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Synthetic and structural chemistry of amidinate-substituted boron halides

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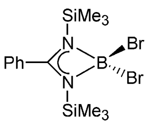
The following new amidinate-substituted boron halides are reported: [PhC{N(SiMe$_3$)}$_2$]BCl$_2$ (**6**), [MeC{NCy}$_2$]BCl$_2$ (**10**), [Mes*C{NCy}$_2$]BCl$_2$ (**11**), [MeC{N^{i}Pr}$_2$]BCl$_2$ (**12**), and [FcC{NCy}$_2$]BBr$_2$ (**13**). Compound **6** was prepared *via* the trimethylsilyl chloride elimination reaction of BCl$_3$ with *N*,*N*,*N′*-tris(trimethylsilyl)benzamidine, and compounds **10–12** were prepared by salt metathesis between the lithium amidinates [RC(NR′)$_2$]Li and BX$_3$. Compound **13** was prepared *via* the insertion of 1,3-dicyclohexylcarbodiimide into the B-C bond of ferrocenyldibromoborane FcBBr$_2$. The molecular structures of **6**, **10**, **11**, **13** and the known compound [PhC{N(SiMe$_3$)}$_2$]BBr$_2$ (**1**) were established by single-crystal X-ray diffraction.

Introduction

The coordination chemistry of amidinate anions [RC(NR′)$_2$]$^-$ with main group, transition metal, lanthanide and actinide elements is well established (R, R′ = alkyl, aryl, silyl).[1] These anions, which function typically as four-electron, N-donor bidentate chelating ligands, have found widespread use due to the ease with which the stereoelectronic properties of the N- and C-atom substituents can be tailored. Moreover, the ligand architecture can be readily modified, for instance to include two amidinate groups, pendant donor atoms, or a chiral center.[2] Several synthetic routes to metal amidinate complexes have been developed, the most prevalent being (i) reaction of a metal halide with an *N*,*N*,*N′*-tris(trimethylsilyl)amidine; (ii) protonolysis of an amidine using a metal alkyl; (iii) carbodiimide insertion into a metal–alkyl bond; and (iv) salt metathesis between a metal halide substrate and a lithium amidinate (generated *in situ* by route (ii) or (iii)).

Within the realm of p-block chemistry, amidinate complexes featuring group 13 metal–alkyl and metal–halide fragments have been the subject of sustained interest during the last decade[3,4] due to the discovery of useful applications in a number of key technological areas. For example, group 13 amidinate complexes represent promising single-source precursors for nitride materials[4c] while amidinate-supported alkylaluminium cations have proved to be active catalysts for olefin polymerization.[5] Considering the rich chemistry displayed by these group 13 species and their relative ease of synthesis, it is remarkable that the coordination chemistry of amidinate ligands with boron substrates remains undeveloped. In fact, examples of such compounds obtained by rational synthetic routes are confined to the dibromo compound **1**,[6] and the chloro–phenyl derivative **2**.[7] A related example is the vinylidene–amidinate compound **3**, which was obtained serendipitously *via* the *in situ* generation of an amidinate fragment, followed by displacement of Cl$^-$ from BCl$_4^-$, during reaction of the propylidyne complex [Cp(CO)$_2$Mn≡CEt][BCl$_4$] with ^{t}BuN=C=NBu^t and NEt$_3$.[8] The bis(trifluoromethyl)-substituted amidinate **4** was formed by rearrangement of an unstable adduct resulting from the [2 + 2] cycloaddition of (CF$_3$)$_2$B=NMe$_2$ to PhN=C=NPh.[9] In the present contribution we report the syntheses and molecular structures of a range of new boron-amidinate complexes.



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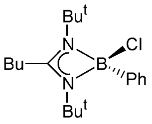

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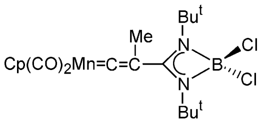

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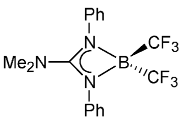

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Experimental

General procedures

All manipulations and reactions were performed under a dry, oxygen-free, catalyst-scrubbed argon atmosphere using a combination of standard Schlenk techniques or in an M-Braun or Vacuum Atmospheres drybox. All glassware was oven-dried and vacuum- and argon flow-degassed before use. All solvents were distilled over sodium benzophenone ketyl, except dichloromethane, which was distilled over CaH$_2$, and degassed prior to use. *N*,*N*,*N′*-Tris(trimethylsilyl)-benzamidine[10] and ferrocenyldibromoborane (FcBBr$_2$)[11] were prepared according to the literature procedures. The compounds 1,3-dicyclohexylcarbodiimide, 1,3-diisopropylcarbodiimide, 1-bromo-2,4,6-tri(*tert*-butyl)benzene (Mes*Br), boron halides, and alkyl lithium solutions were obtained commercially and used without further purification.

Physical measurements

Low-resolution CI mass spectra were obtained on a Finnigan MAT TSQ-700 mass spectrometer and high-resolution CI mass spectra recorded on a VG Analytical ZAB-VE sector instrument. All MS analyses were performed on samples that had been sealed in glass capillaries under an argon atmosphere. ^{1}H, ^{13}C{^{1}H}, and ^{11}B NMR spectra were recorded at 295 K in C$_6$D$_6$ solutions on a GE QE-300 instrument (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz) immediately following removal of the sample from the drybox. ^{1}H and ^{13}C{^{1}H} chemical shift values are reported in parts per million (ppm) relative to SiMe$_4$ (δ 0.00), using residual solvent resonances as internal standards. ^{11}B NMR data are referenced to BF$_3$·OEt$_2$ (δ 0.00). Melting points (uncorrected) were obtained on a Fisher–Johns apparatus after flame-sealing the samples in glass capillaries under argon.

