Synthesis and X-ray structures of amidinate, oxoamidate, and thioamidate complexes of boron

Pierre Blais, Tristram Chivers, Andrew Downard, and Masood Parvez

Abstract: The reactions of $PhBCl_2$ with $Li[CE(N^tBu)(^nBu)]$ or $Li[CS(N^tBu)(NH^tBu)]$ (1:1 molar ratio) in toluene at 23°C produced the heterocycles $Ph(Cl)B(\mu\text{-}N^tBu)(\mu\text{-}E)C(^nBu)$ (**1a**, E = N^tBu; **1b**, E = O; **1c**, E = S) or $Ph(Cl)B(\mu\text{-}N^tBu)(\mu\text{-}S)C(NH^tBu)$ (**2**), which were characterized by ^1H, ^{11}B and ^{13}C NMR and by mass spectra. X-ray structural determinations revealed that **1a**, **1c** and **2** contain four-membered rings. In **2** the thioamidate ligand adopts an *N*,*S* bonding mode. Crystal data: **1a**, monoclinic, space group $P2_1$, a = 8.816(3), b = 11.311(2), c = 10.168(3) Å, β = 98.86(3)°, V = 1001.7(5) Å^3, Z = 2, R = 0.042, and R_w = 0.020; **1c**, monoclinic, space group $P2_1/n$, a = 7.617(2), b = 11.200(1), c = 19.568(2), β = 90.74(2)°, V = 1669.1(5) Å^3, Z = 4, R = 0.046, and R_w = 0.059; **2**, monoclinic, space group $P2_1/a$, a = 11.357(2), b = 12.289(2), c = 12.620(3) Å, β = 95.43(2)°, V = 1753.4(5) Å^3, Z = 4, R = 0.043, and R_w = 0.027.

Key words: boron, amidinate, oxoamidate, thioamidate, X-ray structures.

Résumé : Les réactions entre le $PhBCl_2$ et $Li[(CE(N^tBu)(^nBu)]$ ou $Li[CS(N^tBu)(NH^tBu)]$ (rapport molaire de 1:1), dans le toluène, à 23°C, conduisent à la formation d'hétérocycles $Ph(Cl)B(\mu\text{-}N^tBu)(\mu\text{-}E)C(^nBu)$ (**1a**, E = N^tBu; **1b**, E = O; **1c**, E = S) ou $Ph(Cl)B(\mu\text{-}N^tBu)(\mu\text{-}S)C(NH^tBu)$ (**2**) que l'on a caractérisés par RMN du ^1H, ^{11}B et ^{13}C ainsi que par spectrométrie de masse. La diffraction des rayons appliquée aux produits **1a**, **1c** et **2** révèle qu'ils comportent des cycles à quatre chaînons. Dans le produit **2**, le ligand thioamidate adopte un mode de liaison *N,S*. Les données cristallographiques: **1a**, monoclinique, groupe d'espace $P2_1$, a = 8,816(3), b = 11,311(2) et c = 10,168(3)Å, β = 98,86(3)°, V = 1001,7(5)Å^3, Z = 2, R = 0,042 et R_w = 0,020; **1c**, monoclinique, groupe d'espace $P2_1/n$, a = 7,617(2), b = 11,200(1) et c = 19,568(2)Å, β = 90,74(2)°, V = 1669,1(5)Å^3, Z = 4, R = 0,046 et R_w = 0,059 et **2**, monoclinique, groupe d'espace $P2_1/a$, a = 11,357(2), b = 12,289(2) et c = 12,620(3) Å, β = 95,43(2)°, V = 1753,4(5) Å^3, Z = 4, R = 0,043 et R_w = 0,027.

Mots clés : bore, amidinate, oxoamidate, thiamidate, structures, diffraction des rayons X.

[Traduit par la Rédaction]

Introduction

There is an extensive literature of heterocyclic compounds involving boron–nitrogen (B-N) linkages (1). Four-membered rings are uncommon in comparison with larger ring sizes, but such systems are well established for three-coordinate boron when another heteroatom, e.g., Si(2), P(2–4), Te(5, 6), is incorporated into the ring.

