$_2$N$_2$B unit **A**. In the case of {Li$_2$[RB(N^{t}Bu)$_2$]}$_2$ (R = Ph, ^{n}Bu, ^{t}Bu),[5b,8] two of these units participate in a face-to-face interaction through lithium−nitrogen contacts to give the bicapped cube **B** (R′ = ^{t}Bu). In the unique example of a trimer {Li$_2$[RB(N^{t}Bu)$_2$]}$_3$ (R = Me),[8] three Li$_2$N$_2$B units associate edge-on through lithium−nitrogen contacts to give the tricapped hexagonal prism **C**. The boraamidinate **7a** is the first example of a monomeric dilithio boraamidinate. Each Li$^+$ ion is coordinated by one terminal and one asymmetrically bridging THF molecule. Since all previous boraamidinate structures involve unsolvated Li$^+$ centers,[5b,8] the monomeric structure of **7a** may be the result of solvation of the Li$^+$ ions or the steric bulk of the Dipp substituents on nitrogen (or a combination of both effects). A monomeric structure similar to that of **7a** has been reported for $\{(THF)_3Li_2[PhAs(N^tBu)_2]\}$ in which the smaller ^{t}Bu substituents are attached to the nitrogen atoms.[23] Thus, it seems likely that solvation accounts for the monomeric structure of **7a**.



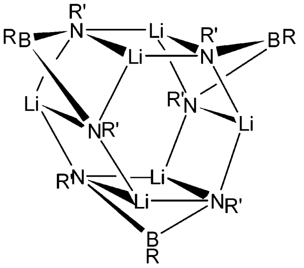
7a



A



B



C

The $[PhB(NR')_2]^{2-}$ framework in **7a** chelates each of the two lithium centers in an *N*,*N*′ manner. However, the B−N bond lengths in the boraamidinate ligand in **7a** differ by ca. 0.03 Å [B(1)−N(1) = 1.415(5) Å; B(1)−N(2) = 1.446(4) Å]. This small difference may be a response to the asymmetric bonding of the bridging THF molecules that, in turn, may result from packing effects. In addition, the bite angle [∠N(1)−B(1)−N(2)] increases from 109.50(18)° in $[Li_2\{PhB(N^tBu)_2\}]_2$[5b] to 111.4(3)° in **7a**, presumably in order to accommodate the bulkier −NDipp groups. Least-squares planes[24] were calculated for the two four-membered rings containing N1−B1−Li1−N2 (plane 1) and N1−B1−Li2−N2 (plane 2), which were found to be puckered rings with the two nitrogen atoms below the plane while the boron and lithium atoms reside above the plane [deviations (Å) from the least-squares planes: plane 1 = −0.154(2) N1, 0.212(3) B1, 0.094(1) Li1, −0.152(2) N2; plane 2 = −0.223(2) N1, 0.331(3) B1, 0.115(1) Li2, −0.224(2) N2]. Furthermore, the two phenyl rings of the Dipp substituents are offset from one another with an angle between the two planes [least-squares planes[25] calculated for plane 3: C7−C12 and for plane 4: C19−24] of 33.8(1)°. In addition, in contrast to the previously reported structures of $\{Li_2[RB(N^tBu)_2]\}_2$ (R = Ph, ^{n}Bu, ^{t}Bu)[5b,8] and $\{Li_2[MeB(N^tBu)_2]\}_3$[8] there are no C(−H)···Li agostic interactions in **7a**.

Synthesis and X-ray Structure of $[Li(OEt_2)_4][In\{PhB(NDipp)_2\}_2]$ (8a). Recent work on group 13 complexes of amidinate anions $[RC(NR')_2]^-$ has revealed novel structural chemistry for In[26] and catalytic activity for cationic Al or Ga complexes.[27] Recently, we reported the first boraamidinate complexes of group 13 elements including $[In\{PhB(N^tBu)_2\}_2Li(OEt_2)]$ in which the spirocyclic anion $[In\{PhB(N^tBu)_2\}_2]^-$ is *N*,*N*′-chelated to a monosolvated lithium cation.[5a] The reaction of $Li_2[PhB(NDipp)_2]$ (**7a**) with $InCl_3$ in a 2:1 stoichiometry also gives a spirocyclic compound $[Li(OEt_2)_4][In\{PhB(NDipp)_2\}_2]$ (**8a**). However, the X-ray structural analysis reveals that this is a solvent-separated ion pair.