X-Ray crystallography

For compounds **1**, **6**, **10**, **11** and **13**, a crystal of suitable quality was removed from a Schlenk flask under positive argon

Table 1 Selected crystal data, data collection and refinement parameters for **1**, **6**, **10**, **11** and **13**

	1	**6**	**10**	**11**	**13**
Formula	$C_{13}H_{23}N_2BBr_2Si_2$	$C_{13}H_{23}N_2BCl_2Si_2$	$C_{14}H_{25}N_2BCl_2$	$C_{37}H_{57}N_2BCl_2$	$C_{23}H_{31}N_2BBr_2Fe$
Formula weight	434.14	345.22	303.07	611.56	561.98
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	15.329(5)	15.026(5)	13.590(5)	13.338(5)	13.953(5)
b/Å	10.887(5)	10.799(5)	7.324(5)	18.972(5)	10.716(5)
c/Å	13.019(5)	12.711(5)	16.451(5)	15.336(5)	15.723(5)
β/°	116.223(5)	114.477(5)	94.622(5)	92.677(5)	103.837
V/Å^3	1949.1(13)	1877.2(13)	1632.1(14)	3867(15)	2282.7(15)
Z	4	4	4	4	4
D_c/g cm^{-3}	1.479	1.222	1.233	1.050	1.635
F(000)	872	728	648	1328	1136
Crystal size/mm	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.30 × 0.30 × 0.20
θ Range/°	2.39–26.99	2.59–26.99	2.48–24.99	1.71–25.00	2.42–27.00
No. of reflns collected	3207	3282	5482	13301	8684
No. of indep. reflns	1718	2045	2883	6811	4966
$R1$ [$I > 2\sigma(I)$]	0.0259	0.0543	0.0435	0.0653	0.0431
wR_2 (all data)	0.0636	0.1569	0.1191	0.1990	0.0849
Peak and hole/e Å^{-3}	0.406 and 0.371	0.485 and −0.325	0.273 and −0.287	0.446 and −0.300	0.699 and −0.643

pressure, covered immediately with degassed hydrocarbon oil and mounted on a glass fiber. The X-ray diffraction data were collected at 153 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device and a graphite-monochromated Mo-Kα radiation source (λ = 0.71073 Å). Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods[12] and refined by full-matrix least-squares cycles on F^2. All non-hydrogen atoms were allowed anisotropic thermal motion, and hydrogen atoms were placed in fixed, calculated positions using a riding model (C–H 0.96 Å). Selected crystal data, and data collection and refinement parameters are listed in Table 1.

CCDC reference numbers 275321–275325.

See http://dx.doi.org/10.1039/b509392a for crystallographic data in CIF or other electronic format.

Preparation of [PhC{N(SiMe$_3$)}$_2$]BBr$_2$ (1). A solution of BBr_3 (10 mmol) in CH_2Br_2 (10 mL) was added to a stirred, equimolar solution of *N*,*N*,*N*′-tris(trimethylsilyl)benzamidine (3.4 g, 10 mmol) in CH_2Br_2 (30 mL) at room temperature. The reaction mixture was warmed to 45 °C for several minutes, then cooled to room temperature and stirred for 6 h. Concentration of the resulting solution (approx. $\frac{1}{2}$ volume) under reduced pressure followed by storage at −30 °C resulted in a crop of colourless crystals which was isolated by filtration. A second crop of crystals formed upon cooling of the filtrate to −30 °C (3.9 g, 90% yield, mp 127–128 °C).

^{1}H NMR (C_6D_6): δ 6.86 (m, 5H, Ph), 0.16 (s, 18H, SiMe$_3$); ^{13}C NMR (C_6D_6): δ 174.36 (N*C*N); 131.63; 128.88; 126.99 (Ph); 0.63 (Si*Me*$_3$); ^{11}B NMR (C_6D_6): δ − 3.84 (s). MS (CI$^+$, CH$_4$): *m*/*z* 435 (M + H), 355 (M − Br). HRMS (CI, CH$_4$): calc. for $C_{13}H_{24}N_2BBr_2$: 434.9917; found: 434.9927.

Preparation of [PhC{N(SiMe$_3$)}$_2$]BCl$_2$ (6). Colourless crystalline **6** (mp 129–131 °C) was prepared in 84% yield from BCl_3 (10 mmol, 10 mL 1.0 M solution in CH_2Cl_2) and *N*,*N*,*N*′-tris(trimethylsilyl)benzamidine (3.4 g, 10 mmol) using the procedure described for **1**. ^{1}H NMR (C_6D_6): δ 6.82 (m, 5H, Ph), 0.14 (s, 18H, SiMe$_3$); ^{13}C NMR (C_6D_6): δ 174.68 (N*C*N); 131.35; 129.02; 125.77 (Ph); 0.66 (Si*Me*$_3$); ^{11}B NMR (C_6D_6): δ 6.04 (s). MS (CI$^+$, CH$_4$): *m*/*z* 344 (M + H), 309 (M − Cl). HRMS (CI, CH$_4$): calc. for $C_{13}H_{24}N_2BCl_2$: 344.0870; found: 344.0871.

