Light group 13 chloride diazadiene complexes: consequences of varying substituent bulk†‡§

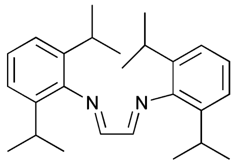
Alan Hinchliffe,[a] Francis S. Mair,*[a] Eric J. L. McInnes,[a] Robin G. Pritchard[a] and John E. Warren[b]

Received 24th August 2007, Accepted 1st October 2007
First published as an Advance Article on the web 23rd October 2007
DOI: 10.1039/b712911d

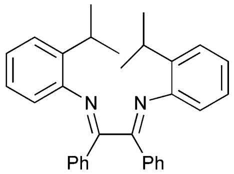
BCl_3 cyclizes diazadiene $(2,6\text{-Pr}^{i}_{2}\text{C}_{6}\text{H}_{3}\text{NCH})_{2}$ **1** through a dichloroborated intermediate $[(2,6\text{-Pr}^{i}_{2}\text{C}_{6}\text{H}_{3}\text{NCHCl})_{2}\text{BCl}]$ **3** to give, in polar aprotic solvents, a spontaneously dehyrochlorinated C-chloro diazaborole **4**. In contrast, reaction of AlCl_3 with **1** forms only acyclic mono- or di-adducts **5a**/**b** and **6**. Alkali metal reductions of **3** gave mixtures of **4** and diazaborole $[(2,6\text{-Pr}^{i}_{2}\text{C}_{6}\text{H}_{3}\text{NCH})_{2}\text{BCl}]$ **7**. Pd(0) reduction cleanly gave diazaborole **7**. Reduction of **6** gave a low yield of the closed shell C–C coupled dimer **8** of the putative diazadiene radical anion $\mathbf{1}\cdot\text{AlCl}_2$ complex monomer. An alternative synthesis for diazadiene $(2,6\text{-Pr}^{i}_{2}\text{C}_{6}\text{H}_{4}\text{NCPh})_{2}$, **2**, is reported. Reduction of $\mathbf{2}/\text{BCl}_3$, in which additional phenyl groups on the diazadiene C-2 and C-3 atoms hinder the radical coupling observed in **8**, gave predominantly diazaborole $\mathbf{2}\cdot\text{BCl}$, (**9a**) contaminated with $\mathbf{2}\cdot\text{BCl}_2$, (**9b**) the first such stable radical diazadiene complex of boron. All compounds **2–9** were characterized by X-ray diffraction and NMR spectroscopy. Stable radical **9b** was additionally characterized by EPR spectroscopy and density functional computation.

Introduction

Complexes of *ortho*-bulky α-diimines (diazabutadienes, DAB) such as **1** and **2** have enjoyed intense interest from main-group and transition metal chemists alike since the discovery of Arduengo's carbenes.[1] Using these ligands, anionic carbene analogues have already been found for heavier group 13 elements.[2,3]



1



2

We were originally motivated by the greater challenge of accessing the lower valencies of the lighter group 13 elements through alkali metal reduction of products of reaction of **1** and **2** with BCl_3 or AlCl_3. While anions $[(\text{DAB})\text{Al}]^-$ and $[(\text{DAB})\text{B}]^-$ have been predicted by computational methods to be preparable,[4] and in the case of boron have very recently proven preparable by reduction of bromides,[5] the chlorides proved remarkably robust to total alkali metal reduction, in confirmation of findings of related work by Weber and Schmid on less bulky variants.[6] However, we found unexpectedly diverse behaviour in addition and partial reduction chemistry. We have already communicated a preliminary account of the unprecedented compound **3**,[7] a result of imine chloroboration, possessed of remarkably long C–Cl bonds (1.84 Å). Here we report some reaction chemistry of **3**, the product of addition of BCl_3 to **1**, the markedly different behaviour of AlCl_3 towards **1**, the products of reaction of **2** with BCl_3, and the products of metal reduction of these compounds.

Experimental

Anilines and chlorinated solvents were distilled from calcium hydride. Hexane was distilled from sodium benzophenenone ketyl with 5% added tetraglyme. Other materials were purchased from commercial vendors and used as received. Ligand **1** was prepared by a literature route.[8] All manipulations except the workup of the ligand synthesis were performed under an argon atmosphere using an argon/vacuum double manifold or argon-filled recirculating glovebox equipped with internally-mounted moisture- and oxygen-scrubbing columns. Details of NMR spectroscopic equipment and referencing procedures are as described elsewhere.[9] X-Band EPR spectra were recorded at 9.5 GHz on a Bruker continuous wave EPR spectrometer from fluid solution by the EPSRC national service. Microanalyses were performed by the UMIST microanalysis service.

