

Diboron complexes of binucleating bis(amidinate) ligands

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Dedicated to Professor Michael F. Lappert in honor of his outstanding contributions to chemistry.

Abstract

The synthesis and X-ray crystal structures of the following bis(amidinate)-substituted boron halides are reported: 1,3- $C_6H_4[C\{N(SiMe_3)\}_2BCl_2]_2$ (**3**), 1,4- $C_6H_4[C\{N(SiMe_3)\}_2BCl_2]_2$ (**4**), 1,4- $C_6H_4[C\{N(SiMe_3)\}_2B(Ph)Cl]_2$ (**5**), 1,4- $C_6H_4[C\{NCy\}_2BCl_2]_2$ (**6**), and 1,4- $C_6H_4[C\{NCy\}_2B(Ph)Cl]_2$ (**7**). Compounds **3–5** were prepared by trimethylsilyl chloride elimination, while **6** and **7** were prepared via salt metathesis reactions of the appropriate dilithium bis(amidinates) with BCl_3 or $PhBCl_2$. The molecular structures of complexes **3**, **5**, and **6** were determined by single-crystal X-ray diffraction, along with that of the free bis(amidinate) **1a**.

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Keywords: Boron; Bis(amidinate); X-ray crystal structure

1. Introduction

Amidinate anions are four-electron, N-donor bidentate chelates of general formula $[RC(NR')_2]^-$. On account of their readily tunable steric and electronic properties, these anions have been widely used as ligands in main group, transition metal and f-block coordination chemistry [1,2]. Early work in this field was focused on the benzamidinate derivative $[PhC\{NSiMe_3\}_2]^-$, which is readily synthesized via the reaction of $LiN(SiMe_3)_2$ with $PhCN$ [3]. More recently, a range of binucleating amidinate ligands have been developed. For example, bimetallic complexes of bis(amidinates) based upon dibenzofuran (**A**) [4–7], 9,9-dimethylxanthene (**B**) [4–7], and 1,2-disubstituted cyclohexyl (**C**) [8–10] frameworks have been reported. In these compounds, the proximity of the two metal fragments is governed by the nature of the structural unit linking the amidinate functional groups, hence such complexes may have applications as bifunctional catalysts. In comparison

with the above systems, the chemistry of the related bisbenzene(amidinate) systems 1,3- and 1,4- $C_6H_4[C(NR)_2]^-$ ($N = SiMe_3$ (**1**), Cy (**2**), $Cy = cyclohexyl$, Chart 1) is less developed. These ligands are readily synthesized and, on account of their rigidity, have the ability to bridge two coordinated metal moieties. However, reports of their coordination chemistry are restricted to a bis(trichlorotin) species [11], a bis(phosphonium) dication [12], a zwitterionic titanium compound [13], and a pair of neutral bimetallic aluminum complexes, 1,4- $C_6H_4[C(N^iPr)_2AlMeX]_2$ ($X = Me, Cl$) [14]. Compounds **1a** and **1b** have also been employed for the preparation of bifunctional 1,2,3,5-dithia- and diselena-diazolyl radicals, a class of compounds which has potential as single component molecular semiconductors [15–17].

Amidinate complexes featuring group 13 metal–alkyl and metal–halide fragments have received sustained interest during the last decade due to the discovery of useful applications for these compounds in key technological areas. For example, amidinate-supported alkylaluminum cations have proved to be active catalysts for the polymerization of olefins, while gallium amidinate complexes have been employed as single-source precursors for nitride mate-

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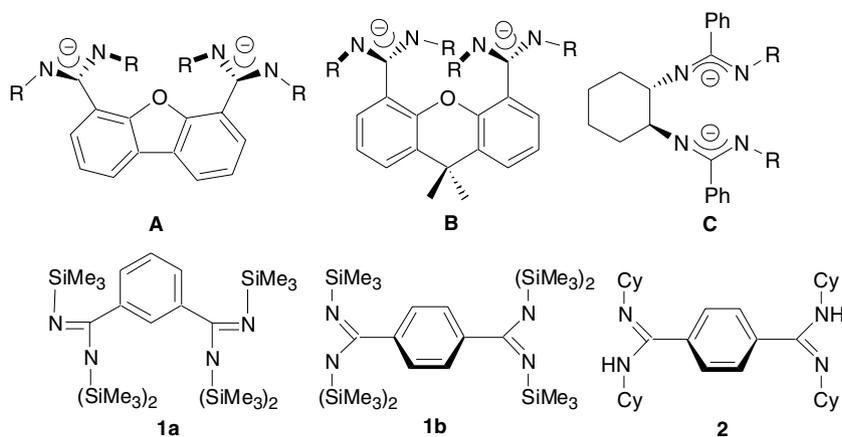