Carbon-containing four-membered B-N heterocycles are relatively rare. Paetzold et al. (7) prepared the three-coordinate boron system $C_6F_5B(\mu\text{-}N^tBu)_2CPh_2$ by the [2+2] cycloaddition of $C_6F_5B \equiv N^tBu$ and $^tBuN = CPh_2$. A similar approach employing iso(thio)cyanates was used by Ansorge et al. (8) to create related four-coordinate boron systems. An interesting feature of the latter is the thermally induced isomerization of the *N*,*N′*-chelated complex to the unsymmetrical (*N*,*E*-chelation) isomer (Scheme 1). This process occurs more readily for E = S than for E = O and it is prevented by bulky *R* groups, e.g., ^tBu (8).

An alternative route to $\overline{\text{BNCN}}$ heterocycles involves the reaction of BX_3 (X = Cl, Br) with $Li[CPh(NSiMe_3)_2]$ which produces $X_2BCPh(NSiMe_3)_2$ (9). Although there have been extensive studies of amidinate complexes of the heavier Group 13 elements (Al, Ga, In, Tl) in recent years (10–18), investigations of boron derivatives are limited to this single report. The chloride was obtained as a yellow oil and the bromide gave yellow crystals, but no structural information was obtained (9).

Here we describe the synthesis and characterization of the series of $\overline{\text{BNCE}}$ (E = N, O, S) heterocycles **1a–c** by the route shown in eq. [1]. The preparation and X-ray structures of the hexameric reagents $\{Li[CE(N^tBu)(^nBu)]\}_6$ (E = O, S) were published very recently (19). Although a few transition-metal complexes of oxoamidate and thioamidate anions $[RC(E)(NR')]^-$ have been reported (E = O (20), S (21)), none of them were generated from these anions by metathetical reactions. Furthermore, heterocycles **1b** and **1c** are, to our knowledge, the first examples of *p*-block element complexes

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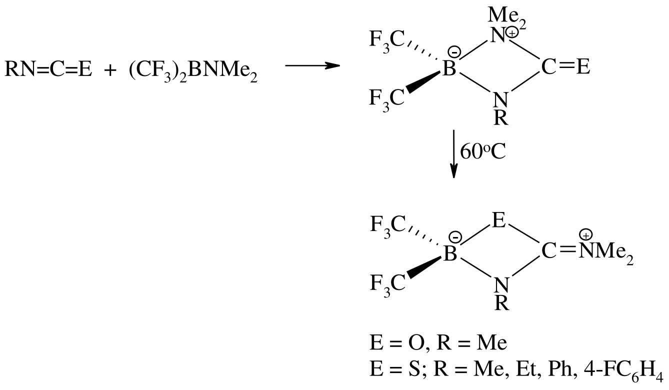
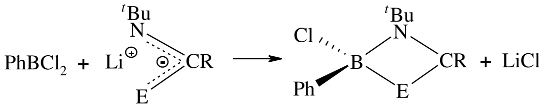
Scheme 1.

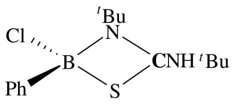


of these bidentate ligands. The structure of the related heterocycle **2** is included for comparison.

[1]



1a, E = N ^{t}Bu, R = ^{n}Bu
1b, E = O, R = ^{n}Bu
1c, E = S, R = ^{n}Bu



2

Experimental

The reagents ^{t}BuNCE (E = N^{t}Bu, O, S), Li^{n}Bu (2.5 M in hexane), ^{t}BuNH$_2$, and PhBCl$_2$ were all obtained from Aldrich and used as received. The reagents Li[CE(N^{t}Bu)^{n}Bu] were prepared by the addition of Li^{n}Bu to an equimolar amount of ^{t}BuNCE (E = N^{t}Bu, O, S) in toluene at 23°C (19, 22). LiNH^{t}Bu was made by the reaction of dry ^{t}BuNH$_2$ with Li^{n}Bu. All solvents were dried with appropriate drying agents and distilled. Deuterated solvents were degassed immediately before use. All reactions and manipulations of moisture and air-sensitive products were carried out using a glove box and Schlenk techniques under an atmosphere of high purity, dried argon.