1,4-(2-isopropylphenyl)-2,3,-diphenyl-1,4-diazadiene 2

In a modification of the general method of Carlson,[10] a solution of TiCl_4 (2.0 mL, 18 mmol) in *n*-hexane (20 mL) was added *via* syringe to a rapidly stirred ice-cooled solution of $2\text{-Pr}^{i}\text{C}_{6}\text{H}_{4}\text{NH}_{2}$ (15.6 mL, 109 mmol) in *n*-hexane (100 mL). After strirring for 30 min, the ice bath was removed, and stirring continued until the mixture reached room-temperature. Powdered PhCOCOPh (7.7 g, 37 mmol) was then added against a strong argon back-flush. The temperature of the solution was raised to 50 °C, and stirring was continued for 18 h. The resulting brown slurry was washed

---

[a] *School of Chemistry, The University of Manchester, Manchester, UK M13 9PL. E-mail: mair@manchester.ac.uk*
[b] *Daresbury Laboratory, Warrington, Cheshire, UK*

† In memory of Dr John H. Morris and his first PhD student, Professor John Leach: two enthusiasts for boron chemistry and for life.

‡ CCDC reference numbers 658384–658391. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712911d

§ Electronic supplementary information (ESI) available: Summary of key results from Unrestricted-Density Functional computations on **9b** and on models. See DOI: 10.1039/b712911d with deionized water and extracted into Et$_2$O. The combined extracts were dried over MgSO$_4$, filtered, and concentrated by rotary evaporation to a yellow oil, which solidified upon trituration with a small volume of *n*-hexane. The resulting yellow solid was re-crystallized from *n*-hexane, isolated by filtration and dried in air to yield yellow crystals of **2** (10.0 g, 22.5 mmol, 60.8%), m.p. 180 °C. ^{1}H NMR (300 MHz, CDCl$_3$) major isomer: δ 7.94 (d, 4H, *o*-Ph), 7.43 (m, 6H, *m*-Ph + *p*-Ph), 6.95 (d, 2H), 6.85 (t, 2H), 6.71 (t, 2H), 6.55 (d, 2H), 2-Pr^{i}C$_6$*H*$_4$, 2.47 (septet, 2H, Me$_2$C*H*), 1.05, 0.65, (two d, 6H each, *Me*$_2$CH$_{A+B}$). Minor isomer (12%): many peaks obscured by major isomer. Observed: 8.13 (broad d, 2H, *o*-Ph) 7.43 (m, 6H, *m*-Ph + *p*-Ph), 6.20 (d, 1H, 2-Pr^{i}C$_6$*H*$_4$), 3.07 (septet, 1H, Me$_2$C*H*$_A$), 2.74 (septet, 1H, Me$_2$C*H*$_B$), 1.1 (d, 6H, *Me*$_2$CH$_A$), 0.90 (d, 6H, *Me*$_2$CH$_B$). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ 162.4 (*C*=N), 146.2 (*C*–N), 142.7 (*C*C=N), 138.7 (*C*–Pr^i), 131.2, 129.1, 128.7, 126.2, 125.9, 125.6, 117.3 (7 × aryl *C*H), 28.1 (*C*HMe$_2$), 23.3, 22.0 (*Me*$_2$CH$_{A+B}$). Found: C, 85.4; H, 7.9; N, 6.6%; C$_{32}$H$_{32}$N$_2$ requires C, 86.4; H, 7.3, N, 6.3%.

N,*N*′-Bis(2,6-diisopropylphenyl)-2,4,5-trichloro-1,3,2-diazaborolidine 3

This compound has previously been reported in a preliminary account.[7] Some of the data was interpreted incorrectly in that account; these errors are corrected here. A three-necked 500 mL round bottomed flask was charged with dry *n*-hexane (150 mL) and cooled to −30 °C. Solutions of 1,4-diaza-1,4-(2,6-diisopropylphenyl)-butadiene **1** (3.76 g, 10 mmol) in 20 mL *n*-hexane and BCl$_3$ (10 mL of a 1 M hexane solution, 10 mmol) were concurrently added dropwise to the flask. The resulting mixture was stirred for 1 h at −30 °C before being allowed to reach ambient temperature. The yellow–orange powder obtained was filtered under argon, washed with *n*-hexane and vacuum dried to give **3a** (1.907 g, 38.6%), m.p. 109–110 °C (dec. with gas evolution); Found: C, 63.05; H, 7.15; N, 5.40; Cl, 21.8%; C$_{26}$H$_{36}$N$_2$BCl$_3$ requires C, 63.25; H, 7.35; N, 5.68; Cl, 21.54%.

The filtrate was refrigerated to produce colourless crystals of **3b** (1.734 g, 35.1%). Microanalysis and NMR in CDCl$_3$ of **3b** were identical to those of **3a**. Single crystal diffraction data were collected for a crystal of **3b**. Powder X-ray diffraction of **3a** matched the Lazy Pulverix-computed pattern[11] from single crystal data for **3b**, *i.e.* **3a** = **3b** = **3**, total yield 73.7%.