Preparation of [MeC{NCy}$_2$]BCl$_2$ (10). Methyllithium (3.1 mL of 1.6 M solution in diethyl ether, 4.85 mmol) was added to a cold (−78 °C) solution of 1,3-dicyclohexylcarbodiimide (1.00 g, 4.85 mmol) in 15 mL of diethyl ether. The stirred colourless reaction mixture was warmed to room temperature, then cooled to −78 °C following which BCl_3 (4.85 mL 1.0 M solution in hexane, 4.85 mmol) was added dropwise. After being stirred at room temperature for 2 h, the reaction mixture was filtered through Celite® and the solvent was stripped from the filtrate to afford a white powder. Recrystallization of this powder from toluene solution afforded a crop of pale yellow crystals of **10** (1.24 g, 85% yield, mp 82–84 °C).

^{1}H NMR (C_6D_6): δ 3.41 (m, 2H); 2.14 (s, 3H); 2.07 (m, 4H); 1.59–1.24 (br m, 10H); 1.18–1.03 (m, 6H); ^{13}C NMR (C_6D_6): δ 173.41 (N*C*N); 52.12 (Cy-*C*$_1$); 33.55 (Cy); 26.95 (Cy); 25.97 (Cy); 10.82 (*Me*C). ^{11}B NMR (C_6D_6): δ 6.01 (s). MS (CI$^+$, CH$_4$): *m*/*z* 302 (M + H), 267 (M − Cl). HRMS (CI, CH$_4$): calc. for $C_{14}H_{25}N_2BCl_2$: 302.1488; found: 302.1488.

Preparation of [Mes*C{NCy}$_2$]BCl$_2$ (11). A solution of ^{n}BuLi (10.2 mmol, 6.4 mL of 1.6 M solution in hexanes) was added to a solution of Mes*Br (10 mmol) in 25 mL of diethyl ether at −78 °C. The stirred reaction mixture was allowed to warm to ambient temperature over a 2 h period. The resulting Mes*Li solution (10 mmol) was chilled to −78 °C and an equimolar solution of 1,3-dicyclohexylcarbodiimide in 10 mL diethyl ether was added dropwise. The reaction mixture was warmed to room temperature and stirred for 2 h, following which it was cooled to −78 °C. Boron trichloride (10 mL of 1.0 M solution in hexanes, 10 mmol) was added dropwise, and the stirred reaction mixture was allowed to warm to room temperature overnight. The resulting white slurry was filtered through Celite® and the solvent was removed from the filtrate under reduced pressure to give a pale yellow residue. Recrystallization of this residue from toluene solution afforded a crop of pale yellow crystals of **11** (3.2 g, 83% yield, mp 178–180 °C).

^{1}H NMR (C_6D_6): δ 6.87 (s, 2H); 3.38 (m, 2H); 1.74 (m, 4H); 1.36–1.26 (m, 10H); 1.19 (s, 27 H); 1.17–1.03 (m, 6H); ^{13}C NMR (C_6D_6): δ 176.43 (N*C*N), 152.13 (Ph); 148.86 (Ph); 126.73 (Ph); 120.03 (Ph); 55.84 (Cy-*C*$_1$); 39.44 (C(*C*H$_3$)$_3$); 35.47 (*C*(CH$_3$)$_3$); 33.14 (Cy); 26.76 (Cy); 25.53 (Cy); ^{11}B NMR (C_6D_6): δ 6.40 (s). MS (CI$^+$, CH$_4$): *m*/*z* 534 (M + H), 497 (M − Cl). HRMS (CI, CH$_4$): calc. for $C_{31}H_{51}N_2BCl_2$: 532.3522; found: 532.3516.

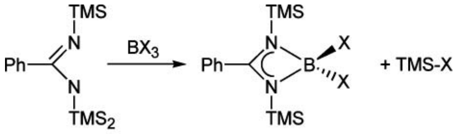
Preparation of [MeC{N^{i}Pr}$_2$]BCl$_2$ (12). Methyllithium (3.8 mL of 1.6 M solution in diethyl ether, 6.0 mmol) was added to a cold (−78 °C) solution of diisopropylcarbodiimide (0.75 g, 5.94 mmol) in 15 mL of diethyl ether. The stirred colourless reaction mixture was allowed to warm to room temperature, following which it was cooled to −78 °C and BCl_3 (6 mL of 1.0 *M* solution in hexane, 6 mmol) was added dropwise. After being stirred at room temperature for 2 h, the reaction mixture was filtered through Celite® and the solvent was stripped from the filtrate to afford a white powder, **12** (1.24 g, 94% yield, mp 38–40 °C). ^{1}H NMR (C_6D_6): 3.43 (sept, 2H); 2.17 (s, 3H); 1.19 (d, 12H); ^{13}C NMR (C_6D_6): 173.80 (N*C*N); 46.17 (*C*HMe$_2$); 23.08 (CH*Me*$_2$); 10.66 (*Me*C); ^{11}B NMR (C_6D_6): 5.78 (s). MS (CI$^+$, CH_4): *m*/*z* 222 (M + H), 187 (M − Cl). HRMS (CI, CH_4): calc. for $C_8H_{17}N_2BCl_2$: 222.0862; found: 222.0863.