^{1}H NMR spectra were recorded on a Bruker ACE200 spectrometer and the chemical shifts are reported relative to Me$_4$Si in C$_6$D$_6$. ^{11}B and ^{13}C NMR spectra were recorded on a Bruker AMX300 spectrometer and the chemical shifts are reported relative to BF$_3$·OEt$_2$ in C$_6$D$_6$ and TMS in C$_6$D$_6$, respectively. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary. IR spectra were obtained as Nujol mulls on a Mattson 4030 FTIR spectrophotometer. Mass spectra (EI, 70eV) were measured on a Kratos MS80RFA instrument.

Preparation of Ph(Cl)B(μ-N^{t}Bu)$_2$C^{n}Bu (1a)

A solution of PhBCl$_2$ (0.925 g, 5.82 mmol) in toluene (5 mL) was added dropwise via a stainless steel cannula to a solution of Li[C(N^{t}Bu)$_2$^{n}Bu] (1.267 g, 5.29 mmol) in toluene (10 mL) at 23°C. The mixture was stirred for 2 h to give a white precipitate and a pale yellow solution. Lithium chloride was removed by filtration and removal of solvent yielded a viscous yellow oil, which was washed with diethyl ether (2 × 5 mL) to give pale yellow crystals of **1a** (1.46 g, 4.36 mmol, 82%); mp 76–79°C. ^{1}H NMR (in C$_6$D$_6$, 25°C, δ): 8.1–7.2 (m, 5H, C$_6$*H*$_5$), 2.14 (m, 2H, C*H*$_2$), 1.60 (m, 2H, C*H*$_2$), 1.17 (s, 18H, C(C*H*$_3$)$_3$), 1.11 (m, 2H, C*H*$_2$), 0.73 (t, 3H, C*H*$_3$). ^{13}C NMR (in C$_6$D$_6$, 25°C, δ): 176.3 (s, *C*(N^{t}Bu)$_2$^{n}Bu), 134.0–128.2 (m, *C*$_6$H$_5$B-), 54.1 (s, -*C*(CH$_3$)$_3$), 31.6 (s, -C(*C*H$_3$)$_3$), 49.3 (s, *C*H$_2$CH$_2$CH$_2$CH$_3$), 30.4 (s, CH$_2$*C*H$_2$CH$_2$CH$_3$), 24.4 (s, CH$_2$CH$_2$*C*H$_2$CH$_3$), 6.4 (s, -CH$_2$CH$_2$CH$_2$*C*H$_3$). ^{11}B NMR (in C$_6$D$_6$, 25°C, δ): 6.8 (s). EIMS: *m*/*z* 334 (M$^+$, $C_{19}H_{32}N_2{}^{11}B^{35}Cl$; good agreement between calculated and observed isotopic distribution). Anal. calcd. for $C_{19}H_{32}N_2BCl$: C 68.16, H 9.65, N 8.37; found: C 67.76, H 9.97, N 8.45.

Preparation of Ph(Cl)B(μ-N^{t}Bu)(μ-O)C^{n}Bu (1b)