Clean NMR spectra were not obtainable for **3**, which instead converted to **4** in all NMR solvents in which it was soluble, *vide infra*.

N,*N*′-Bis(2,6-diisopropylphenyl)-2,4-dichloro-1,3,2-diazaborole 4

A solution of **1** (2.28 g, 6 mmol), in dichloromethane (60 mL) was chilled to −10 °C and stirred during dropwise addition of BCl$_3$ (6.2 mL of a 1.0 M solution in *n*-hexane). A dark purple solid precipitated instantaneously. The mixture was allowed to reach room temperature and stirred for 2 d. Solvent was removed *in vacuo*. The remaining purple solid was re-suspended in *n*-hexane (60 mL), filtered *in vacuo*, washed with *n*-hexane (3 × 5 mL) and dried *in vacuo* to yield a lilac powder (0.37 g). Concentration of the filtrate produced a further 2.28 g of identical lilac powder, combined yield 2.89 g, 88%) of **4**, m.p. 106–108 °C. NMR spectra were identical to those obtained by dissolution of **3** in CDCl$_3$. A crystal of **4** was obtained by evaporation of CDCl$_3$ from an NMR sample of **3**. The powder obtained as described matched the single crystal by comparison of measured powder diffraction and simulation from single-crystal data (Lazy Pulverix).[11] ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K) 7.31 (t, 7.6 Hz, 1H, *p*-aryl C*H*$_a$), 7.26 (t, 1H, 7.8 Hz, 1H, *p*-aryl C*H*$_b$), 7.17 (d, 7.8 Hz, 2H, *m*-aryl C*H*$_b$), 7.14 (d, 7.6 Hz, 2H, *m*-aryl C*H*$_a$), 6.15 (s, 1H, *H*C=CCl), 2.89 (septet, 2H, 6.82 Hz, *H*CMe$_2$) 2.79 (septet, 7.07 Hz, 2H, *H*CMe$_2$), 1.17 (two d, overlapped, 7.07 Hz, 12H, HC*Me*$_2$), 1.11 (two d, overlapped, 6.82 Hz, 12H, HC*Me*$_2$); ^{11}B NMR (CD$_3$CN, 64.2 MHz, 298 K): 21.7 (s); ^{13}C NMR: (CDCl$_3$, 75.47 MHz, 298 K): 147.0, 146.2 (2 × aryl *C*–N), 135.8, 132.8 (2 × aryl *C*–Pr^i), 128.6, 128.1, 123.5, 123.4 (4 × aryl *C*H), 115.8 (Cl*C*=CH), 115.0 (ClC=*C*H), 28.75, 28.49 (2 × *C*HMe$_2$), 24.06, 23.98, 23.87, 23.43 (4 × CH*Me*$_2$). Found: C, 68.6; H, 7.9; N, 6.1; Cl, 15.9%; C$_{26}$H$_{35}$N$_2$BCl$_2$ requires C, 68.29; H, 7.71; N, 6.12; Cl, 15.50%.

[η^1-*N*-{*E*,*E*-*N*,*N*′-Bis(2,6-diisopropylphenyl)-1,4-diazadiene}trichloroaluminium(III)] 5a, [η^1-*N*-{*E*,*Z*-*N*,*N*′-bis(2,6-diisopropylphenyl)1,4-diazadiene}trichloroaluminium(III)] 5b, and [η^2-*N*,*N*′-{*E*,*E*-*N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diazadiene}bis{trichloroaluminium(III)}] 6

These three compounds were isolated as single crystals selected from complex mixtures containing dark tars and orange–red crystals. None were isolated as pure bulk materials. A typical procedure is given:

To a vigorously stirred suspension of AlCl$_3$ (0.35 g, 2.64 mmol) in *n*-hexane (60 mL) held at −70 °C was added a *n*-hexane solution of **1** (1.0 g, 2.66 mmol in 60 mL *n*-hexane), in 10 mL aliquots. An orange colouration developed rapidly. The solution was allowed to reach room temperature and stirred for 3 d, during which time the orange colour deepened. Concentration *in vacuo* to 50% of original volume, followed by overnight refrigeration (−20 °C), afforded a crop of large orange crystals of **5**/**6**, which were isolated by filtration (0.27 g). Further concentration and refrigeration of the filtrate produced a further 0.51 g, combined yield 0.78 g, of a mixture of **5** and **6**, m.p. 120–125 °C. Selection of crystals from different batches of **5** for X-ray diffraction gave the structures of the two isomers, *E*,*E* **5a** and *E*,*Z* **5b**, and of the doubly substituted **6**. NMR spectra from all batches were identical, all containing mixtures of **5** and **6** in solution, in approximate molar ratio 55% : 45%. Reported integrals are normalized. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K) peaks assigned to **5a**/**5b** (isomers not observed at room temperature): 9.08 (d, 1H, J = 8 Hz, N=*H*C–CH=N), 7.66 (d, 1H, J = 8 Hz, N=HC–C*H*=N), 3.01 (septet, 2H, J = 6.8 Hz, Me$_2$C*H*$_a$) 2.77 (septet, 2H, J = 6.8 Hz, Me$_2$C*H*$_b$), 1.34 (d, 6H, J = 6.8 Hz, *Me*$_a$Me$_b$CH$_a$), 1.11 (d, 6H, J = 6.8 Hz, Me$_a$*Me*$_b$CH$_a$), 1.07 (d, 12H, J = 6.8 Hz, *Me*$_2$CH$_b$); peaks assigned to **6**: 8.71 (s, 2H, N=*H*C–C*H*=N), 3.04 (septet, 4H, J = 6.8 Hz, Me$_2$C*H*), 1.27 (d, 12H, J = 6.8 Hz, *Me*$_2$CH). Peaks not unambiguously assignable to **5** or **6**: 7.12–7.49 (unresolved m, aryl CH). ^{13}C NMR (CDCl$_3$, 75.47 MHz, 298 K): **5**/**6** mixture: 175.1 (AlN=*C*), 153.9 (N=*C*), 146.0, 141.1 (aryl *C*–N), 139.3, 138.2 (aryl *C*–Pr^i), 130.0, 128.8, 128.4, 124.9, 124.1, 123.9 (aryl *C*H), 29.0, 28.7, 28.1 (*C*H(CH$_3$)$_2$), 24.0, 23.8, 23.6, 23.5, (CH(*C*H$_3$)$_2$).

Similar reaction of **1** (1.0 g, 2.66 mmol) with two equivalents of AlCl$_3$ (0.71 g, 5.32 mmol) produced dark red powder, 1.46 g, m.p.

158–160 °C, with NMR trace enriched in peaks assigned to **6**, but still containing some **5**.

N,*N*′-Bis(2,6-diisopropylphenyl)-2-chloro-1,3,2-diazaborole 7

Method 1. From **3** and lithium: To a stirred Schlenk flask containing 1.0 g (2.0 mmol) of **3** and lithium sand (0.05 g, 7.2 mmol) at −10 °C, dry *n*-hexane (40 mL) was added, forming a grey–tan suspension. After 3 d of stirring at room temperature, a black precipitate was removed by filtration to yield a pale tan solution. This was concentrated to 25% of its original volume *in vacuo* and stored at −20 °C for 3 d to yield large prismatic crystals. A small sample was collected for X-ray diffraction analysis, which proved the formulation as **7**, *vide infra*. The remaining solution was concentrated *in vacuo* to yield impure crystals of **7** (0.82 g) contaminated with some **4** and some silicone grease, as determined by NMR and microanalysis. m.p. 164–168 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K), minor peaks assignable to silicone grease and **4** (*vide supra*) were observed, in addition to: 7.25 (t, 7.6 Hz, 2H, *p*-aryl C*H*), 7.16 (d, 4H, 7.6 Hz, *m*-aryl C*H*), 6.16 (s, 2H, *H*C=C*H*), 2.91 (septet, 6.8 Hz, 4H, *H*CMe$_2$), 1.12 (two d, overlapped, 6.8 Hz, 24H, HC*Me*$_2$), ^{11}B NMR (CD_3CN, 64.2 MHz, 298 K): 21.5 (s); ^{13}C NMR: ($CDCl_3$, 75.47 MHz, 298 K): peaks for **4** (*vide supra*) plus 146.3 (aryl *C*–N), 136.7 (aryl *C*–Pr^i), 127.8, 123.45 (2 × aryl *C*H), 118.8 (H*C*=*C*H), 28.46 (*C*HMe$_2$), 24.07, 23.88 (2 × CH*Me*$_2$).

Found: C, 64.75; H, 8.00; N, 5.15; Cl, 12.4%; $C_{26}H_{36}N_2BCl$ requires C, 73.85; H, 8.58; N, 6.62; Cl, 8.38%. Compound **7** could not be isolated in good yield free of **4** by this route.

Method 2. From **3** and $Pd(Ph_3P)_4$: A stirred Schlenk flask containing **3** (0.20 g, 0.41 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.47 g, 0.41 mmol) in toluene (40 mL) was heated under reflux for 3 h, allowed to cool, then filtered. The filtrand was washed with cold toluene (3 × 5 mL) yielding a yellow crystalline solid, $[(Ph_3P)_2PdCl_2]$, identified by crystallography,[12] and a white powder. Evacuation of the combined filtrates to dryness gave a yellow tar which was taken up in dry hexanes (10 mL) and held at −20 °C for 6 d to yield crystals of **7** (0.11 g, 62%). NMR as above, but without contamination with **4**. Found: C, 73.11; H, 8.60; N, 6.37; Cl, 7.95%; $C_{26}H_{36}N_2BCl$ requires C, 73.85; H, 8.58; N, 6.62; Cl, 8.38%.