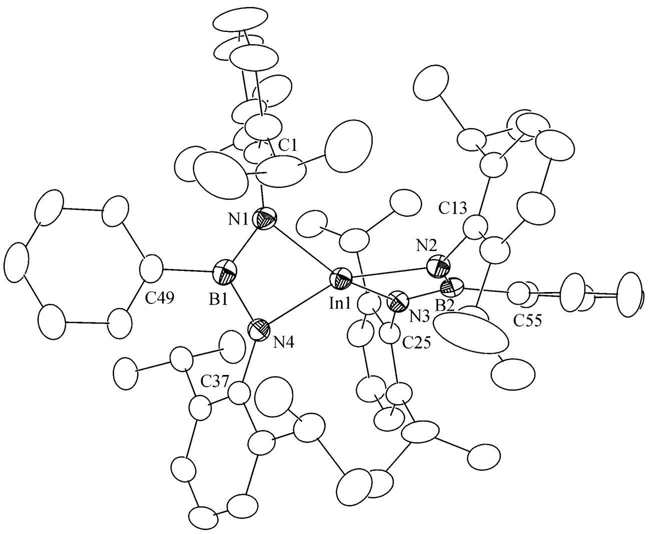


Figure 3. Thermal ellipsoid plot of the anion in $[Li(OEt_2)_4][In\{PhB(NDipp)_2\}_2]$ (**8a**). For clarity, H atoms are omitted.

Table 4. Selected Bond Lengths and Bond Angles for $[Li(OEt_2)_4][In\{PhB(NDipp)_2\}_2]\cdot(C_7H_8)_2$ (**8a**)

Bond Distances (Å)			
In(1)−N(2)	2.123(4)	N(1)−B(1)	1.437(7)
In(1)−N(1)	2.129(4)	N(2)−B(2)	1.442(6)
In(1)−N(4)	2.132(3)	N(3)−B(2)	1.427(6)
In(1)−N(3)	2.133(3)	N(4)−B(1)	1.431(6)

Bond Angles (deg)			
B(1)−N(1)−In(1)	91.3(3)	N(4)−B(1)−N(1)	110.3(4)
B(1)−N(4)−In(1)	91.4(3)	N(4)−B(1)−C(49)	124.4(4)
B(2)−N(2)−In(1)	90.9(3)	N(4)−In(1)−N(3)	125.7(1)
B(2)−N(3)−In(1)	90.9(3)	C(1)−N(1)−B(1)	131.0(4)
N(1)−B(1)−C(49)	125.3(4)	C(1)−N(1)−In(1)	135.1(3)
N(1)−In(1)−N(3)	143.3(1)	C(13)−N(2)−B(2)	129.5(4)
N(1)−In(1)−N(4)	67.1(1)	C(13)−N(2)−In(1)	134.5(3)
N(2)−B(2)−C(55)	124.3(4)	C(25)−N(3)−B(2)	131.3(4)
N(2)−In(1)−N(1)	127.0(1)	C(25)−N(3)−In(1)	135.3(3)
N(2)−In(1)−N(3)	67.4(1)	C(37)−N(4)−B(1)	132.7(4)
N(2)−In(1)−N(4)	141.8(2)	C(37)−N(4)−In(1)	134.2(3)
N(3)−B(2)−N(2)	110.8(4)		
N(3)−B(2)−C(55)	124.9(4)		

The molecular geometry and atomic numbering scheme for **8a** are shown in Figure 3, and pertinent structural parameters are summarized in Table 4. The spirocyclic anion $[In\{PhB(NDipp)_2\}_2]^-$ is presumably stabilized by the steric bulk provided by the four Dipp substituents attached to the nitrogen atoms, while the lithium cation is solvated by four

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(23) Briand, G. G.; Chivers, T.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3785.

(24) x, y, z in crystal coordinates: plane 1 (Å) = $-1.92(3)x + 4.74(5)y + 17.61(2)z = 6.17(2)$; plane 2 (Å) = $-6.68(2)x + 10.50(4)y - 10.14(5)z = 0.62(3)$.

(25) x, y, z in crystal coordinates: plane 3 (Å) = $-6.28(1)x + 15.63(2)y + 6.00(2)z = 6.593(6)$; plane 4 (Å) = $-8.176(9)x + 12.34(2)y - 3.48(3)z = 2.63(2)$.