A solution of PhBCl$_2$ (0.889 g, 5.60 mmol) in toluene (5 mL) was added dropwise to a solution of Li[CO(N^{t}Bu)^{n}Bu] (0.885 g, 5.42 mmol) in toluene (10 mL) at 23°C. Observations and work-up procedure were similar to those described for **1a**. The crude product was washed with cold (–80°C) hexane (5 mL) (6 × 5 mL) to give **1b** as a yellow solid (1.03 g, 3.69 mmol, 68%); mp 111–112°C. ^{1}H NMR (in C$_6$D$_6$, 25°C, δ): 8.3–7.2 (m, 5H, C$_6$*H*$_5$), 1.93 (m, 2H, C*H*$_2$), 1.42 (m, 2H, C*H*$_2$), 1.14 (m, 2H, C*H*$_2$), 0.98 (s, 9H, C(C*H*$_3$)$_3$), 0.70 (t, 3H, C*H*$_3$). ^{13}C NMR (in C$_6$D$_6$, 25°C, δ): 184.2 (s, *C*O(N^{t}Bu)^{n}Bu), 136–127 (m, *C*$_6$H$_5$B-), 54.1 (s, -*C*(CH$_3$)$_3$), 29.9 (s, -C(*C*H$_3$)$_3$), 31.0 (s, -*C*H$_2$CH$_2$CH$_2$CH$_3$), 27.1 (s, -CH$_2$*C*H$_2$CH$_2$CH$_3$), 23.1 (s, -CH$_2$CH$_2$*C*H$_2$CH$_3$), and 14.5 (s, -CH$_2$CH$_2$CH$_2$*C*H$_3$). ^{11}B NMR (in C$_6$D$_6$, 25°C, δ): 11.6 (s). FAB–MS: *m*/*z* 280 [(M+H)$^+$]. Anal. calcd. for $C_{15}H_{23}NOBCl$: C 64.56, H 8.33, N 5.02; found: C 63.91, H 8.41, N 4.67.

Preparation of Ph(Cl)B(μ-N^{t}Bu)(μ-S)C^{n}Bu (1c)

A solution of PhBCl$_2$ (0.997 g, 6.28 mmol) in hexane (5 mL) was added dropwise to a solution of Li[CS(N^{t}Bu)^{n}Bu] (0.880 g, 4.91 mmol) in hexane (10 mL) at 23°C. Observations and work-up procedure were similar to those described for **1a**. The crude product was washed with diethyl ether (2 × 3 mL) to give **1c** as a yellow powder (0.455 g, 1.54 mmol, 31%); mp 67–69°C. ^{1}H NMR (in C$_6$D$_6$, 25°C, δ): 8.4–7.0 (m, 5H, C$_6$*H*$_5$), 2.23 (m, 2H, C*H*$_2$), 1.40 (m, 2H, C*H*$_2$), 1.11 (m, 2H, C*H*$_2$), 1.07 (s, 9H, C(C*H*$_3$)$_3$), 0.71 (t, 3H, C*H*$_3$). ^{13}C NMR (in C$_6$D$_6$, 25°C, δ): 203.7 (s, *C*S(N^{t}Bu)^{n}Bu), 136–128 (m, *C*$_6$H$_5$B-), 60.5 (s, -*C*(CH$_3$)$_3$), 29.5 (s, -C(*C*H$_3$)$_3$) and (CH$_2$*C*H$_2$CH$_2$CH$_3$), 37.0 (s, -*C*H$_2$CH$_2$CH$_2$CH$_3$), 22.8 (s, -CH$_2$CH$_2$*C*H$_2$CH$_3$), and 14.2 (s, -CH$_2$CH$_2$CH$_2$*C*H$_3$). ^{11}B NMR (in C$_6$D$_6$, 25°C, δ): 6.5 (s). EIMS: *m*/*z* 295 (M$^+$). Anal. calcd. for $C_{15}H_{23}NSBCl$: C 60.92, H 7.86, N 4.74; found: C 61.82, H 8.49, N 4.55.

Preparation of Ph(Cl)B(μ-N^{t}Bu)(μ-S)CN(H)^{t}Bu (2)

A solution of *tert*-butyl isothiocyanate (1.94 g, 16.8 mmol) in toluene (10 mL) was added dropwise to a slurry of LiNH^{t}Bu (2.68 g, 33.9 mmol) in toluene (15 mL) at 20°C. The reaction mixture was stirred for 18 h. Solvent and

Table 1. Crystallographic data for **1a**, **1c,** and **2**.

	1a	**1c**	**2**
Formula	$C_{19}H_{32}N_2BCl$	$C_{15}H_{23}NBClS$	$C_{15}H_{24}N_2BClS$
*F*w	334.74	295.68	310.69
Space group	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)
a, Å	8.816 (3)	7.617 (2)	11.357 (2)
b, Å	11.311 (2)	11.200 (1)	12.289 (2)
c, Å	10.168 (3)	19.568 (2)	12.620 (3)
β, deg	98.86 (3)	90.74 (2)	95.43 (2)
V, Å^3	1001.7 (5)	1669.1 (5)	1753.4 (5)
Z	2	4	4
T, °C	–103.0	–103.0	–103.0
λ, Å	0.71069	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.110	1.177	1.177
μ, cm^{-1}	1.92	3.35	3.29
R^a	0.042	0.046	0.043
$R_w{}^b$	0.020	0.059	0.027

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma w\delta^2/\Sigma wF_o{}^2]^{1/2}$.