Preparation of [FcC{NCy}$_2$]BBr$_2$ (13). A solution of FcBBr$_2$ (0.89 g, 2.5 mmol) in 20 mL of hexane was added to a cold (−78 °C) solution of 1,3-dicyclohexylcarbodiimide (0.52 g, 2.5 mmol) in 15 mL of hexane. The resulting yellow reaction mixture was stirred at room temperature for 2 h, following which the solvent and volatiles were removed under reduced pressure to give an orange powder, **13**. Recrystallization of the crude product from toluene afforded orange–red block crystals of **13** (0.98 g, 71% yield, mp 177–179 °C). ^{1}H NMR (C_6D_6): δ 4.83–4.03 (br, 9H); 3.64 (m, 2H); 2.20–1.11 (m, 20H); ^{13}C{^{1}H} NMR (C_6D_6): δ 75.13; 72.90; 71.17; 70.54; 69.55; 68.63; 56.03; 33.89; 26.46; 25.95 (N*C*N resonance not observed due to low intensity); ^{11}B NMR (C_6D_6): δ −4.05 (s). MS (CI$^+$, CH_4): *m*/*z* 562 (M + H), 483 (M − Br). HRMS (CI, CH_4): calc. for $C_{23}H_{31}N_2BBr_2Fe$: 560.0296; found: 560.0295.

Results and discussion

The coordination chemistry of boron amidinates is ripe for development since, apart from intrinsic interest in their molecular and electronic structures, complexes such as [RC(NR′)$_2$]BX$_2$ (X = Cl, Br) represent potentially valuable starting materials for the synthesis of new classes of boron-containing compounds.

Our initial approach to the synthesis of amidinate-substituted boron halides focused on the elimination of trimethylsilyl halide from the readily prepared ligand precursor *N*,*N*,*N*′-tris(trimethylsilyl)benzamidine (**5**).[10] Thus, treatment of a methylene dihalide solution of **5** with an equimolar amount of BX$_3$ (X = Cl, Br) at room temperature resulted, after work-up of the reaction mixtures, in high yields of pale yellow, thermally stable crystalline solids **1** and **6**.



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X = Br (**1**)
X = Cl (**6**)
TMS = Me$_3$Si

Although **1** has been reported previously,[6] the characterization of this compound was based solely on an infrared spectrum and microanalytical data. Curiously, in the same report, it was mentioned that attempts to prepare **6** resulted in the isolation of an uncharacterized yellow oil.[6] However, we found that crystalline **6** is indefinitely stable under an inert atmosphere and shows no sign of reverting to an oil, even upon gentle heating.

In order to assess the structural and bonding features, single-crystal X-ray diffraction experiments were performed on **1** and **6**. Both compounds crystallize as monomers in the monoclinic space group *C*2/*c*, and have very similar unit cell dimensions. The molecular structure of **1** is illustrated in Fig. 1 along with the numbering scheme. An identical numbering scheme was employed for **6**. Individual molecules of **1** and **6**, which reside on a two-fold axis passing through atoms B(1)–C(1)–C(2)–C(5), feature a four-membered B–N–C–N chelate ring and a phenyl group which is orthogonal to the B(1)–N(1)–C(1)–N(1A) plane. The B–X, B–N, and C–N bond distances in **1** and **6** are similar to those reported for **2–4**, and the related amido-pyridyl compounds **7** and **8**.[13,14] The C(1)–N(1) bond distances for **1** and **6** are 1.339(3) and 1.332(4) Å, respectively. These values are approximately intermediate between typical C–N double bond and C–N single bond distances. Moreover, the B–N–C–N torsion angles for both compounds are zero, indicating delocalization about the N–C–N junction. The B–N bond distances of 1.559(4) (**1**) and 1.580(5) Å (**6**) fall within the typical range of 1.55–1.61 Å for a B–N bond derived from a four-coordinate boron atom bound to a three-coordinate nitrogen atom.[15] In comparison, the B–N bond distances in **9**, an amido boron compound containing a base-stabilized, three-coordinate boron atom, are 1.535(8) and 1.635(8) Å.[16] The bite angles of the amidinate fragment (N(1)–B(1)–N(1A)) are 85.2(3) (**1**) and 86.1(3)° (**6**), and thus *ca.* 4° wider than the equivalent angle (81.6°) in **2**,[7] but closer to the mean bite angles of 84.0° in **3** and 83.8° in **4** (angles averaged for two crystallographically independent molecules in the asymmetric units of **3** and **4**).[8,9] By contrast, the N–Al–N bond angle in the congeneric complex [PhC{N(TMS)}$_2$]AlCl$_2$ is 72.9(2)° and the Al–N bond distance is 1.882(3) Å.[6] The average N–B–X bond angle is 114.6° in **1** and 114.8° in **6**, hence the geometry about the boron atom is appreciably distorted from that of a regular tetrahedron.

