ChemComm

A new route to dilithio boraamidinates: formation and X-ray structures of the dimeric and trimeric clusters $\{Li_2[RB(NBu^t)_2]\}_x$ (R = Bu^n, x = 2 and R = Me, x = 3)

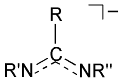
Justin K. Brask, Tristram Chivers* and Gabriele Schatte

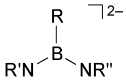
Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary, Alberta, Canada T2N 1N4.
E-mail: chivers@ucalgary.ca

Received (in Cambridge, UK) 20th July 2000, Accepted 18th August 2000

The dilithio boraamidinate complexes $\{Li_2[RB(NBu^t)_2]\}_x$ (R = Bu^n, x = 2 and R = Me, x = 3), prepared unexpectedly by treating $B[N(H)Bu^t]_3$ with 3 equiv. LiR, represent the first structurally characterized s-block metal derivatives of the boraamidinate ion.

Amidinate ions $[RC(NR')(NR'')]^-$ **1** have been investigated extensively as ligands for both transition metal and main group element centers.[1] In the presence of Lewis bases, *e.g.* THF or HMPA, the lithium derivatives of these important reagents form dimeric step-shaped structures.[2,3] This structural motif is also evident in the lithio ligands of the lithium oxide complex $\{Li[Bu^nC(NBu^t)_2]\}_4{\cdot}Li_2O$.[4] By contrast, the isoelectronic boraamidinate ions $[RB(NR')(NR'')]^{2-}$ **2** have received little attention. The reagent $\{Li_2[PhB(NBu^t)_2]\}_n$, prepared by dilithiation of $PhB[N(H)Bu^t]_2$, has been used in metathetical reactions to generate several main group derivatives, *e.g.* $[PhB(\mu\text{-}NBu^t)_2]_2Te$[5] and $[PhB(\mu\text{-}NBu^t)_2Pb]_2$,[6] and the transition-metal derivative $[PhB(\mu\text{-}NBu^t)_2]_2Ti$.[7] The X-ray structures of these complexes were reported, but s-block metal derivatives of **2** have not been structurally characterized. We describe here the unexpected formation and X-ray structures of dimeric and trimeric dilithio boraamidinates $\{Li_2[RB(NBu^t)_2]\}_x$ (**3**: R = Bu^n, x = 2; **4a**: R = Me, x = 3) from the reaction of $B[N(H)Bu^t]_3$ with LiR (R = Bu^n or Me, respectively).


1


2

Treatment of the trisaminoborane $B[N(H)Bu^t]_3$ with 3 equiv. $LiBu^n$ in *n*-hexane gives a 1:2 mixture of the dimer $\{Li_2[Bu^nB(NBu^t)_2]\}_2$ **3** and $LiN(H)Bu^t$ [eqn. (1)]. Complex **3** is the first product to crystallize from *n*-hexane at 0 °C and it can be isolated in 71% yield free from $LiN(H)Bu^t$.† The ^1H NMR spectrum of **3** in C_6D_6 consists of a single Bu^t resonance at δ 1.25 as well as resonances corresponding to a Bu^n group ($Bu^n{:}Bu^t \approx 1{:}2$). The ^7Li and ^{11}B NMR spectra each exhibit single resonances at δ −0.63 and 36.6 ppm, respectively.

$$3\,LiR + B[N(H)Bu^t]_3 \rightarrow {}^1/_x\,\{Li_2[RB(NBu^t)_2]\}_x + LiN(H)Bu^t + 2\,RH$$

3: R = Bu^n, x = 2
4a: R = Me, x = 3
4b: R = Me, x = 2 (1)

X-Ray structure analysis revealed a 10-atom $Li_4B_2N_4$ cluster core for **3** (Fig. 1),‡ isostructural with the $Li_4Si_2N_4$ framework in $\{Li_2[(Me)_2Si(NBu^t)_2]\}_2$.[8] Although no crystallographic symmetry is imposed on the molecule, **3** displays near D_{2d} symmetry with the S_4-axis parallel to the B(1)–B(2) vector. This structure is consistent with the solution NMR data. The B–N distances for **3** [mean 1.458(4) Å, range 1.451(4)–1.464(4) Å] are similar to those found in $[PhB(\mu\text{-}NBu^t)_2]_2Ti$ [mean 1.464(10) Å, range 1.453(9)–1.475(10) Å],[7] while the Li–N distances [mean 2.037(6) Å, range 2.009(6)–2.091(5) Å] fall in the range for those of $\{Li_2[(Me)_2Si(NBu^t)_2]\}_2$ [mean 2.075(7) Å, range 2.003(6)–2.129(6) Å].[8] The distortion of the central Li_4N_4 cube along the S_4-axis [Li–N–Li: mean 75.42(20)°, range 68.30(18)–88.3(2)°; N–Li–N: mean 97.15(30)°, range 70.99(18)–110.8(2)°; Li(2)–N(1)–Li(1)–N(2) 46.16(18)°, Li(4)–N(4)–Li(3)–N(3) = 46.22(18)°] is attributed to the rigidity of the boraamidinate ions **2** (R = Bu^n, R′ = R″ = Bu^t). The geometry at the three-coordinate boron atoms of these dianions is essentially planar [Σ B(1) = Σ B(2) = 359.9(3)°]. The agostic C(–H)···Li contacts in **3** (mean 2.41 Å) are considerably shorter than those reported for the cluster complex $\{Li_3[Sb(NBu^t)_3]\}_2$ (mean 2.65 Å),[9] but longer than those observed for $\{Li_2[(Me)_2Si(NBu^t)_2]\}_2$ (mean 2.34 Å).[8]