^{t}BuNH$_2$ were removed under vacuum and the product was washed with *n*-hexane (2 × 5 mL) to give $Li_2[CS(N^tBu)_2]$ as a very moisture-sensitive yellow powder (2.26 g, 67%). ^{1}H NMR (in C_6D_6, 25°C, δ) 1.18 [s, C(CH_3)$_3$].

A solution of $PhBCl_2$ (0.318 g, 2.00 mmol) in hexane (5 mL) was cooled to –35°C and added dropwise to a slurry of $Li_2[CS(N^tBu)_2]$ (0.400 g, 2.00 mmol) in hexane (10 mL) at –35°C. The reaction mixture was stirred for 5 h at –35°C. The mother liquor was decanted by cannula from the white precipitate and stored at –25°C for 3 days to give colourless crystals of **2** (0.055 g, 15%); mp 124–126°C. The precipitate was extracted with diethyl ether (2 × 20 mL) to give $(PhBS)_3$ (0.075 g, 31% based on boron); EIMS: *m/z* 360 (M$^+$). ^{1}H NMR (in C_6D_6, 25°C): δ 8.2–7.3 (m, 5H, C_6H_5), 5.2 (s, 1H, N*H*), 1.09 (s, 9H, C(CH_3)$_3$), 1.00 [s, 9H, C(CH_3)$_3$)]. ^{13}C NMR (in C_6D_6, 25 °C, δ): 172.3 [*C*S(N^{t}Bu)(NH^{t}Bu)], 136–128 (m, C_6H_5B), 56.3 [HN*C*(CH$_3$)$_3$], 54.6 [N*C*(CH$_3$)$_3$], 29.6 [HNC(*C*H$_3$)$_3$], 28.8 [NC(*C*H$_3$)$_3$]. ^{11}B NMR (in C_6D_6, 25°C, δ): 6.5 (s). EIMS: *m/z* 312 [(M+1)$^+$]. Anal. calcd. for $C_{15}H_{24}BClN_2S$: C 57.99, H 7.79, N 9.02; found: C 57.83, H 7.31, N 8.53.

X-ray analysis

Crystal data for **1a, 1c**, and **2** are summarized in Table 1.[2]

1a

A colourless, prismatic crystal (0.45 × 0.40 × 0.55 mm) was obtained from a mixture of pentane and diethyl ether (1:1) at 23°C. It was coated with epoxy and mounted on a glass fibre. Accurate cell dimensions and a crystal orientation matrix were obtained on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 25 reflections in the range 18.39° < 2θ < 23.96°. Intensity data were collected by the ω/2θ method using a scan speed of 4.0° min^{-1}, scan width (1.31 + 0.34 tan θ)°, and monochromatic MoK$_\alpha$ radiation in the range 4.0° < 2θ < 55.1°.

The intensities of 2443 unique reflections were measured of which 1346 had $I > 3\sigma(I)$. Data were corrected for Lorentz-polarization and absorption effects. The structure was solved by direct methods (23) and expanded using Fourier techniques (24). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Scattering factors were those of Cromer and Waber (25) and allowance was made for anomalous dispersion (26). All calculations were performed using teXsan.[3]

1c

A colourless, prismatic crystal (0.50 × 0.48 × 0.45 mm) was obtained from pentane–Et$_2$O at –14°C. Data collection, structure solution and refinement procedures were similar to those described for **1a** except for the use of a different direct methods program (27). Range of data collected 4.0° < 2θ < 55.1°, scan speed 8.0° min^{-1}, scan width (1.57 + 0.34 tan θ)°, 4063 unique reflections of which 2431 had $I > 3\sigma(I)$.