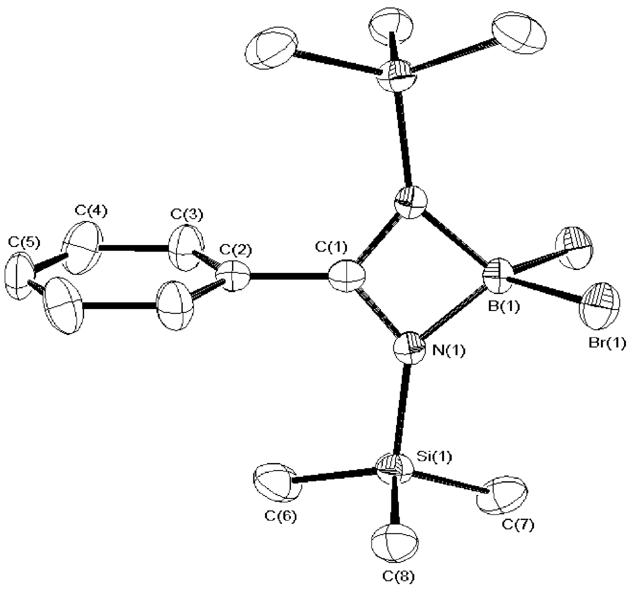
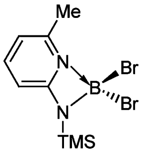


Fig. 1 ORTEP diagram of **1** with thermal ellipsoids at 40% probability and H-atoms omitted for clarity.



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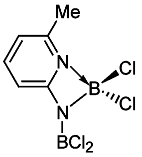

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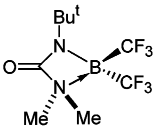

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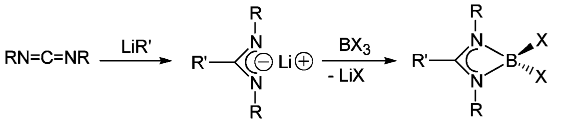
The ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra of **1** and **6** confirm that the C_{2v}-symmetric structures observed in the solid-state are retained in solution. The ^{11}B NMR spectra exhibit intense singlet resonances at δ −3.8 (**1**) and 6.0 (**6**), values which are typical for a four-coordinate boron atom.[17] The ^{1}H and ^{13}C{^{1}H} spectra exhibit peaks due to the phenyl group and two equivalent trimethylsilyl groups. A low-intensity ^{13}C{^{1}H} peak attributable to the carbon atom of the NCN fragment was detected at δ 174.

Although the trimethylsilyl halide elimination method proved to be effective for the preparation of the [RC(NR′)$_2$]BX$_2$ complexes described above, it was necessary to employ a different synthetic strategy to extend the range of these compounds. In this context, the salt metathesis reaction between BX$_3$ and a lithium amidinate [RC(NR′)$_2$]Li seemed like a more versatile approach for the introduction of a wide variety of R and R′ groups, thereby offering the possibility of tuning the steric environment of the BX$_2$ fragment. Indeed, the validity of this approach has already been demonstrated by the successful synthesis of mono- and bis(amidinate) complexes of aluminium and gallium.[3,4]

The requisite lithium amidinates were prepared by addition of diethyl ether solutions of LiMe or LiMes* (Mes* = 2,4,6-tri(*tert*-butyl)phenyl) to cold (−78 °C) diethyl ether solutions of either 1,3-dicyclohexylcarbodiimide or 1,3-diisopropylcarbodiimide. Subsequent treatment with one equivalent of BX_3 and work-up of the reaction mixtures afforded good yields of the desired boron amidinate complexes **10–12** as colourless solids.



10: X = Cl, R' = Me, R = Cy
11: X = Cl, R' = Mes*, R = Cy
12: X = Cl, R' = Me, R = ^{i}Pr

Single crystals of **10** and **11** suitable for X-ray diffraction experiments were obtained by recrystallization from toluene solution. The molecular structures of **10** and **11** (Fig. 2) are very similar to those of the boron amidinates discussed above, in the sense that the ligand is chelated to the BCl_2 fragment in a symmetrical bidentate fashion, resulting in a planar, four-membered B–N–C–N heterocycle with a delocalized N–C–N moiety. As expected, the bond distances and angles for **10** and **11** are also similar to those for **1** and **6**. Likewise, the N(1)–B(1)–N(2) bite angles and average N–B–Cl bond angles of 82.17(2) and 115.23° for **10**, and 82.1(4) and 115.4° for **11**, indicate substantial distortion from the ideal tetrahedral value. However, the N(1)–C(1)–N(2) bond angles of 101.24(3) and 100.7(3)° in **10** and **11**, respectively, are slightly more acute that those in **1** and **6** (av. 104°).

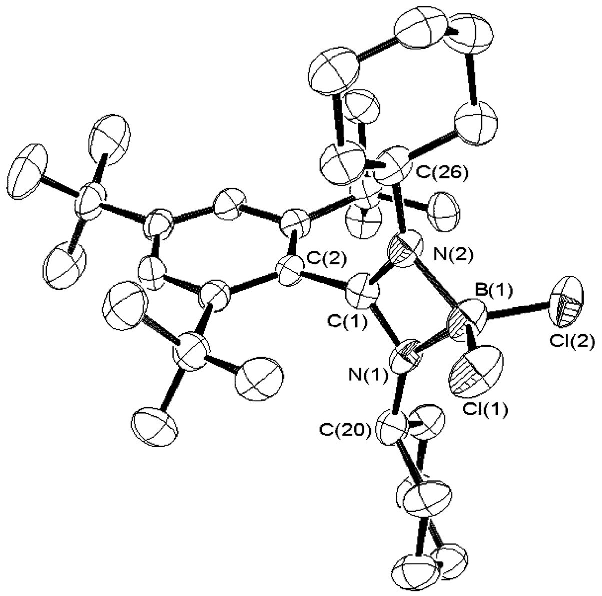
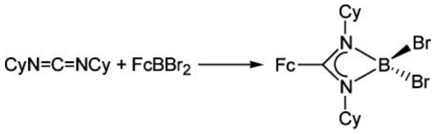


Fig. 2 ORTEP diagram of **11** with thermal ellipsoids at 40% probability and H-atoms omitted for clarity.