(26) (a) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1996**, *35*, 1423. (b) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1996**, *35*, 2448.

(27) Dagome, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274 and references therein.

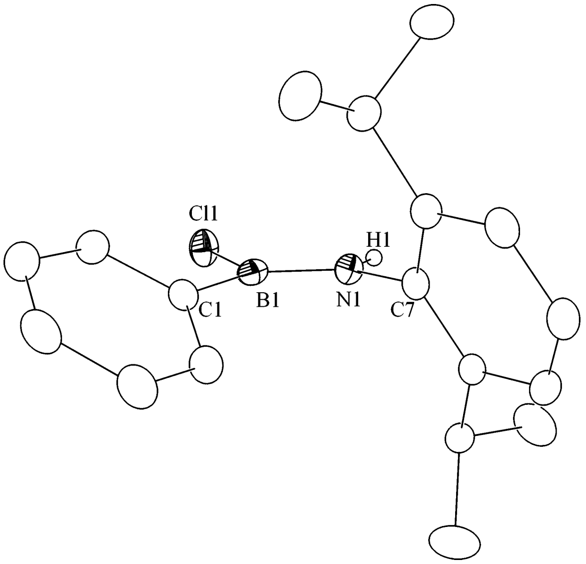

Figure 4. Thermal ellipsoid plot of PhBCl[N(H)Dipp] (**9a**). For clarity, H atoms are omitted except H1 on N1.

molecules of diethyl ether. The boron atoms in **8a** adopt a distorted trigonal planar geometry ($\Sigma\angle B = 360.0°$) with bond angles $\angle$N−B−N of 110.3(4) and 110.8(4)°. In the contact ion-pair [In{PhB(N^{t}Bu)$_2$}$_2$Li(OEt$_2$)], there is a significant difference (ca. 0.13 Å) in the two B−N bond distances in the planar, four-membered BN$_2$In rings, which is related to the different coordination numbers of the nitrogen atoms in this complex. Consistently, the B−N bond distances in **8a**, in which all nitrogen atoms are three-coordinate, are approximately equal. The bond angles at the central In atom in **8a** deviate markedly from tetrahedral (range ca. 67−141°).

The reaction of **7a** with GaCl$_3$ (2:1 stoichiometry) gave a similar product [Li(OEt$_2$)$_x$][Ga{PhB(NDipp)$_2$}$_2$] (**8b**), which has been characterized by multinuclear (^{1}H, ^{11}B, ^{7}Li, and ^{13}C) NMR spectroscopy. Integration of the resonances due to the diethyl ether molecules (with respect to those of the alkyl and aryl of the anion moiety) in the ^{1}H NMR spectrum indicates $x = 4$.

Synthesis and X-ray Structure of PhBCl[N(H)Dipp] (9a). During the synthesis of PhB[N(H)Dipp]$_2$ (**6a**) (eq 2), it was found that incomplete reaction yields the monoamido derivative PhBCl[N(H)Dipp] (**9a**). The bis(amino)borane **6a** is isolated as a viscous oil that slowly crystallizes over 24 h. When incomplete reaction occurs, the monosubstituted product **9a** crystallizes first and can be separated from **6a**. Crystals of **9a** were isolated and characterized by CHN analysis and multinuclear (^{1}H, ^{11}B, and ^{13}C) NMR spectroscopy. As expected, successive replacement of the chlorine atoms on the central boron atom by organoamino groups causes an upfield shift of the ^{11}B NMR resonance {PhBCl$_2$: δ 63; PhBCl[N(H)Dipp]: δ 40; PhB[N(H)Dipp]$_2$: δ 29}. The solid-state structure of **9a** was determined by X-ray crystallography. The molecular geometry and atomic numbering scheme are shown in Figure 4, and pertinent structural parameters are summarized in Table 5. The boron−nitrogen bond length of 1.386(3) Å is significantly shorter than those of typical triaminoboranes[28] [cf. B−N = 1.432 Å in tris(2-pyridylamino)borane[29]]. This shortening is most likely due to the electronegative chlorine atom attached to the central boron atom, which enhances B−N π-bonding. The boron−chlorine bond length in **9a** [B(1)−Cl(1) = 1.798(2) Å] is comparable to those in Me$_2$N−N[B(Mes)Cl]$_2$ [B(1)−Cl(1) = 1.843(4) Å; B(1)−Cl(2) = 1.796(5) Å].[30]