2

A colourless, prismatic crystal (0.50 × 0.35 × 0.30 mm) was obtained from diethyl ether at –18°C. Data collection, structure solution and refinement procedures were similar to those described for **1c**. Range of data collected 4.0° < 2θ < 51.0°, scan speed 8.0° min $^{-1}$, scan width (1.63 + 0.34 tan θ)°, 4241 unique reflections of which 2330 had $I > 3\sigma(I)$.

Results and discussion

Compounds **1a**–**c** were obtained as moisture-sensitive pale yellow solids by the metathetical reaction illustrated in eq. [1]. They were characterized by elemental analyses and

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[2] Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Tables of hydrogen atom coordinates and bond lengths and angles involving hydrogen atoms have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

[3] teXsan. Single crystal structure analysis software. Version 1.2. Molecular Structure Corp., The Woodlands, Tex. 1992.

Fig. 1. ORTEP drawing of PhB(Cl)(μ-N^{t}Bu)$_2$C^{n}Bu (**1a**).

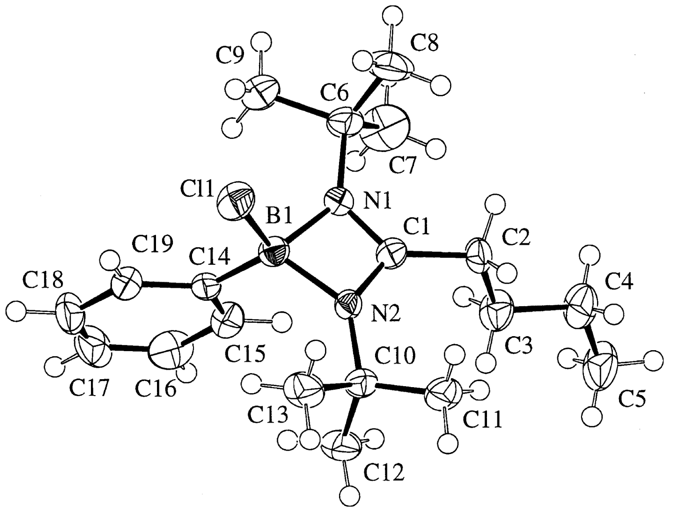
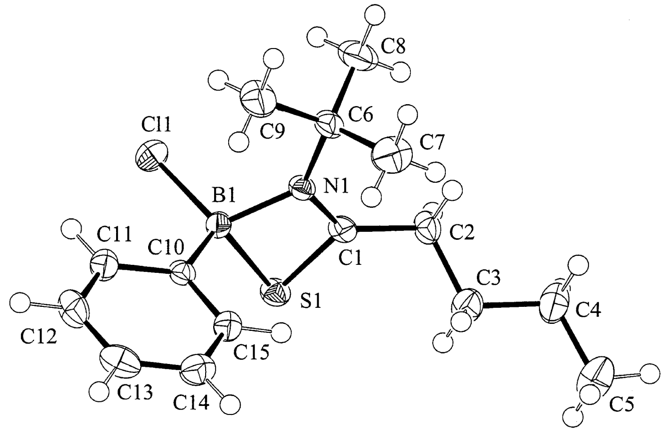


Fig. 2. ORTEP drawing of PhB(Cl)(μ-N^{t}Bu)(μ-S)C^{n}Bu (**1c**).



by ^{1}H, ^{13}C, and ^{11}B NMR spectra. The ^{11}B NMR chemical shifts are in the range δ 6–12 ppm consistent with tetracoordinate boron (28). The highest molecular ions observed in the EI and FAB mass spectra indicate monomeric structures in the solid state. We note, however, that four-coordinate boron compounds involving the [Me$_2$P(S)NR]$^-$ ligand, cf. [RC(S)N^{t}Bu]$^-$, exist in solution as an equilibrium mixture of monomers and dimers (29).