The formation of **3** requires cleavage of a B–N bond in favor of a B–C bond. In effect, the added $LiBu^n$ functions as a base to deprotonate two $N(H)Bu^t$ groups per $B[N(H)Bu^t]_3$ molecule and as a nucleophile to displace the third $N(H)Bu^t$ group in the form of $LiN(H)Bu^t$. A similar displacement was observed in the reaction of $[(THF)_2Li]_2[Nb(NMes)_3(NHMes)]$ with 1 equiv. $LiBu^n$ to produce the alkyl complex $[(THF)_2Li]_2[Bu^nNb(NMes)_3]$ and LiN(H)Mes in a 1:1 molar ratio.[10] In order to gauge the versatility of this novel methodology for preparing dilithio boraamidinates, $B[N(H)Bu^t]_3$ was treated with 3 equiv. LiMe in diethyl ether. After removal of $LiN(H)Bu^t$, recrystallization of the product mixture from *n*-pentane gave $\{Li_2[MeB(NBu^t)_2]\}_3$ **4a** in 28% yield [eqn. (1)].†

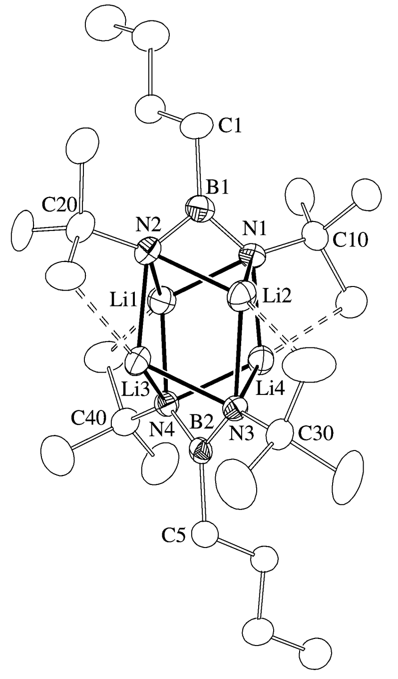


Fig. 1 Molecular structure of $\{Li_2[Bu^nB(NBu^t)_2]\}_2$ **3** (40% probability ellipsoids). For clarity, H atoms are omitted and only one orientation of the disordered Bu^t group centered at C(20) is shown. Relevant bond distances and bond angles are provided in the text.

DOI: 10.1039/b005852l

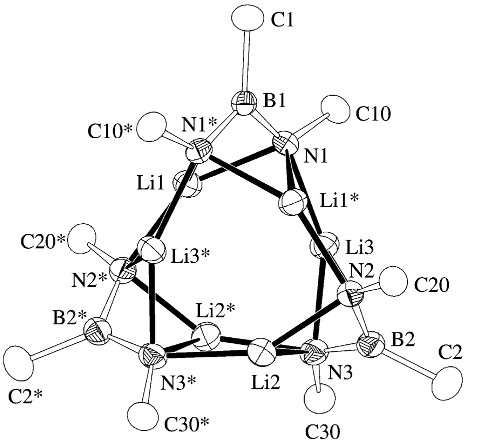


Fig. 2 Molecular structure of $\{Li_2[MeB(NBu^t)_2]\}_3$ **4a** (40% probability ellipsoids). For clarity, H atoms are omitted and only the α-carbon atoms of the Bu^t groups are shown. Starred atoms are related by the symmetry transformation: $-x + 1, y, -z + {}^1/_2$. Selected bond distances (Å) and angles (°): B(1)–N(1) 1.452(3), B(1)–C(1) 1.604(4), B(2)–N(2) 1.456(3), B(2)–N(3) 1.451(3), B(2)–C(2) 1.608(3), Li–N [mean 2.051(4), range 2.001(4)–2.100(4)]; N(1)–B(1)–N(1*) 110.0(2), N(1)–B(1)–C(1) 125.02(12), N(2)–B(2)–N(3) 110.51(19), N(2)–B(2)–C(2) 124.4(2), N(3)–B(2)–C(2) 125.0(2).