Method 3. From **3** and Na–K alloy: To a Schlenk flask containing **3** (0.50 g, 1.0 mmol) and Na–K alloy (0.11 g, 1.8 mmol, 3.2 mmol reducing equivalents) and a glass-coated magnetic stir-bar were added hexanes (20 mL) with rapid stirring to produce a grey–tan suspension. Stirring at room temperature was continued for 5 d, after which filtration removed a black precipitate. Concentration of the filtrate *in vacuo* to dryness yielded a tan glass with NMR and microanalysis characteristics as for Method 1. Recrystallization from cold hexanes gave crystals for X-ray diffraction, identical to those from Method 2.

[η^2:η^2-*N*,*N*′*N*″,*N*″-{Bis-1,6-*N*,*N*′-(2,6-diisopropylphenyl)-bis-3,4-(2,6-diisopropylphenylamido)-1,6-diazahexa-1,5-diene}-bis{dichloroaluminium(III)}] 8

To a vigorously stirred solution of $AlCl_3$ (0.70 g, 5.25 mmol) in hexanes (100 mL) was added **1** (2.03 g, 5.39 mmol), under a strong argon back-flush, instantly producing an orange solution. The solution was stirred for 0.5 h then transferred by cannula to a cold water-jacketed Schlenk flask containing lithium sand (0.09 g, 12.97 mmol) in hexanes (18 mL). The mixture was stirred for 3 weeks, filtered, the filtrate concentrated *in vacuo* to half-volume then refrigerated for 6 d at −20 °C, during which time orange–red crystals formed. These were isolated by filtration to yield **8**, (0.25 g, 10%). m.p. 191–193 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): only weak signals attributable to impurities **5**/**6** were well-resolved. Broad features centred at 7.23 (aryl C–*H*), 2.98 (*H*CMe$_2$) and 2.24 (*Me*$_2$CH) were also apparent.

[*N*,*N*′-Bis(2,6-diisopropylphenyl)-2-dichloro-4,5-diphenyl-1,3,2-diazaborolium]/[*N*,*N*′-bis(2,6-diisopropylphenyl)-2-chloro-4,5-diphenyl-1,3,2-diazaborole] 9

To an ice-cooled solution of **2** (0.79 g, 1.78 mmol) in hexanes (60 mL) and dichloromethane (2 mL) was added BCl_3 (1.8 mL of a 1 M solution in hexanes), producing an orange solution. An orange suspension formed upon warming to room temperature. The solvent volume was reduced by half *in vacuo*, and stirring at room temperature continued for a further 2 d to yield an orange powder which was isolated by filtration, washed with hexanes, and dried to yield 0.77 g of an impure form of borolium salt. This was used without further purification. Impure borolium salt (0.3 g, approx. 0.5 mmol) and lithium sand were combined in a Schlenk tube, then suspended in hexanes (20 mL). Stirring at room temperature for 5 d gave an olive green–brown suspension. Filtration gave a pale orange filtrate which was concentrated by half *in vacuo*. Standing overnight at room temperature caused deposition of a few yellow crystals of **2**, which were manually removed, and some fine orange solid. Further concentration *in vacuo*, followed by heating to redissolve the orange solid, followed by slow cooling, furnished a few orange crystals of **9** in low yield. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): *anti* conformer: 7.38 (d, 2H, NCC*H*CHCHCHCPr^i), 7.25 (AB dd, 4H, NCCHC*H*C*H*CHCPr^i), 7.14 (d, 2H, NCCHCHCHC*H*CPr^i), 7.00 (d, 4H, *o*-Ph), 6.96 (t, 2H, *p*-Ph), 6.91 (t, 4H, *m*-Ph), 2.81 (sept. $J = 6.8$ and 7.1 Hz, 2H, C*H*Me$_2$), 1.08 (d, $J = 7.1$ Hz, 6H, *Me*$_2$CH) and 0.58 (d, $J = 6.8$ Hz, 6H, *Me*$_2$CH); *syn* conformer: 7.25 (AB dd, 4H, as above), 7.14 (d, 2H, as above, + overlapping d, 2H, NCC*H*CHCHCHCPr^i), 7.00, 6.96, 6.91 (Ph, as above), 3.09 (sept., $J = 6.8$ and 7.1 Hz, 2H Me$_2$C*H*), 1.19 (d, $J = 6.8$ Hz, 6H, *Me*$_2$CH), 1.00 (d, $J = 7.1$ Hz, 6H, *Me*$_2$CH). ^{13}C NMR (298 K, $CDCl_3$, 75.47 MHz) (both conformers): 146.32, 145.97 137.24, 137.19, 131.83, 131.75, (quaternary C,{C–N, C–Pr$_i$, *ipso*-C–Ph,} × 2), 130.80, 129.93, 129.54, 127.85, 127.57, 127.40, 127.37, 126.46, 126.37, 126.02, 125.99, 125.73 (aryl C–H, 2 × Pr^{i}C$_6$H$_4$, 2 × *o*-Ph, *m* + *p*-Ph), 27.85, 27.71 (2 × *C*HMe$_2$), 24.85, 24.24, 22.78, 21.60 (2 × CH*Me*$_2$). EPR (293 K, $CDCl_3$): $g = 2.011$, 14-line multiplet, see discussion.