Table 5. Selected Bond Lengths and Bond Angles for PhBCl[N(H)Dipp] (**9a**)

Bond Distances (Å)			
B(1)−N(1)	1.386(3)	N(1)−C(7)	1.447(2)
B(1)−C(1)	1.559(3)	B(1)−Cl(1)	1.798(2)
Bond Angles (deg)			
B(1)−N(1)−C(7)	128.0(2)	N(1)−B(1)−Cl(1)	115.9(2)
N(1)−B(1)−C(1)	126.0(2)	C(1)−B(1)−Cl(1)	118.1(2)

In view of the possible application of **9a** and related derivatives in the preparation of new ligand systems, it was desirable to have a high-yield synthesis. This is achieved through the reaction of 2 equiv of DippNH$_2$ with phenyldichloroborane, which produces **9a** in 93% yield (eq 4).

$$\mathrm{PhBCl_2 + 2DippNH_2 \rightarrow \underset{\mathbf{9a}}{PhBCl[N(H)Dipp]} + [DippNH_3]Cl} \tag{4}$$

Synthesis and X-ray Structure of [Li$_2${PhB(NDipp)(N^{t}Bu)}(OEt$_2$)$_2$] (7b). With a direct method to the reagent PhBCl[N(H)Dipp] available, it was possible to prepare [Li$_2${PhB(NDipp)(N^{t}Bu)}(OEt$_2$)$_2$] (**7b**), the first boraamidinate with different substituents attached to the two nitrogen atoms. The borane PhB[N(H)Dipp][N(H)^{t}Bu] (**6b**) was prepared by the reaction of an excess of Li[N(H)^{t}Bu] with PhBCl[N(H)Dipp]. The ^{1}H NMR spectrum of **6b** exhibits one septet for the two equivalent methine hydrogens and a pair of doublets of equal intensity for the diastereotopically inequivalent ^{i}Pr methyl pairs consistent with a C_s structure in solution. The reaction of 2 equiv of ^{n}BuLi with **6b** in boiling *n*-hexane solution provided off-white amorphous Li$_2${PhB(NDipp)(N^{t}Bu)}. Dissolution of Li$_2${PhB(NDipp)(N^{t}Bu)} in diethyl ether yielded colorless crystals of **7b**, which were characterized by CHN analyses, multinuclear (^{1}H, ^{11}B, ^{7}Li, and ^{13}C) NMR spectroscopy, and a single-crystal X-ray diffraction experiment. The ^{1}H NMR spectrum showed resonances for the Ph, ^{t}Bu, and Dipp substituents with the appropriate relative intensities. Two separate methine signals are observed in the spectrum and four doublets for the ^{i}Pr methyl groups, reflecting both the lower symmetry of the molecule and hindered rotation of the N-aryl groups in solution. Deprotonation was indicated by the lack of an N−H stretch in the IR spectrum.

The molecular geometry and atomic numbering scheme for **7b** are shown in Figure 5, and pertinent structural parameters are summarized in Table 6. The [PhB(NDipp)(N^{t}Bu)]$^{2-}$ framework in **7b** chelates each of the two lithium atoms in an *N,N′* manner with each lithium center solvated by one molecule of diethyl ether. As in the case of **7a**, this solvation prevents further association. The boron atom in

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(28) Nöth, H. *Z. Naturforsch., Teil B* **1983**, *38*, 692.

(29) Braun, U.; Habereder, T.; Nöth, H.; Piotrowski, H.; Warchhold, M. *Eur. J. Inorg. Chem.* **2002**, 1132.

(30) Diemer, S.; Nöth, H.; Storch, W. *Eur. J. Inorg. Chem.* **1999**, 1765.

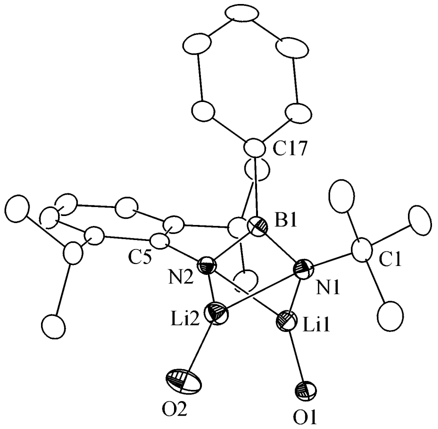
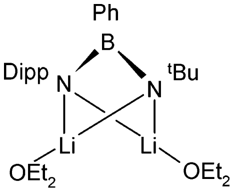


Figure 5. Thermal ellipsoid plot of [Li$_2${PhB(NDipp)(N^{t}Bu)}(OEt$_2$)$_2$] (**7b**). For clarity, H atoms are omitted and only the oxygen atoms of the OEt$_2$ molecules are shown.