The ^1H NMR spectrum of **4a** in C_6D_6 shows Bu^t and Me resonances at δ 1.29 and 0.85 in a 2 : 1 ratio, respectively. Single resonances are observed at δ −0.86 and 35.5 in the ^7Li and ^{11}B NMR spectra, respectively. A more soluble product, tentatively identified as the dimer $\{Li_2[MeB(NBu^t)_2]\}_2$ **4b**, was characterized by ^1H, ^7Li and ^{11}B NMR spectra.† The molar ratio of **4a** : **4b** was *ca.* 1 : 3 based on the integrated intensities of the resonances in the ^1H NMR spectrum of the mixture.

X-Ray structure analysis of **4a** disclosed a novel trimeric arrangement based on a severely distorted $Li_6(NBu^t)_6$ hexagonal prism, for which alternate Li_2N_2 rings are *N*,*N*′-capped by a BMe unit (Fig. 2).‡ The resulting 15-atom $Li_6B_3N_6$ core provides the first example of a tricapped hexagonal prismatic cluster. Although only a C_2-axis is imposed on the molecule crystallographically [through C(1), B(1) and the centre of the Li(2)N(3)Li(2*)N(3*) ring], **4a** displays near D_3 symmetry. The capped Li_2N_2 rings in **4a** deviate greatly from planarity [Li(1*)–N(1)–Li(1)–N(1*) = 44.99(16)°, Li(3)–N(2)–Li(2)–N(3) 45.14(13)°] as compared with their non-capped counterparts [Li(2*)–N(3)–Li(2)–N(3*) 10.9(2)°, Li(1*)–N(1)–Li(3)–N(2) −11.60(16)°], demonstrating the dominance of the dianion **2** in structure formation, *cf.* structural direction by the trianions $[Sb(NR)_3]^{3-}$.[11]

The reaction of readily accessible trisaminoboranes, $B[N(H)R]_3$ (R = alkyl or aryl),[12] with the appropriate organolithium reagent is a potentially versatile method for generating dianionic ligands **2** with variable steric requirements. Unlike the lithiation of bisaminoboranes $RB[N(H)R']_2$,[7] this new route to dilithio boraamidinates does not require the preparation of RCl_2 reagents.

We thank Dr R. McDonald (University of Alberta) for assistance with the X-ray data collection for **3** and **4a** and NSERC (Canada) for financial support.

Notes and references

† *Synthesis*: **3**: a 2.5 M solution of $LiBu^n$ in hexanes (2.49 mL, 6.33 mmol) was added slowly to a solution of $B[N(H)Bu^t]_3$[12] (0.48 g, 2.11 mmol) in *n*-hexane (30 mL) at 23 °C and the mixture was stirred for 2.5 h. Concentration (*ca.* 3 mL), by removal of solvent *in vacuo*, and subsequent cooling (0 °C for 1 h) of the resulting solution yielded colorless blocks of **3** (0.33 g, 0.74 mmol, 71%); mp 109–110 °C. Anal. Calc. for $BC_{12}H_{27}Li_2N_2$: C, 64.33; H, 12.15; N, 12.50. Found: C, 63.80; H, 11.64; N, 12.65%. ^1H NMR (C_6D_6, 23 °C): δ 1.68 [m, 4 H, $CH_2(CH_2)_2CH_3$], 1.35 [m, 2 H, $CH_2(CH_2)_2CH_3$], 1.25 (s, 18 H, Bu^t), 1.11 [t, 3 H, $CH_2(CH_2)_2CH_3$]. ^7Li NMR (C_6D_6, 23 °C): δ −0.63 (s). ^{11}B NMR (C_6D_6, 23 °C): δ 36.6 (s). A 1 mL aliquot of the initial *n*-hexane reaction mixture was pumped to dryness *in vacuo* and taken up in C_6D_6. The ^1H and ^7Li NMR spectra indicated the presence of **3** and $LiN(H)Bu^t$ [^1H NMR: δ 1.36 (s, Bu^t), *cf.* lit.:[13] 1.37, ^7Li NMR: δ 0.14 (s)] in a 1:2 molar ratio [eqn. (1)].

4a: a 1.4 M solution of LiMe in diethyl ether (4.52 mL, 6.33 mmol) was added slowly to a solution of $B[N(H)Bu^t]_3$[12] (0.48 g, 2.11 mmol) in diethyl ether (30 mL) at 23 °C and the mixture was stirred for 2.5 h. The resulting cloudy reaction mixture was filtered to remove $LiN(H)Bu^t$ [^1H and ^7Li NMR (*vide supra*)] and subsequently pumped to dryness by removal of solvent *in vacuo*. The white powder obtained was redissolved in *n*-pentane (5 mL) and the solution was cooled (−20 °C for 4 days), yielding colorless blocks of **4a** (0.11 g, 0.20 mmol, 28%); mp 124–125 °C (decomp.). Anal. Calc. for $BC_9H_{21}Li_2N_2$: C, 59.40; H, 11.63; N, 15.39. Found: C, 58.76; H, 11.21; N, 14.68%. ^1H NMR (C_6D_6, 23 °C): δ 1.29 (s, 18 H, Bu^t), 0.85 (s, 3 H, Me). ^7Li NMR (C_6D_6, 23 °C): δ −0.86 (s). ^{11}B NMR (C_6D_6, 23 °C): δ 35.5 (br).