Crystallography‡

Data collection for **3** previously communicated.[7] Single crystals of compounds **2** and **4–9** were coated in an inert perfluoropolyether oil (1800 fomblin), mounted on a glass fibre then placed on a Nonius Kappa CCD Diffractometer. Data were recorded at −123 °C (Oxford Cryostream) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$) with the CCD detector placed at a minimum distance of 33 mm from the sample. Data was collected *via* a mixture of 1° φ and ω scans at different θ and κ settings using the program COLLECT.[13] The raw data were processed to produce conventional data using the program DENZO-SMN.[14] The data sets were corrected for absorption using the program SORTAV.[15] All structures were solved by using SIR92[16] and were refined by full matrix least squares refinement using SHELXL-97.[17] All non-hydrogen atoms were refined with anisotropic displacement parameters. Table 1 lists key structural parameters; those for **5a**, a geometric isomer of **5b**, are available in the ESI§. Data collection and refinement information for **2**, **4**, **5b**, **6**, **8** and **9a/b** is summarised in Table 2.

Computation

Energy minimisations using Unrestricted Density Functional B3LYP methods on **9b** using GAUSSIAN[18] were performed with 6-311G (d,p) basis sets, starting from the crystallographic geometry. A full vibrational analysis was done in every case in order to characterize the stationary points.

Results & discussion

Proligand synthesis

While ligand **1** is conveniently prepared by direct acid-catalysed condensation,[8] we find with benzil-derived diazadienes that the $TiCl_4$-mediated condensation is advantageous. In this way, good yields of proligand **2** are obtained. This method has previously been employed for a wide range of imine syntheses.[9,10,19] Ligand **2** had been previously reported using a simple acid-condensation route,[20] as an intermediate to its cyclodehydrogenated dihydrophenanthrene form, but no data for **2** were reported in that paper. We found it necessary to use $TiCl_4$, because in our hands the simple acid-catalysed route required forcing conditions under which cyclization to 1,2-dihydro quinoxalines is a major side-reaction.[21] Compound **2** adopts the *Z-s-cis-Z* conformation in the solid state (Fig. 1), and its ^1H NMR spectrum indicates that this conformation is retained in solution, in addition to another minor conformer. As prochiral groups in an environment lacking C_s symmetry in any conformation, the two methyls are anisochronous.[22]

The two isopropyl groups are in an *anti* disposition in the solid state. Adoption of a C_s transient conformer is impeded in the *Z*,*Z* conformation, due to unfavourable interactions between aryl hydrogens from the N-aryl and the α-phenyl (chart 1). In the *E* conformation, this restriction is relaxed, as shown in Chart 1, because analogous interaction between N-aryl and *ipso*-phenyl are less-severe. Consequently, the minor component is assigned an *E*/*Z* geometry. A free exchange of *E* and *Z* geometries in imines during and prior to co-ordination is known.[23] Observation of cross-peaks between the sets of doublets in an 2-D EXSY NMR experiment provided such evidence in this case. These results differ from those found for the dihydrophenanthrene form, which was reported to exist mainly as *E*/*Z*, with some *E*/*E* conformer in solution.[20]

Reaction chemistry 1: addition

The normal path of reaction of a group 13 chloride with a diazadiene is bidentate co-ordination of the diazadiene ligand with

Table 1 Selected bond lengths (Å) and angles (°) in **2**, **4**, **5b**, **6**, **7**, **8**, and **9**