Chart 1.

rials [18–31]. We have recently extended the range of group 13 amidinates to include boron halide derivatives, a relatively unexplored area prior to our work [32–34]. In the present contribution, we describe the synthetic and structural chemistry of a series of diboron amidinates derived from **1** and **2**.

2. Experimental

2.1. 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. Compounds **1a**, **1b** and **2** were prepared according to the literature procedures [14,35]. The reagents 1,3- and 1,4-dicyanobenzene, 1,4-dibromobenzene, lithium bis(trimethylsilyl)amide, 1,3-dicyclohexylcarbodiimide, boron halides and *n*-butyl lithium solutions were obtained commercially and used as received.

2.2. Spectroscopic measurements

Low-resolution CI mass spectra were obtained on a Finnigan MAT TSQ-700 mass spectrometer and high-resolution CI mass spectra were 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. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{11}B NMR spectra were obtained at 295 K in C_6D_6 or CDCl_3 solutions on a GE QE-300 instrument (^1H , 300 MHz; ^{13}C , 75 MHz, ^{11}B , 96 MHz) immediately following removal of the samples from the drybox. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR 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 $\text{BF}_3\cdot\text{OEt}_2$ (δ 0.00).

2.3. Single crystal X-ray structure determinations

For compounds **1a**, **3**, **5**, and **6** a crystal of suitable quality was removed from a Schlenk flask under positive argon pressure, placed on a glass slide, covered immediately with degassed hydrocarbon oil and mounted on a thin 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 $\text{K}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$). Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods [36] 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.

2.4. Synthesis of 1,3- C_6H_4 [$\text{C}\{N(\text{SiMe}_3)\}_2\text{BCl}_2$] $_2$ (**3**)

BCl_3 (10 mL, 1.0 M in hexane, 10 mmol) was added to a stirred solution of **1a** (3.0 g, 5 mmol) in 20 mL of toluene at room temperature. After being stirred overnight, 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 dichloromethane solution afforded a crop of colorless crystals of **3** (91% yield).

^1H NMR (CDCl_3): δ 7.69 (m, Ph, 3H), 7.50 (s, Ph, 1H), 0.170 (s, SiMe_3 , 36H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 169.37 (NCN), 132.96, 129.72, 129.13, 124.12 (Ph), 0.35 (SiMe_3); ^{11}B NMR (CDCl_3): δ 5.73. MS (CI+, CH_3): m/z $[\text{M} + \text{H}]^+$ 612, $[\text{M} - \text{Cl}]^+$ 576. HRMS (CI, CH_4) Calc. for $\text{C}_{20}\text{H}_{40}\text{N}_4\text{B}_2\text{Si}_4\text{Cl}_4$, 610.1270. Found: 610.1278.

Table 1
Selected crystal data, data collection and refinement parameters for **1a**, **3**, **5**, and **6**