Table 6. Selected Bond Lengths and Bond Angles for [Li$_2${PhB(NDipp)(N^{t}Bu)}(OEt$_2$)$_2$] (**7b**)

Bond Distances (Å)			
B(1)−N(1)	1.428(3)	N(2)−Li(1)	2.010(4)
B(1)−N(2)	1.451(3)	N(2)−Li(2)	2.003(4)
B(1)−C(17)	1.601(3)	N(2)−C(5)	1.397(3)
N(1)−Li(1)	1.988(4)	O(1)−Li(1)	1.921(4)
N(1)−Li(2)	1.985(5)	O(2)−Li(2)	1.937(4)
N(1)−C(1)	1.468(3)		

Bond Angles (deg)			
B(1)−N(1)−C(1)	128.1(2)	N(2)−B(1)−C(17)	119.7(2)
B(1)−N(1)−Li(2)	79.3(2)	C(1)−N(1)−Li(2)	130.2(2)
B(1)−N(1)−Li(1)	79.5(2)	C(1)−N(1)−Li(1)	139.1(2)
B(1)−N(2)−C(5)	125.3(2)	C(5)−N(2)−Li(2)	140.2(2)
B(1)−N(2)−Li(1)	78.2(2)	C(5)−N(2)−Li(1)	133.6(2)
B(1)−N(2)−Li(2)	78.2(2)	Li(2)−N(1)−Li(1)	78.7(2)
N(1)−B(1)−N(2)	109.9(2)	Li(2)−N(2)−Li(1)	77.8(2)
N(1)−B(1)−C(17)	130.3(2)		



7b

7b adopts a distorted trigonal planar geometry ($\Sigma\angle B = 359.9°$) with a bond angle ∠N−B−N of 109.9(2)°. The B−N bond lengths in **7b** differ by 0.023 Å with the longer bond [B(1)−N(2) = 1.451(3) Å] attributed to the steric influence of the bulkier Dipp substituent on N(2). There are no C(−H)···Li agostic interactions in the structure of **7b**.

Synthetic Approaches to Hybrid Boraamidinate/Amidinate (bamam) Ligands. Two approaches to the synthesis of the novel bamam ligands **2** were investigated. The first makes use of the reaction of lithium amidinates with organoamino(chloro)phenyl boranes (**9**) (Scheme 1). The reaction of PhBCl[N(H)Dipp] (**9a**) and Li{^{n}BuC(N^{t}Bu)$_2$} (**4a**) in a 1:1 stoichiometry in *n*-hexane produced {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} (**10a**) in 88% yield. The product was characterized by a single-crystal X-ray diffraction experiment in addition to CHN analysis, multinuclear (^{1}H, ^{11}B, and ^{13}C) NMR spectra, and IR spectroscopy. The ^{1}H NMR spectrum indicates the presence of the amino proton (δ 4.13), which is also supported by IR analysis (3420 cm^{-1} [ν(N−H)]), along with the equivalence of the N^{t}Bu groups (δ 1.03). The ^{11}B NMR chemical shift (δ 5.3 ppm) is consistent with a tetracoordinate boron environment, suggesting a cyclic structure.[31]

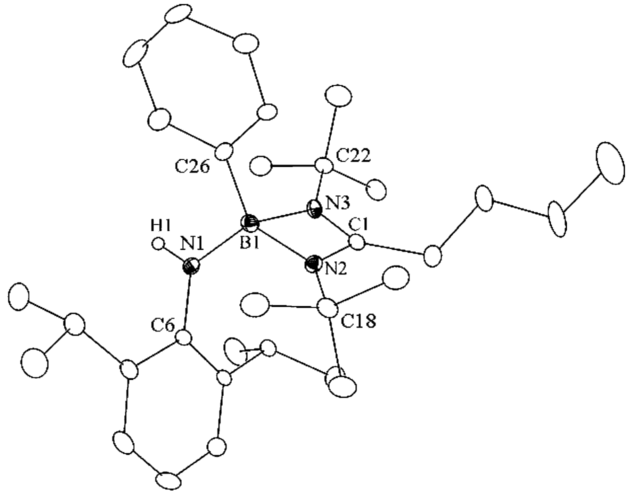


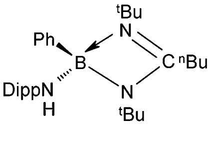
Figure 6. Thermal ellipsoid plot of {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$ C^{n}Bu} (**10a**). For clarity, H atoms are omitted except H1 on N1.