The insertion of a carbodiimide into a metal–hydrogen or metal–alkyl bond has proved to be a facile route to amidinate complexes of the heavier group 13 elements Al, Ga, and In. For example, 1,3-bis(trimethylsilyl)carbodiimide reacts with MMe_3 (M = Al, Ga, In) to afford the insertion products $[MeC\{N(SiMe_3)\}_2]MMe_2$.[18] A similar reaction occurs when 1,3-diisopropylcarbodiimide is treated with $AlMe_3$, and a recent elegant theoretical study has provided insight into the mechanism of carbodiimide insertion into Al–C and Al–N bonds.[19] However, to the best of our knowledge this type of reaction has not been employed previously for the synthesis of boron amidinates.

Interestingly, the reaction of 1,3-dicyclohexylcarbodiimide with BEt_3 was unsuccessful and resulted in a thick, colourless oil which did not exhibit a ^{11}B resonance. However, the reaction of equimolar quantities of 1,3-dicyclohexylcarbodiimide and ferrocenyldibromoborane $FcBBr_2$ in hexane solution at room temperature afforded, upon work-up, orange crystalline **13** in good yield. A similar carbodiimide insertion reaction takes place with $PhBCl_2$.[20] The question of whether or not such insertions occur therefore appears to depend upon the Lewis acidity of the borane (*i.e.* on the ability to form a Lewis acid–base complex with the carbodiimide). The ^{11}B NMR spectrum of **13** revealed an intense resonance at δ −4.05, which falls in a similar region to that observed for **1**, thus suggesting that the desired insertion reaction had occurred. ^1H and $^{13}C\{^1H\}$ NMR data were also consistent with such a suggestion (the NCN bridgehead carbon atom was not observed due to weak intensity).



13

Recrystallization of **13** from toluene solution produced a crop of orange block crystals suitable for X-ray diffraction experiments. The X-ray crystal structure (Fig. 3) confirmed the structure proposed for **13**. Although carbodiimide insertion into an M-alkyl bond is well known, to our knowledge this is the first example of such a process occurring at a p-block-aryl bond (contrary to the assertion of Barry *et al.*,[19b] the $[PhC\{N(TMS)\}_2]AlCl_2$ complex[6] was prepared *via* trimethylsilyl chloride elimination). As in the case of the boron amidinates discussed earlier, the B–N–C–N heterocycle is planar and the boron atom possesses a distorted tetrahedral geometry (bite angle 83.5(2)°, and a mean N–B–Br bond angle of 114.9°. The other metrical parameters are very similar to those of **1**, **6**, **10**, and **11** (Table 2).

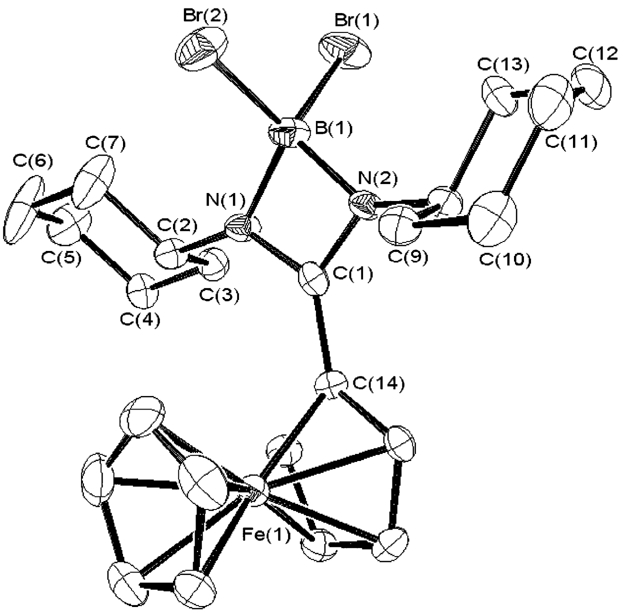


Fig. 3 ORTEP diagram of **13** with thermal ellipsoids at 40% probability and H-atoms omitted for clarity.

The incorporation of a ferrocene unit into the framework of an amidinate ligand has precedent in the work of Arnold *et al.*,[21,22] who prepared a ferrocene-substituted amidine *via* the reaction of FcLi with 1,3-dicyclohexylcarbodiimide and subsequently explored its coordination chemistry with Fe(II), Co(II) and Rh(I) halides. To our knowledge, **13** represents the first example of a p-block complex of the ferrocenylamidinate, and also constitutes the first report of the insertion of a carbodiimide ligand into a Cp–group 13 element bond.