	1a	3	5	6
Formula	C ₂₆ H ₅₈ N ₄ Si ₆	C ₂₀ H ₄₀ N ₄ B ₂ Cl ₄ Si ₄	C ₃₂ H ₅₀ N ₄ B ₂ Cl ₄ Si ₄	C ₃₂ H ₄₈ N ₄ B ₄ Cl ₄
Formula weight	595.30	612.34	695.64	652.16
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	C2/c	Pca21	P2 ₁ /c	Pbcn
a/Å	27.732(5)	21.111(5)	10.293(5)	13.870(3)
b/Å	9.515(5)	12.901(5)	12.988(5)	14.466(3)
c/Å	17.665(5)	12.380(5)	16.781(5)	19.406(4)
α/°	90	90	90	90
β/°	124.245(5)	90	115.973(5)	90
γ/°	90	90	90	90
V/Å ³	3853(2)	3372(2)	2016.8(14)	3893(5)
Z	4	4	2	4
ρ _{calc} /g cm ⁻³	1.026	1.206	1.146	1.113
F(000)	1304	1288	740	1384
Crystal size/mm	0.30 × 0.30 × 0.30	0.20 × 0.15 × 0.10	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.15
θ range/°	1.78–27.51	1.93–27.41	2.63–27.52	2.29–27.49
Number of reflections collected	6793	12923	14344	8409
Number of independent reflections	4331	7169	4593	4452
R ₁ [I > 2σ(I)]	0.0633	0.0544	0.0972	0.0655
wR ₂ (all data)	0.1900	0.1347	0.3215	0.1864
Peak and hole/e Å ⁻²	0.365 and -0.322	0.492 and -0.432	0.580 and -0.724	0.443 and -0.488

2.5. Synthesis of 1,4-C₆H₄ [C{N(SiMe₃)₂BCl₂]₂ (**4**)

Colorless crystalline **4** was prepared in 90% yield from BCl₃ (10 mL, 1.0 M in hexane, 10 mmol) and **1b** (3.0 g, 5 mmol) using the procedure described for **3**.

¹H NMR (CDCl₃): δ 7.47 (m, Ph, 4H), 0.15 (s, SiMe₃, 36H); ¹³C{¹H} NMR (C₆D₆): δ 168.95 (NCN), 136.40, 122.20 (Ph), 0.32 (SiMe₃); ¹¹B NMR (CDCl₃): δ 5.62. MS (CI+, CH₃): m/z [M + H]⁺ 612, [M - Cl]⁺ 576. HRMS (CI, CH₄) Calc. for C₂₀H₄₀N₄B₂Si₄Cl₄, 610.1270. Found: 610.1280.

2.6. Synthesis of 1,4-C₆H₄ [C{N(SiMe₃)₂B(Ph)Cl]₂ (**5**)

Colorless crystalline **5** was prepared in 91% yield from PhBCl₂ (1.6 g, 10 mmol) and **1b** (3.0 g, 5 mmol) in 20 mL of toluene using the procedure described for **3**.

¹H NMR (CDCl₃): δ 7.45 (m, Ph, 14H), -0.05 (s, SiMe₃, 36H); ¹³C{¹H} NMR (CDCl₃): δ 178.85 (NCN), 140.78, 136.11, 133.66, 132.14 (Ph), 0.42 (SiMe₃); ¹¹B NMR (CDCl₃): δ 9.05. MS (CI+, CH₃): m/z [M + H]⁺ 695, [M - Cl]⁺ 660, [M - Ph]⁺ 617. HRMS (CI, CH₄) Calc. for C₃₂H₅₀N₄B₂Si₄Cl₂, 694.2676. Found: 694.2678.

2.7. Synthesis of 1,4-C₆H₄ [C{NCy}₂BCl₂]₂ (**6**)

ⁿBuLi (4 mL of 2.5 M in hexanes, 10 mmol) was added dropwise to a solution of **2** (1.67 g, 5 mmol) in 30 mL of toluene at room temperature. The resulting slurry was stirred for 2 h, after which BCl₃ (10 mL, 1.0 M in hexane, 10 mmol) was added dropwise. After being stirred overnight, 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

dichloromethane solution afforded a crop of colorless crystals of **6** (92% yield).

¹H NMR (CDCl₃): δ 7.71 (m, Ph, 4H), 3.44 (m, NCH, 4H), 1.76–1.12 (m, Cy, 40H); ¹³C{¹H} NMR (C₆D₆): δ 173.25 (NCN), 138.60, 120.19 (Ph), 54.87 (Cy-C1), 33.45 (Cy), 25.49, 25.25 (Cy); ¹¹B NMR (CDCl₃): δ 5.97. MS (CI+, CH₃): m/z [M + H]⁺ 652, [M - Cl]⁺ 617. HRMS (CI, CH₄) Calc. for C₃₂H₄₈N₄B₂Cl₄, 650.2819. Found: 650.2822.