Table 7. Selected Bond Lengths and Bond Angles for {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu}(**10a**)

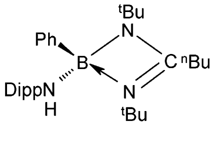
Bond Distances (Å)			
B(1)−N(3)	1.633(5)	N(3)−C(22)	1.481(5)
B(1)−N(2)	1.606(5)	N(2)−C(18)	1.487(4)
B(1)−N(1)	1.499(5)	N(2)−C(1)	1.336(5)
B(1)−C(26)	1.618(5)	N(1)−C(6)	1.424(5)
N(3)−C(1)	1.330(4)		

Bond Angles (deg)			
C(1)−N(3)−B(1)	89.4(3)	N(2)−B(1)−N(3)	79.0(2)
C(1)−N(2)−B(1)	90.3(2)	N(1)−B(1)−N(2)	117.2(3)
C(6)−N(1)−B(1)	128.3(3)	N(1)−B(1)−N(3)	118.7(3)
N(3)−C(1)−N(2)	101.2(3)	N(1)−B(1)−C(26)	112.5(3)

An X-ray structural analysis confirmed that **10a** contains a four-membered BNCN ring. The molecular geometry and atomic numbering scheme are shown in Figure 6, and selected bond lengths and bond angles are summarized in Table 7. The heterocyclic ring is essentially planar with a torsion angle [B(1)−N(3)−C(1)−N(2)] of 3.0(3)°. The C−N bond distances [1.330(4) and 1.336(5) Å] are almost equal, approximately intermediate between C−N double-bond and C−N(sp^2) single-bond values. The sums of the bond angles at the three-coordinate N and C centers are ca. 360°. These structural features indicate delocalized bonding in the NCN unit with approximately equal contributions from the two canonical forms **D** and **E**.



D



E

Consistently, the endocyclic B−N bond lengths are also approximately equal [1.633(5) and 1.606(5) Å], but are

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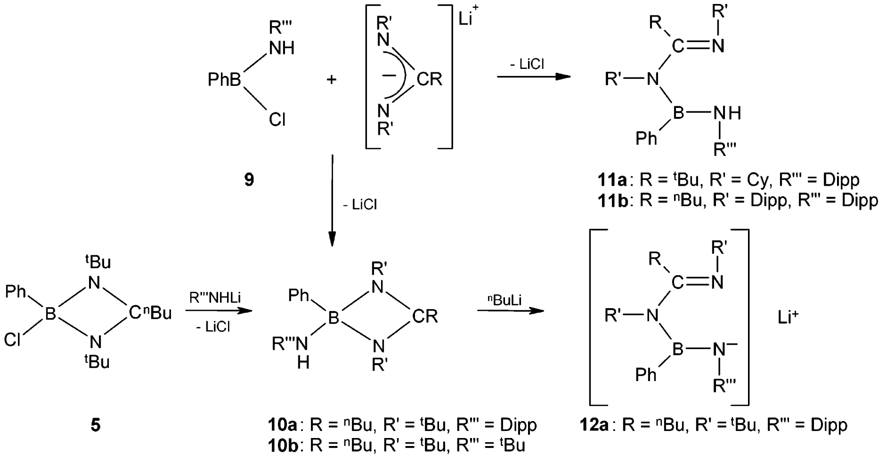
[31] Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, 1978; pp 74−101.

Scheme 1. Syntheses of Hybrid Boraamidinate/Amidinate (BAMAM) Ligands **2**.



significantly longer than those in $\{Cl(Ph)B(\mu\text{-}N^tBu)_2C^nBu\}$ (**5**) [1.567(6) and 1.590(6) Å][15] and fall just outside the range of 1.55−1.61 Å found for B−N bonds involving four-coordinate boron linked to three-coordinate nitrogen.[32] These structural features indicate that the [DippN(H)]PhB unit in **10a** is coordinated more weakly by the amidinate ligand than the (Cl)PhB unit in **5**,[15] likely as a result of stronger π-donation from the exocyclic [DippN(H)] group to boron in **10a**. The exocyclic B−N bond length is shorter [ca. 0.12 Å] than the mean endocyclic B−N length and is slightly shorter [by ca. 0.051 Å] than the mean B−N bond distances involving four-coordinate boron linked to three-coordinate nitrogen.