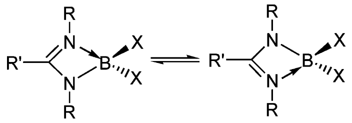
Table 2 Selected bond distances (Å) and angles (°) for **1**, **6**, **10**, **11** and **13**

1		**6**		**10**		**11**		**13**	
B(1)–Br(1)	2.001(2)	B(1)–Cl(1)	1.829(3)	B(1)–Cl(1)	1.821(3)	B(1)–Cl(1)	1.830(4)	B(1)–Br(1)	2.009(4)
B(1)–N(1)	1.559(4)	B(1)–N(1)	1.580(3)	B(1)–Cl(2)	1.846(3)	B(1)–Cl(2)	1.835(4)	B(1)–Br(2)	2.009(4)
N(1)–C(1)	1.339(8)	N(1)–C(1)	1.332(4)	B(1)–N(1)	1.559(3)	B(1)–N(1)	1.554(5)	B(1)–N(1)	1.545(5)
N(1)–Si(1)	1.767(2)	N(1)–Si(1)	1.768(3)	B(1)–N(2)	1.568(3)	B(1)–N(2)	1.569(5)	B(1)–N(2)	1.545(5)
C(1)–C(2)	1.476(5)	C(1)–C(2)	1.481(7)	N(1)–C(1)	1.330(3)	N(1)–C(1)	1.332(4)	N(1)–C(1)	1.347(4)
				N(1)–C(2)	1.329(3)	N(1)–C(2)	1.331(4)	N(2)–C(1)	1.337(4)
				N(1)–C(3)	1.463(3)	N(1)–C(20)	1.470(4)	N(1)–C(2)	1.458(4)
				N(2)–C(9)	1.456(3)	N(2)–C(26)	1.463(4)	N(2)–C(8)	1.465(4)
				C(1)–C(2)	1.479(3)	C(1)–C(2)	1.480(4)	C(1)–C(14)	1.450(4)
N(1)–B(1)–N(1A)	85.2(3)	N(1)–B(1)–N(1A)	83.5(4)	Cl(1)–B(1)–Cl(2)	111.11(15)	Cl(1)–B(1)–Cl(2)	110.5(2)	Br(1)–B(1)–Br(2)	111.1(4)
N(1)–C(1)–N(1A)	104.0(3)	N(1)–C(1)–N(1A)	104.3(4)	N(1)–B(1)–N(2)	82.17(17)	N(1)–B(1)–N(2)	82.1(2)	N(1)–B(1)–N(2)	83.5(2)
Br(1)–B(1)–Br(1A)	110.9(1)	Cl(1)–B(1)–Cl(1A)	111.5(3)	N(1)–C(1)–N(2)	101.24(3)	N(1)–C(1)–N(2)	100.7(3)	N(1)–C(1)–N(2)	100.2(3)
N(1)–B(1)–Br(1)	114.2(4)	N(1)–B(1)–Cl(1)	114.1(3)	N(1)–B(1)–Cl(1)	115.89(18)	N(1)–B(1)–Cl(1)	116.9(3)	N(1)–B(1)–Br(1)	114.3(3)
C(1)–N(1)–B(1)	85.4(4)	C(1)–N(1)–B(1)	86.1(3)	N(1)–B(1)–Cl(2)	114.52(18)	N(1)–B(1)–Cl(2)	114.7(2)	N(1)–B(1)–Br(2)	115.3(2)
				N(2)–B(1)–Cl(1)	116.19(18)	N(2)–B(1)–Cl(1)	113.4(2)	N(2)–B(1)–Br(1)	114.1(2)
				N(2)–B(1)–Cl(2)	114.33(18)	N(2)–B(1)–Cl(2)	116.7(3)	N(2)–B(1)–Br(2)	116.1(3)

The C_5H_5 plane of the Fc moiety is almost coplanar with the NCN plane of the amidinate ligand (torsion angles N(1)–C(1)–C(14)–C15) 10.0(5)°, N(2)–C(1)–C(14)–C(18) 15.1(6)°), which may indicate some degree of π–π interaction between the two fragments (C(1)–C(14) 1.450(4) Å) This arrangement contrasts with that of the uncomplexed ferrocene-substitued amidine, on which the Fc group is approximately perpendicular to the NCN plane (corresponding torsion angles ~60°), and those of the Fe(II), Co(II) and Rh(I) complexes in which the torsion angle is ~45°.[21,22]

Conclusions

We have demonstrated that a range of complementary synthetic routes are applicable for the preparation of boron amidinate compounds. On the basis of NMR and X-ray structural data, the bonding in the four-membered B–N–C–N heterocycles may be described in terms of equal contributions from two diaza-allyl resonance forms, giving rise to delocalization about the N–C–N junction.



Although the presence of bulky Mes* and Fc groups in **11** and **13** does not exert any marked effect upon the key metrical parameters of the B–N–C–N chelate ring, we anticipate that the use of sterically demanding N- and C-substituents will have an influence on the subsequent chemistry of these complexes. Moreover, the presence of the electrochemically active ferrocene group in **13** may impart some intriguing redox properties upon this compound. Studies of the reactivity patterns of these and other boron amidinate complexes are currently in progress.

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References

1 (*a*) F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; (*b*) J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.

2 (*a*) J. R. Hagadorn, M. J. McNevin, G. Wiedenfeld and R. Shoemaker, *Organometallics*, 2003, **22**, 4818; (*b*) J. Grundy, M. P. Coles and P. B. Hitchcock, *J. Organomet. Chem.*, 2002, **662**, 178; (*c*) C.-T. Chen, C.-A. Huang, Y.-R. Tzeng and B.-H. Huang, *Dalton Trans.*, 2003, 2585; (*d*) C.-T. Chen, L. H. Rees, A. R. Cowley and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 2001, 1761; (*e*) D. Doyle, Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2000, 4093; (*f*) J. R. Hagadorn and J. Arnold, *Angew. Chem., Int. Ed.*, 1998, **37**, 1729.