2.8. Synthesis of 1,4-C₆H₄ [C{NCy}₂B(Ph)Cl]₂ (**7**)

Colorless crystalline **7** was prepared in 93% yield from ⁿBuLi (4 mL of 2.5 M in hexanes, 10 mmol), PhBCl₂ (1.6 g, 10 mmol) and **2** (1.67 g, 5 mmol) in 30 mL of toluene using the procedure described for **6**.

¹H NMR (CDCl₃): δ 8.17 (d, Ph, 4H), 7.49–7.25 (m, Ph, 10H), 3.29 (m, NCH, 4H), 1.90–0.74 (m, Cy, 40H); ¹³C{¹H} NMR (CDCl₃): δ 169.54 (NCN), 146.74, 138.62, 135.49, 133.20, 130.19 (Ph), 54.83 (Cy-C1), 34.51, 33.95, 25.49, 25.23 (Cy); ¹¹B NMR (CDCl₃): δ 9.69. MS (CI+, CH₃): m/z [M + H]⁺ 736, [M - Cl]⁺ 698. HRMS (CI, CH₄) Calc. for C₄₄H₅₈N₄B₂Cl₂, 734.4225. Found: 734.4222.

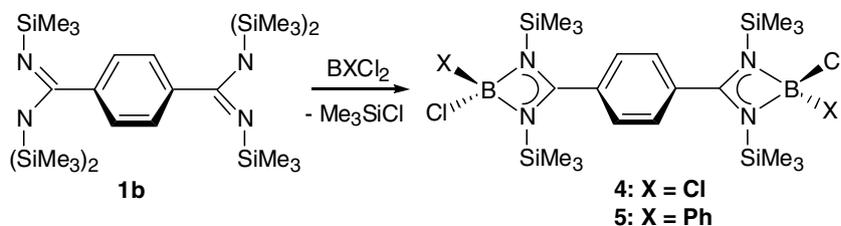
3. Results and discussion

Several methods have been reported for the synthesis of metal amidinate complexes, including: (i) insertion of carbodiimides into metal-alkyl or metal-amide bonds; (ii) protonolysis reactions employing neutral amidines; (iii) salt metathesis reactions of lithium amidinates (prepared by treatment of carbodiimides with alkyl lithium reagents) with metal halides; (iv) reaction of metal halides with *N,N,N'*-tris(trimethylsilyl)amidines.

The reaction of **1a** or **1b** with two equivalents of BXCl_2 ($\text{X} = \text{Cl}, \text{Ph}$) at room temperature proceeded via trimethylsilyl chloride elimination and afforded compounds **3–5** as colorless crystalline solids in high yields (Scheme 1). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these compounds are similar, and show signals due to equivalent trimethylsilyl groups and the bridging phenyl group, along with a weak $^{13}\text{C}\{^1\text{H}\}$ resonance at δ 169 attributable to electron delocalization within the N–C–N fragment. The ^{11}B NMR spectra exhibit strong singlet resonances at δ 5.73 for **3**, δ 5.62 for **4**, and δ 9.05 for **5**, values that fall in the typical range for four-coordinate boron atoms [37]. The mass spectra of **3–5** indicated the binding of two BXCl fragments to the binucleating bis(amidinate) ligand. In order to gain further insight into the molecular structures of these compounds, we undertook single crystal X-ray diffraction experiments on **3** and **5**.

Crystalline samples of **3** and **5** suitable for X-ray diffraction studies were obtained by recrystallization from dichloromethane solutions. The molecular structure of **3** is shown in Fig. 1, experimental data are detailed in Table 1 and selected metrical parameters are summarized in Table 2.