The monoamino borane $PhBCl[N(H)^tBu]$ (**9b**) was obtained in 93% yield from the reaction of $PhBCl_2$ and 2 equiv of *tert*-butylamine and characterized by CHN elemental analyses and ^1H, ^{11}B, and ^{13}C NMR spectroscopy. Attempts to make the related ring system **10b** by the reaction of **9b** with $Li\{^nBuC(N^tBu)_2\}$ (**4a**) resulted in incomplete reaction, even after prolonged reflux according to ^1H and ^{11}B NMR spectra of the reaction mixture. Subsequently, **10b** was prepared using a different synthetic approach (vide infra).

The reactions of PhBCl[N(H)Dipp] (**9a**) and $Li\{^tBuC(NCy)_2\}$ (**4b**) or $Li\{^nBuC(NDipp)_2\}$ (**4c**) in a 1:1 stoichiometry in *n*-hexane proceed to completion to produce **11a** and **11b** in 89% and 76% yields, respectively (Scheme 1). In contrast to the observations for **10a**, the ^{11}B NMR spectra for **11a** and **11b** exhibit a major, broad resonance at ca. 30−32 ppm, indicative of a three-coordinate boron[31] (i.e., an acyclic structure as depicted in Scheme 1), and a sharp, minor resonance at ca. 1.5 ppm attributable to the cyclic isomer, cf. **10a**. Variable temperature ^{11}B NMR spectra of **11a** in C_6D_6 in the range 280−342 K show that the broad resonance at 30 ppm grows at the expense of the sharp singlet at 1.5 ppm as the temperature is increased. We infer that, in C_6D_6, there is an equilibrium between the acyclic and cyclic forms of **11a** and that, as expected, the former is increasingly favored at high temperatures. At room temperature, the integration of the resonances in the ^{11}B NMR spectra indicates that the three-coordinate form represents ca. 90% of the mixture. Although a comparison of **10b** and **11b** suggests that the steric influence of the two Dipp substituents induces an acyclic structure, steric effects cannot explain the formation of an acyclic arrangement in **11a**, which has cyclohexyl groups attached to both nitrogens. Attempts to monolithiate **11a** and **11b** have been unsuccessful.

The second synthetic approach to bamam ligands involves the nucleophilic replacement of the exocyclic chloro substituent in $\{Cl(Ph)B(\mu\text{-}N^tBu)_2C^nBu\}$ (**5**) by an organoamino group followed by deprotonation with *n*-butyllithium (Scheme 1). The reaction of **5** with Li[N(H)Dipp] in a 1:1 molar ratio was unsuccessful even in boiling THF. When a 1:2 molar ratio was employed, however, a mixture of $\{[DippN(H)](Ph)B(\mu\text{-}N^tBu)_2C^nBu\}$ (**10a**) and Li[N(H)Dipp] was obtained according to multinuclear (^1H, ^{11}B, and ^{13}C) NMR analyses, but this mixture could not be separated. When the analogous reaction of **5** with $Li[N(H)^tBu]$ was carried out in a 1:2 molar ratio at room temperature, $\{[^tBuN(H)](Ph)B(\mu\text{-}N^tBu)_2C^nBu\}$ (**10b**) was obtained in 51% yield. The derivative **10b** was characterized by CHN and multinuclear (^1H, ^{13}C, and ^{11}B) NMR analyses, which indicated a four-coordinate boron center and exhibited the expected resonances for ^nBu, ^tBu, and Ph groups with the appropriate relative intensities.