2^{a}		**4**^{b}		**5b**		**6**^{c}		**7**		**8**^{c}		**9a/b**^{a}	
N(1)–C(2)	1.2828(19)	Cl(1)–B(1)	1.757(3)	Cl(1)–Al(1)	2.1144(11)	N(1)–C(2)	1.276(7)	Cl(1)–B(1)	1.7565(14)	Cl(1)–Al(1)	2.115(2)	Cl(1a)–B(1)	1.753(3)
N(1)–C(10)	1.4172(19)	Cl(2)–C(2)	1.6250(19)	Cl(2)–Al(1)	2.0996(10)	N(1)–C(10)	1.467(7)	N(1)–C(2)	1.4037(16)	Cl(2)–Al(1)	2.100(2)	Cl(1b)–B(1)	1.893(6)
C(2)–C(20)	1.489(2)	N(1)–C(2)	1.403(2)	Cl(3)–Al(1)	2.1010(12)	N(1)–Al(1)	2.003(5)	N(1)–B(1)	1.4159(17)	Al(1)–N(4)	1.824(4)	N(1)–C(2)	1.418(2)
C(2)–C(2)$^{\#}$	1.511(3)	N(1)–B(1)	1.420(2)	Al(1)–N(1)	1.965(2)	Cl(1)–Al(1)	2.104(3)	N(1)–C(10)	1.4479(15)	Al(1)–N(1)	1.953(4)	N(1)–B(1)	1.421(3)
		N(1)–C(10)	1.435(2)	N(1)–C(2)	1.285(3)	Cl(2)–Al(1)	2.096(2)	N(4)–C(3)	1.4052(16)	N(1)–C(2)	1.286(6)	N(1)–C(10)	1.439(2)
		C(2)–C(2)$^{\#}$	1.313(4)	N(1)–C(10	1.479(3)	Cl(3)–Al(1)	2.100(2)	N(4)–B(1)	1.4199(17)	N(1)–C(10)	1.467(6)	C(2)–C(2)$^{\#}$	1.371(4)
				N(4)–C(3)	1.259(3)	C(2)–C(2)$^{\#}$	1.489(12)	N(4)–C(40)	1.4320(15)	N(4)–C(40)	1.422(6)	C(2)–C(20)	1.479(3)
				N(4)–C(40)	1.441(4)			C(2)–C(3)	1.3408(18)	N(4)–C(3)	1.462(6)		
				C(2)–C(3)	1.467(4)					C(2)–C(3)	1.498(7)		
										C(3)–C(3)$^{\#}$	1.585(9)		
C(2)–N(1)–C(10)	123.28(14)	C(2)–N(1)–B(1)	106.32(14)	N(1)–Al(1)–Cl(2)	104.64(8)	C(2)–N(1)–C(10)	120.6(5)	C(2)–N(1)–B(1)	107.62(10)	N(4)–Al(1)–N(1)	87.78(18)	C(2)–N(1)–B(1)	108.06(16)
N(1)–C(2)–C(20)	118.20(15)	C(2)–N(1)–C(10)	122.50(14)	N(1)–Al(1)–Cl(3)	105.05(8)	C(2)–N(1)–Al(1)	119.7(4)	C(2)–N(1)–C(10)	122.48(10)	N(4)–Al(1)–Cl(2)	117.65(16)	C(2)–N(1)–C(10)	125.16(16)
N(1)–C(2)–C(2)$^{\#}$	124.31(12)	B(1)–N(1)–C(10)	130.48(14)	Cl(2)–Al(1)–Cl(3)	114.94(5)	C(10)–N(1)–Al(1)	119.7(3)	B(1)–N(1)–C(10)	129.88(10)	N(1)–Al(1)–Cl(2)	111.47(14)	B(1)–N(1)–C(10)	126.55(17)
C(20)–C(2)–C(2)$^{\#}$	117.49(12)	N(1)–B(1)–N(1)$^{\#}$	106.97(19)	N(1)–Al(1)–Cl(1)	105.26(8)	N(1)–Al(1)–Cl(2)	106.85(16)	C(3)–N(4)–B(1)	106.98(10)	N(4)–Al(1)–Cl(1)	115.22(15)	N(1)–B(1)–N(1)$^{\#}$	106.5(2)
		N(1)–B(1)–Cl(1)	126.51(10)	Cl(2)–Al(1)–Cl(1)	113.13(5)	N(1)–Al(1)–Cl(3)	101.33(15)	C(3)–N(4)–C(40)	120.62(10)	N(1)–Al(1)–Cl(1)	109.17(16)	N(1)–B(1)–Cl(1a)	126.73(12)
		C(2)$^{\#}$–C(2)–N(1)	110.19(10)	Cl(3)–Al(1)–Cl(1)	112.63(5)	Cl(2)–Al(1)–Cl(3)	115.41(10)	B(1)–N(4)–C(40)	132.09(10)	Cl(2)–Al(1)–Cl(1)	112.65(9)	N(1)–B(1)–Cl(1b)$^{\#}$	113.9(2)
		C(2)$^{\#}$–C(2)–Cl(2)	120.43(7)	C(2)–N(1)–C(10)	118.4(2)	N(1)–Al(1)–Cl(1)	103.31(16)	N(1)–B(1)–N(4)	106.60(11)	C(2)–N(1)–C(10)	118.8(4)	N(1)–B(1)–Cl(1b)	111.1(2)
		N(1)–C(2)–Cl(2)	129.36(15)	C(2)–N(1)–Al(1)	121.24(19)	Cl(2)–Al(1)–Cl(1)	113.99(10)	N(1)–B(1)–Cl(1)	127.06(10)	C(2)–N(1)–Al(1)	109.6(3)	Cl(1b)–B(1)–Cl(1b) $^{\#}$	100.4(5)
				C(10)–N(1)–Al(1)	120.36(17)	Cl(3)–Al(1)–Cl(1)	113.99(10)	N(4)–B(1)–Cl(1)	126.33(10)	C(10)–N(1)–Al(1)	131.6(3)	C(2)$^{\#}$–C(2)–N(1)	108.64(10)
				C(3)–N(4)–C(40)	117.1(2)	N(1)–C(2)–C(2)$^{\#}$	123.7(7)	C(3)–C(2)–N(1)	109.02(11)	C(40)–N(4)–C(3)	120.6(4)	C(2)$^{\#}$–C(2)–C(20)	128.73(10)
				N(1)–C(2)–C(3)	125.7(3)			C(2)–C(3)–N(4)	109.78(11)	C(40)–N(4)–Al(1)	122.7(3)	N(1)–C(2)–C(20)	122.60(16)
				N(4)–C(3)–C(2)	118.7(3)					C(3)–N(4)–Al(1)	111.9(3)		
										N(1)–C(2)–C(3)	119.3(4)		
										N(4)–C(3)–C(2)	109.0(4)		
										N(4)–C(3)–C(3)$^{\#}$	113.6(5)		
										C(2)–C(3)–C(3)$^{\#}$	107.0(5)		