3 (*a*) M. L. Cole, C. Jones, P. C. Junk, M. Kloth and A. Stasch, *Chem. Eur. J.*, 2005, **11**, 4482; (*b*) V. Amo, R. Andres, E. de Jesus, F. J. de la Mata, J. C. Flores, R. Gomez, M. P. Gomez-Sal and J. F. C. Turner, *Organometallics*, 2005, **24**, 2331; (*c*) R. T. Boere, M. L. Cole and P. C. Junk, *New. J. Chem.*, 2005, **29**, 128; (*d*) B. Clare, N. Sarker, R. Shoemaker and J. R. Hagadorn, *Inorg. Chem.*, 2004, **43**, 1159; (*e*) H. A. Jenkins, D. Abeysekera, D. A. Dickie and J. A. C. Clyburne, *J. Chem. Soc., Dalton Trans.*, 2002, 3919; (*f*) D. Abeysekera, K. N. Robertson, T. S. Cameron and J. A. C. Clyburne, *Organometallics*, 2001, **20**, 5532; (*g*) K. Kincaid, C. P. Gerlach, G. R. Giesbrecht, J. R. Hagadorn, G. D. Wheeler, A. Shafir and J. Arnold, *Organometallics*, 1999, **18**, 5360; (*h*) C. C. Chang, C. S. Hsiung, H. L. Su, B. Srinivas, M. Y. Chiang, G. H. Lee and Y. Wang, *Organometallics*, 1998, **17**, 1595; (*i*) M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1998, **17**, 4042; (*j*) M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1997, **16**, 5183.

4 (*a*) J. T. Patton, M. M. Bokota and K. A. Abboud, *Organometallics*, 2002, **21**, 2145; (*b*) S. Dagorne, R. F. Jordan and V. G. Young, *Organometallics*, 1999, **18**, 4619; (*c*) J. Barker, N. C. Blacker, P. R. Phillips, N. W. Alcock, W. Errington and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1996, 431; (*d*) Y. Zhou and D. S.

Richeson, *Inorg. Chem.*, 1996, **35**, 2448; (*e*) Y. Zhou and D. S. Richeson, *Inorg. Chem.*, 1996, **35**, 1423.

5 (*a*) R. J. Meier and E. Koglin, *J. Phys. Chem. A*, 2001, **105**, 3867; (*b*) S. Dagorne, I. A. Guzei, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 274; (*c*) M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125; (*d*) R. Duchateau, A. Meetsma and J. H. Teuben, *J. Chem. Soc., Chem. Commun.*, 1996, 223.

6 C. Ergezinger, F. Weller and K. Dehnicke, *Z. Naturforsch., Teil B*, 1988, **43**, 1621.

7 P. Blais, T. Chivers, A. Downard and M. Parvez, *Can. J. Chem.*, 2000, **78**, 10.

8 M. R. Terry, L. A. Mercando, C. Kelley, G. L. Geoffroy, P. Nombel, N. Lugen, R. Mathieu, R. L. Ostrander, B. E. Owens-Waltermire and A. L. Rheingold, *Organometallics*, 1994, **13**, 843.

9 D. J. Brauer, S. Buchheim-Spiegel, H. Burger, R. Gielen, G. Pawelke and J. Rothe, *Organometallics*, 1997, **16**, 5321.

10 R. T. Boere, R. G. Hicks and R. T. Oakley, *Inorg. Synth.*, 1997, **31**, 94.

11 T. Renk, W. Ruf and W. Siebert, *J. Organomet. Chem.*, 1976, **120**, 1.

12 G. M. Sheldrick, *SHELL-PC Version 5;03*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, USA, 1994.

13 S. Aldridge, R. J. Calder, D. L. Coombs, C. Jones, J. W. Steed, S. Coles and M. B. Hursthouse, *New. J. Chem.*, 2002, **26**, 677.

14 L. M. Engelhardt, G. E. Jacobson, P. C. Junk, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1990, 89.

15 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1–S19.

16 A. Ansorge, D. J. Brauer, H. Bürger, F. Dorrenbach, T. Hagen, G. Pawlke and W. Weuter, *J. Organomet. Chem.*, 1991, **407**, 283.

17 H. Nöth and B. Wrackmeyer, in *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer Verlag, Berlin, 1978, ch. 7, pp. 74–101.

18 R. Lechler, H.-D. Hausen and J. Weidlein, *J. Organomet. Chem.*, 1989, **359**, 1.

19 (*a*) A. P. Kenney, G. P. A. Yap, D. S. Richeson and S. T. Barry, *Inorg. Chem.*, 2005, **44**, 2926; (*b*) C. N. Rowley, G. A. DiLabio and S. T. Barry, *Inorg. Chem.*, 2005, **44**, 1983.

20 N. J. Hill, J. A. Moore, M. Findlater and A. H. Cowley, manuscript submitted.

21 J. R. Hagadorn and J. Arnold, *Inorg. Chem.*, 1997, **36**, 132.

22 J. R. Hagadorn and J. Arnold, *J. Organomet. Chem.*, 2001, **637–639**, 521.