Interestingly, when the reaction of **5** with $Li[N(H)^tBu]$ was carried out in a 1:2 molar ratio under reflux in THF, the known amidinate complex $\{(Li[^nBuC(N^tBu)_2])_2{\cdot}LiCl{\cdot}THF\}$ was formed and identified by comparison of the ^1H NMR spectrum and unit cell parameters with the literature data.[33] The other product was identified by ^1H NMR spectroscopy data as the bis(amino)borane $PhB[N(H)^tBu]_2$.[5b] Thus, it appears that, under these reaction conditions, the second equivalent of $Li[N(H)^tBu]$ acts as a nucleophile rather than a base toward $\{[^tBuN(H)](Ph)B(\mu\text{-}N^tBu)_2C^nBu\}$ (**10b**) to generate the observed products (Scheme 2). This conclusion was confirmed by a separate reaction in which treatment of **10b** with $Li[N(H)^tBu]$ in THF was shown by ^1H NMR to produce the known products $(Li[^nBuC(N^tBu)_2])_2$ (**4a**)[14a] and $PhB[N(H)^tBu]_2$.[5b]

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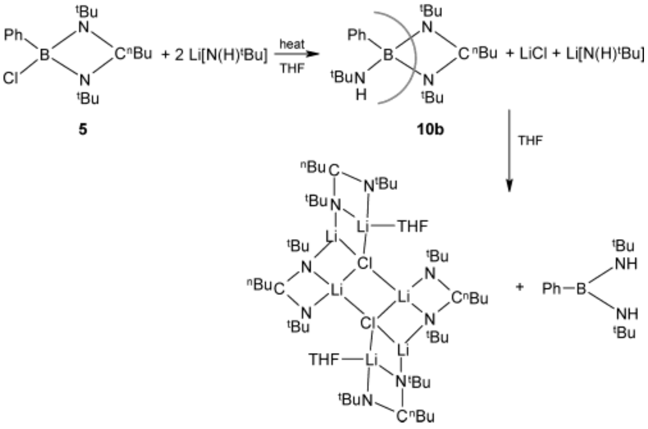
(32) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(33) Chivers, T.; Downard, A.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 4347.

Scheme 2. Displacement of the Amidinate Ligand in **5** by a ^{t}BuNH Group.



Treatment of **10a** with *n*-butyllithium produces the lithiated bamam ligand {Li[DippN]PhB(N^{t}Bu)C^{n}Bu(N^{t}Bu)} (**12a**) in a 62% yield. The product has been characterized by CHN elemental analyses, and multinuclear (^{1}H, ^{13}C, ^{11}B, and ^{7}Li) NMR and IR spectroscopy. Monolithiation was indicated by the lack of an N−H stretch in the IR spectrum and the ^{7}Li NMR resonance at δ 0.13. Deprotonation promotes opening of the four-membered BN_2C ring in **10a** as indicated by ^{11}B NMR chemical shifts (δ 29 for **12a** vs δ 5 for **10a**) and ^{1}H NMR data (inequivalence of the N^{t}Bu groups in **12a**: δ 1.40 and 0.99 vs equivalent N^{t}Bu groups in **10a**: δ 1.03). The NMR spectra reveal that **12a** can be isolated in a reasonably pure form with **10a** as a minor (<8%) impurity. Variation of the reaction temperature, reaction time, or purification method of the isolated product has little effect on the purity or yield of the product. Crystals of **12a** were obtained from THF, but these crystals are unstable in the absence of solvent and attempts to mount them on the diffractometer have been unsuccessful. Nevertheless, the NMR data indicate that the bamam ligand is *N*(R′),*N*(R‴)-chelated to Li as expected.

Conclusions

The first monomeric dilithium boraamidinates have been prepared and structurally characterized. Unlike previously reported dilithio boraamidinates, the lithium ions in these new derivatives are solvated and this structural feature, rather than the bulkiness of the Dipp substituent, may account for the monomeric structures. The preparation of hybrid boraamidinate/amidinate ligands by two different routes has revealed that either four-membered BNCN rings, with an exocyclic amido (NHR) substituent, or an acyclic NBNCN chelating ligand are formed depending on the substituents attached to the nitrogen or carbon atoms. These structural isomers are readily distinguished by their characteristic ^{11}B NMR chemical shifts, which fall in the range δ 0−5 for the cyclic systems (four-coordinate boron) and δ 30−35 for the acyclic ligands (three-coordinate boron). Monolithiation of the exocyclic amido substituent on the ring system in {[DippN(H)](Ph)B(μ-N^{t}Bu)$_2$C^{n}Bu} provides the alkali derivative {Li[DippN]PhB(N^{t}Bu)C^{n}Bu(N^{t}Bu)}. Future studies will focus on magnesium complexes of this ligand.

Supporting Information Available: X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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