The related complex **2** was obtained unexpectedly, and in low yield, from the reaction of PhBCl$_2$ with Li$_2$[CS(N^{t}Bu)$_2$]. A major by-product of this reaction is (PhBS)$_3$ (30),[4] which accounts for the low yield of **2**.[5] Surprisingly, we were unable to obtain **2** from the reaction of PhBCl$_2$ with Li[CS(NH^{t}Bu)(N^{t}Bu)] (prepared from the reaction of ^{t}BuNCS with LiNH^{t}Bu in a 1:1 molar ratio). The ^{1}H and ^{13}C NMR spectra of **2** both show the presence of inequivalent N^{t}Bu environments and the ^{1}H NMR spectrum also exhibits a broad singlet at δ 5.2 attributable to the N*H* group. The ^{11}B NMR chemical shift for **2** is 6.5 ppm consistent with tetracoordinate boron.

Fig. 3. ORTEP drawing of PhB(Cl)(μ-N^{t}Bu)(μ-S)CN(H)^{t}Bu (**2**).

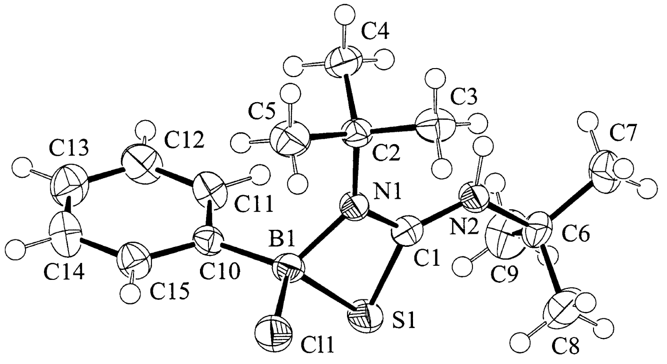


Table 2. Selected bond lengths (Å), bond angles (deg) for **1a**, **1c**, and **2**.

	1a	**1c**	**2**
B—C$_{ar}$^{a}	1.589(6)	1.581(5)	1.581(4)
B—Cl	1.882(6)	1.847(4)	1.872(3)
B—N(1)	1.567(6)	1.571(5)	1.546(4)
B—E^b	1.590(6)	2.032(4)	2.008(3)
C(1)—N(1)	1.321(6)	1.302(4)	1.323(3)
C(1)—E^b	1.341(6)	1.740(4)	1.742(3)
C(1)—C(2)	1.522(7)	1.493(5)	—
N(1)—C(6)	1.491(5)	1.503(4)	1.495(3)
N(2)—C(10)	1.470(5)	—	—
C(1)—N$_{exo}$^{c}	—	—	1.323(3)
C$_{Ar}$-B-Cl	113.8(4)	115.6(3)	113.2(2)
N(1)-B-E^b	81.6(3)	83.7(2)	84.9(2)
B-N(1)-C(1)	89.2(4)	100.1(3)	99.9(2)
C(1)-N(1)-C(6)	132.5(4)	128.9(3)	127.8(2)
B-N(1)-C(6)	137.8(4)	131.3(3)	131.9(2)
B-E^b-C(1)	87.6(4)	71.2(2)	71.4(1)
B-N(2)-C(10)	136.0(4)	—	—
C(1)-N(2)-C(10)	135.2(4)	—	—
N(1)-C(1)-E^b	101.6(4)	105.0 (3)	103.7 (2)
N(1)-C(1)-C(2)	128.4(5)	131.3 (3)	—
E^b-C(1)-C(2)	130.0(5)	123.7 (3)	—
N(1)-C(1)-N$_{exo}$	—	—	128.8 (3)
E^b-C(1)-N$_{exo}$	—	—	127.4 (2)

^{a}C$_{Ar}$ = *ipso* carbon of C$_6$H$_5$ group.
^{b}**1a**, E = N(2); **1c**, E = S; **2**, E = S.
^{c}N$_{exo}$ = exocyclic N atom.

The monomeric, four-membered ring structures of **1a**, **1c**, and **2** were confirmed by X-ray crystallography (see Figs. 1–3). Numerous attempts to obtain crystals of **1b** suitable for X-ray crystallography were unsuccessful. Pertinent metrical parameters for these heterocyclic systems are compared in Table 2. All three ring systems are essentially planar with torsion angles (BNCE) of –1.9(4)°, 1.2(3)°, and –3.9(2)° for

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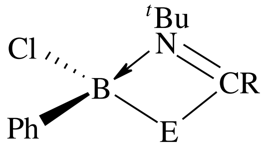
[4] In one experiment a small amount of the five-membered ring (PhB)$_2$S$_3$ was isolated and identified by X-ray crystallography. This structure has been reported previously in a review (31).