The white powder, prior to the recrystallization step, contains a second product **4b**: ^1H NMR (C_6D_6, 23 °C): δ 1.20 (s, 18 H, Bu^t), 0.81 (s, 3 H, Me). ^7Li NMR (C_6D_6, 23 °C): δ −0.69 (s). ^{11}B NMR (C_6D_6, 23 °C): δ 35.5 (br). The CHN analyses for the mixture of **4a** and **4b** were consistent with the empirical formula $Li_2[MeB(NBu^t)_2]$.

‡ *Crystal data*: for **3**: $C_{24}H_{54}B_2Li_4N_4$, M = 448.09, monoclinic, a = 12.671(5), b = 17.562(5), c = 14.026(5) Å, β = 98.825(5)°, V = 3084.2(9) Å^3, T = 193(2) K, space group $P2_1/n$ [a non-standard setting of $P2_1/c$ (no. 14)], Z = 4, μ(Mo-Kα) = 0.053 mm^{-1}, D_c = 0.965 g cm^{-3}, 9679 reflections measured, 5898 unique (R_{int} = 0.0791), 2277 observed [$I > 2\sigma(I)$]. The final R_1 and $wR_2(F^2)$ were 0.0641 [$I > 2\sigma(I)$] and 0.1678 (all data), respectively.

For **4a**: $C_{27}H_{63}B_3Li_6N_6$, M = 545.90, monoclinic, a = 17.3587(13), b = 12.0750(8), c = 19.2718(14) Å, β = 116.0730(14)°, V = 3628.4(4) Å^3, T = 193(2) K, space group $C2/c$ (no. 15), Z = 4, μ(Mo-K$_\alpha$) = 0.055 mm^{-1}, D_c = 0.999 g cm^{-3}, 10 572 reflections measured, 3104 unique (R_{int} = 0.0388), 2302 observed [$I > 2\sigma(I)$]. The final R_1 and $wR_2(F^2)$ were 0.0611 [$I > 2\sigma(I)$] and 0.1775 (all data), respectively.

CCDC 182/1749. See http://www.rsc.org/suppdata/cc/b0/b005852l/ for crystallographic files in .cif format.

1 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.
2 D. Stalke, M. Wedler and F. T. Edelmann, *J. Organomet. Chem.*, 1992, **431**, C1.
3 J. Barker, D. Barr, N. D. R. Barnett, W. Clegg, I. Cragg-Hine, M. G. Davidson, R. P. Davies, S. M. Hodgson, J. A. K. Howard, M. Kilner, C. W. Lehmann, I. Lopez-Solera, R. E. Mulvey, P. R. Raithby and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1997, 951.
4 T. Chivers, A. Downard and M. Parvez, *Inorg. Chem.*, 1999, **38**, 4347; T. Chivers, A. Downard and G. P. A. Yap, *J. Chem. Soc., Dalton Trans.*, 1998, 2603.
5 H.-J. Koch, H. W. Roesky, S. Besser and R. Herbst-Irmer, *Chem. Ber.*, 1993, **126**, 571.
6 A. Heine, D. Fest, D. Stalke, C. D. Habben, A. Meller and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1990, 742.
7 D. Fest, C. D. Habben, A. Meller, G. M. Sheldrick, D. Stalke and F. Pauer, *Chem. Ber.*, 1990, **123**, 703.
8 D. J. Brauer, H. Bürger and G. R. Liewald, *J. Organomet. Chem.*, 1986, **308**, 119.
9 M. A. Beswick, N. Choi, C. N. Harmer, A. D. Hopkins, M. McPartlin, M. A. Paver, P. R. Raithby, A. Steiner, M. Tombul and D. S. Wright, *Inorg. Chem.*, 1998, **37**, 2177.
10 D. P. Smith, K. D. Allen, M. D. Carducci and D. E. Wigley, *Inorg. Chem.*, 1992, **31**, 1319.
11 M. A. Beswick, M. E. G. Mosquera and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 2437.
12 D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 1959, 2927.
13 N. D. R. Barnett, W. Clegg, L. Horsburgh, D. M. Lindsay, Q.-Y. Liu, F. M. Mackenzie, R. E. Mulvey and P. G. Williard, *Chem. Commun.*, 1996, 2321.