Compound **3** is monomeric in the solid state and features two planar, four-membered B–N–C–N chelate rings linked by a phenyl group. The chelate rings are arranged in a perpendicular fashion with respect to the bridging phenyl group. The boron atoms are bound to two chlorine and two nitrogen atoms, giving rise to an overall distorted tetrahedral coordination environment. The B–N, B–Cl, and N–C bond distances and internal bond angles of the four-membered ring are very similar to those observed for the parent boron amidinate $[\text{PhC}\{\text{NSiMe}_3\}_2\text{BCl}_2]$, and are indicative of electron delocalization within the N–C–N junction [32]. The molecular structure of **5** is that predicted on the basis of spectroscopic data. However, disorder within the phenyl and trimethylsilyl groups prevented a satisfactory refinement of the data set, thus precluding a detailed comparison of the metrical parameters with those of **3**. The molecular structure of the free amidine **1a** was also determined (Fig. 2). The molecule contains two crystallographically identical amidine groups, with N(1)–C(5) and N(2)–C(5) bond lengths of 1.402(4) and 1.279(4) Å, respectively, which are indicative of localized C–N and C=N bonds. For comparison, the corresponding bond



Scheme 1. Preparation of **4** and **5** by the Me_3SiCl elimination method.

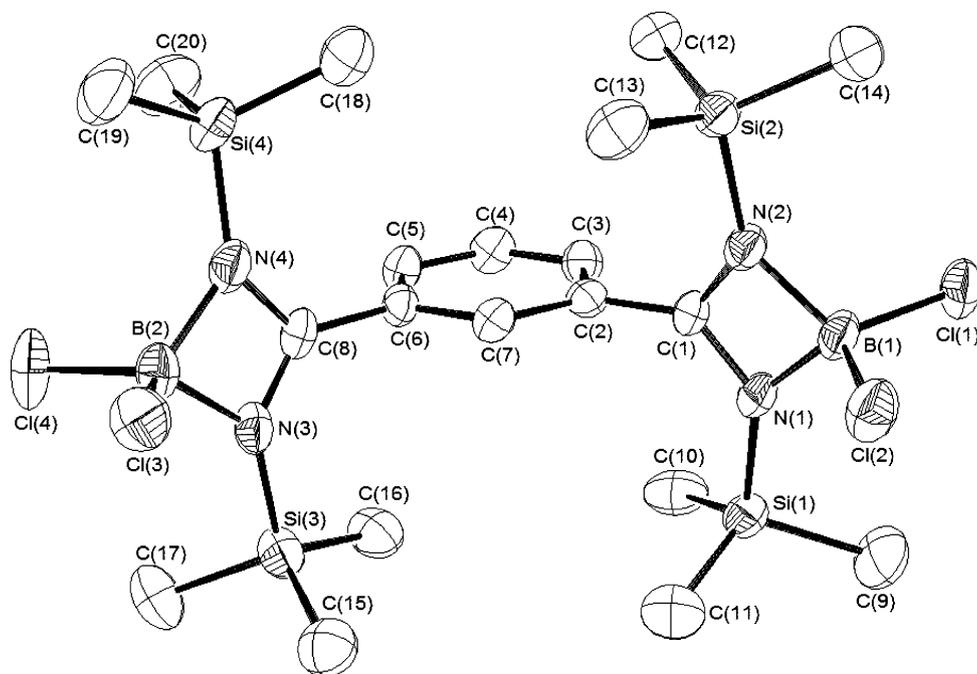


Fig. 1. ORTEP diagram of **3** with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity.

Table 2
Selected bond distances (Å) and bond angles (°) for **1a**, **3**, **5** and **6**