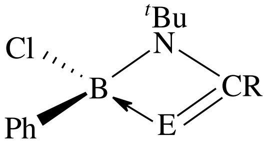
[5] The metathetical reactions of Li$_2$[CSN^{t}Bu]$_2$ with other organometallic halides also produce the corresponding sulfides. For example, (Cp$_2$ZrS)$_2$ (32) and (Me$_2$SnS)$_3$ (33) were obtained from the reactions with Cp$_2$ZrCl$_2$ and Me$_2$SnCl$_2$, respectively, and identified by comparison of spectroscopic data with those reported in the literature (P. Blais and T. Chivers, unpublished results).

1a, **1c,** and **2**, respectively. The anionic ligand in **2** is chelated to boron in an *N*,*S* rather than *N*,*N′* bonding mode consistent with the previous observations of Ansorge et al. (8) for related ligands in four-coordinate boron complexes.

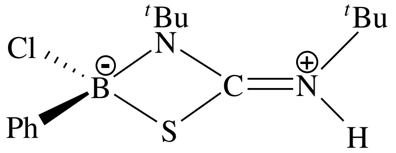
The C—N bond distances (1.321(6) and 1.341(6) Å) in the amidinate **1a** are almost equal, approximately intermediate between C—N double-bond and C—N(sp^2) single-bond values. The sums of the bond angles at the three-coordinate N and C centres are ca. 360° (as is the case for the other two heterocycles **1c** and **2**). These structural features indicate delocalized bonding in the NCN unit with approximately equal contributions from the two canonical forms **A** and **B** (E = $\mathrm{N}^t\mathrm{Bu}$). Consistently, the B—N bond lengths are also approximately equal (1.590(6) and 1.567(6) Å) and fall within the range of 1.55–1.61 Å found for B—N bonds involving four-coordinate boron linked to three-coordinate nitrogen (34). Interestingly, the endocyclic and exocyclic C—N bond lengths in **2** are identical at 1.323(3) Å. The shortness of the exocyclic bond suggests a significant contribution from the resonance form **C** to the overall structure (cf. Scheme 1 (8)).



A



B



C

The C—S bond lengths in **1c** and **2** are equal at 1.74 Å, which is close to the typical single-bond distance for sp^2-carbon atoms attached to two-coordinate sulfur (34). This observation and the relatively short (1.302(4) Å) C—N bond distance suggest that resonance form **A** (E = S) is a much more important contributor than **B** to the structure of **1c**. The B—S bond lengths in **1c** and **2** (2.032(4) and 2.008(3) Å, respectively) are somewhat longer than the mean single-bond value of 1.90 Å for four-coordinate boron attached to two-coordinate sulfur (34). This may reflect the relatively weak affinity of the hard Lewis acid boron for a soft Lewis base donor, sulfur, compared to nitrogen, a hard Lewis base centre.

The endocyclic bond angles at boron and carbon fall within the narrow ranges of 81.6(3)–84.9(2)° and 101.6(4)–105.0(3)°, respectively. However, there are substantial differences in the other two endocyclic bond angles for the S-containing rings **1c** and **2** compared to the corresponding values for **1a** as a result of the ability of two-coordinate sulfur to accommodate relatively small bond angles. Thus the endocyclic bond angles are ca. 71° at sulfur and ca. 100° at nitrogen in **1c** and **2**, cf. 88–89° at the N atoms in **1a**.

Conclusions

The first *p*-block element complexes of oxo- and thioamidate anions have been prepared by metathetical reactions using the novel reagents $\mathrm{Li[CE(N^tBu)(^nBu)]}$ (E = O, S). By analogy with the extensive chemistry of amidinates it is likely that this approach can be applied to the synthesis of a wide range of main group element and transition metal complexes of these hetero-bidentate ligands.

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