1a		3		5		6	
N(1)–C(5)	1.402(4)	B(1)–Cl(1)	1.835(4)	B(1)–Cl(1)	1.869(8)	B(1)–Cl(1)	1.843(4)
N(2)–C(5)	1.279(4)	B(1)–Cl(2)	1.839(5)	B(1)–N(1)	1.613(8)	B(1)–Cl(2)	1.828(4)
N(1)–Si(1)	1.774(3)	B(1)–N(1)	1.576(6)	B(1)–N(2)	1.573(8)	B(1)–N(1)	1.552(5)
N(1)–Si(2)	1.769(3)	B(1)–N(2)	1.568(5)	B(1)–C(2)	1.580(10)	B(1)–N(2)	1.567(5)
N(2)–Si(3)	1.729(3)	N(1)–C(1)	1.343(5)	N(1)–C(1)	1.326(6)	N(1)–C(1)	1.331(4)
C(2)–C(5)	1.503(5)	N(1)–C(2)	1.335(5)	N(1)–C(2)	1.331(6)	N(1)–C(2)	1.332(4)
N(1)–C(5)–N(2)	119.8(3)	N(1)–Si(1)	1.766(3)	N(1)–C(3)	1.463(3)	N(1)–C(5)	1.473(4)
Si(1)–N(1)–Si(2)	123.1(5)	N(2)–Si(2)	1.767(3)	N(1)–Si(1)	1.760(5)	N(2)–C(11)	1.459(4)
Si(1)–N(1)–C(5)	122.1(2)	C(1)–C(2)	1.472(5)	N(2)–Si(2)	1.731(5)	C(1)–C(2)	1.466(4)
Si(2)–N(1)–C(5)	113.1(2)	Cl(1)–B(1)–Cl(2)	112.5(2)	Cl(1)–B(1)–C(2)	114.5(5)	Cl(1)–B(1)–Cl(2)	110.5(2)
Si(3)–N(2)–C(5)	136.6(3)	N(1)–B(1)–N(2)	84.4(3)	N(1)–B(1)–N(2)	82.7(4)	N(1)–B(1)–N(2)	83.1(2)
C(5)–C(2)–C(1)	120.2(4)	N(1)–C(1)–N(2)	104.2(3)	N(1)–C(1)–N(2)	104.8(4)	N(1)–C(1)–N(2)	101.9(3)
C(5)–C(2)–C(3)	121.2(3)	N(1)–B(1)–Cl(1)	114.1(3)	N(1)–B(1)–Cl(1)	112.5(5)	N(1)–B(1)–Cl(1)	115.4(2)
		N(1)–B(1)–Cl(2)	113.9(3)	N(1)–B(1)–C(2)	113.4(5)	N(1)–B(1)–Cl(2)	115.4(2)
		N(2)–B(1)–Cl(1)	114.3(3)	N(2)–B(1)–Cl(1)	112.25(5)	N(2)–B(1)–Cl(1)	114.5(2)
		N(2)–B(1)–Cl(2)	114.8(3)	N(2)–B(1)–C(2)	117.6(7)	N(2)–B(1)–Cl(2)	114.5(2)

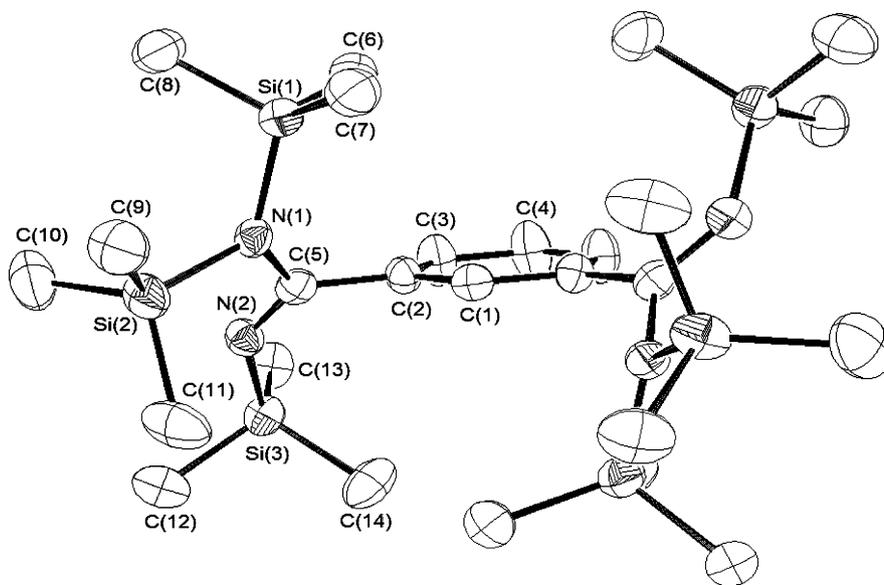
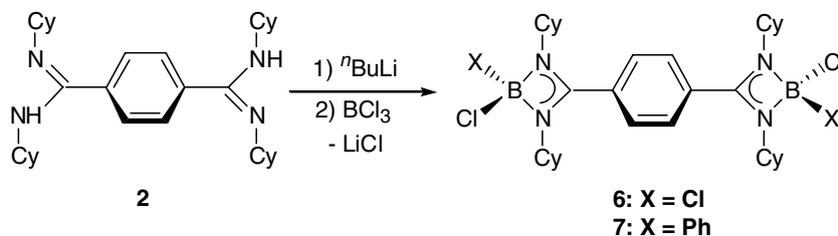


Fig. 2. ORTEP diagram of **1a** with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity.

distances in the 5-*tert*-butyl analog of **1a** are 1.410(5) and 1.264(5) Å, respectively [17], while those in **1b** are 1.413(3) and 1.271(3) Å, respectively [38].

Treatment of bis(amidene) **2** with two equivalents of ⁿBuLi, followed by addition of the requisite boron halide furnished, after workup, **6** and **7** as colorless crystalline

solids in high yields (Scheme 2). Multinuclear NMR and mass spectral data again indicated the formation of binuclear complexes, and this indication was confirmed by an X-ray diffraction study on a single crystal of **6** (Fig. 3). The molecular structure of **6** is very similar to those of **3** and **5**, in the sense that a BCl₂ fragment is bound by each



Scheme 2. Preparation of **6** and **7** by salt metathesis reactions.

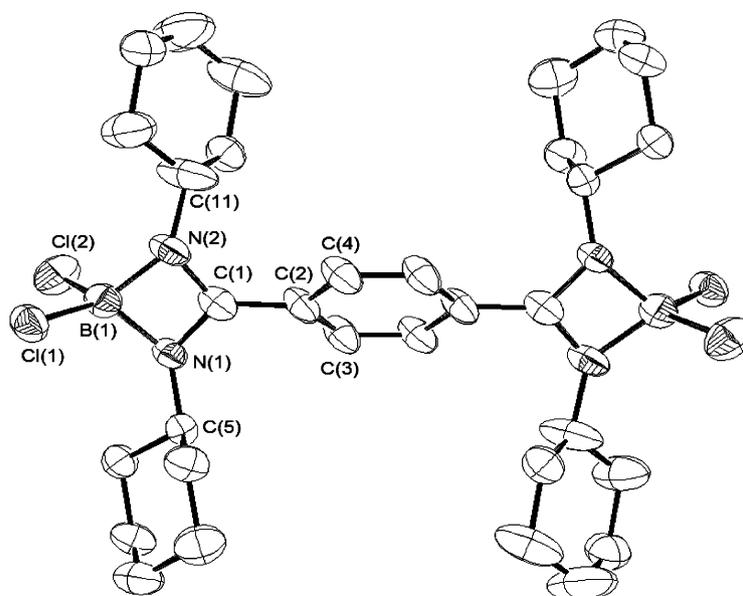


Fig. 3. ORTEP diagram of **6** with thermal ellipsoids at 40% probability. All hydrogen atoms have been omitted for clarity.

of the two N-donors of the amidinate in a symmetrical bidentate fashion thereby resulting in a planar B–N–C–N ring. The B–Cl, B–N and C–N bond distances and angles in **6** are similar to those in **3** and the bulky boron amidinate [Mes**C*{NCy}₂BCl₂] (Mes* = 2,4,6-tri(*tert*-butyl)phenyl) [32].

In summary, we have extended the range of boron amidinates to include binuclear complexes. On the basis of spectroscopic and X-ray structural data, the bonding in the four-membered B–N–C–N chelate rings in these compounds can be described in terms of equal contributions from two diaza-allyl resonance forms which results in electron delocalization at the N–C–N junctions. This structural feature is characteristic of the majority of group 13 amidinate compounds [18–34]. Bridged binuclear compounds such as **3–7** may find use as synthons for the construction of coordination networks and advanced materials.

Acknowledgments

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Appendix A. Supplementary material

Full crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 294839 (**3**), 294840 (**5**), 294841 (**6**), and 294842 (**1a**). Copies of this information can be obtained free of charge upon request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or

www.ccdc.cam.ac.uk), by quoting the publication citation and the deposition number. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.02.008.

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