Symmetry transformations used to generate equivalent atoms:[a] $-x, y, -z + 1/2$. [b] $x, -y + 3/2, z$. [c] $-x + 1, -y + 1, -z + 1$.

Table 2 X-Ray data collection and refinement details

Compound	**2**	**4**	**5a**	**5b**	**6**	**7**	**8**	**9a/b**
Formula	$C_{32}H_{32}N_2$	$C_{26}H_{35}BCl_2N_2$	$C_{26}H_{36}AlCl_3N_2$	$C_{26}H_{36}AlCl_3N_2$	$C_{26}H_{36}Al_2Cl_6N_2$	$C_{26}H_{36}BClN_2$	$C_{52}H_{72}Al_2Cl_4N_4$	$C_{32}H_{32}BCl_{1.11}N_2$
M_w	444.60	457.27	509.90	509.90	643.23	422.83	948.90	494.67
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic
a/Å	13.7318(5)	11.7771(5)	12.6140(15)	10.7200(3)	8.4674(4)	19.3586(5)	10.8043(12)	21.7735(14)
b/Å	10.9074(5)	20.7881(9)	12.6754(17)	13.5827(4)	9.3576(5)	6.8550(2)	12.4962(13)	9.7868(7)
c/Å	16.9606(8)	10.9245(5)	19.166(3)	19.0756(8)	11.0134(6)	20.0253(5)	12.6503(18)	13.2216(10)
α/°	90	90	90	90	79.379(2)	90	118.224(7)	90
β/°	102.097(2)	90	108.712(5)	90	77.968(2)	101.033(1)	90.425(7)	99.065(4)
γ/°	90	90	90	90	66.034(4)	90	115.297(6)	90
Space group	$C2/c$	$Pnma$	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/c$
Z	4	4	4	4	1	4	1	4
Temp./K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
μ/mm^{-1}	0.069	0.258	0.362	0.378	0.631	0.160	0.296	0.170
Reflns measd	11 695	19 705	15 175	15 122	10 201	15 984	10 147	8904
Reflns obsd^a (R_{int})	2833 (0.0844)	2762 (0.0782)	5067 (0.1084)	6136 (0.0691)	2670 (0.0733)	4948 (0.0420)	4556 (0.0761)	2976 (0.0455)
R_1(observed)	0.0527	0.0530	0.0841	0.0504	0.1020	0.0638	0.0840	0.0552
wR_2(all data)^b	0.1154	0.1307	0.1925	0.0871	0.2361	0.1545	0.2141	0.0964

[a] $I = I > 2\sigma(I)$. [b] $wR_2 = \{\sigma[w(F_o{}^2 - F_c{}^2)^2]/\sigma[w(F_o{}^2)^2]\}^{1/2}$.

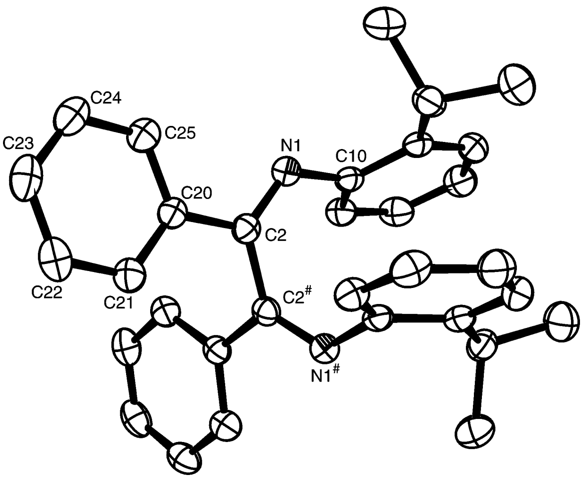


Fig. 1 Crystal and molecular structure of proligand **2**. The asymmetric unit comprises one half-molecule; symmetry-equivalent atoms are labelled with #. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 50% probability level.

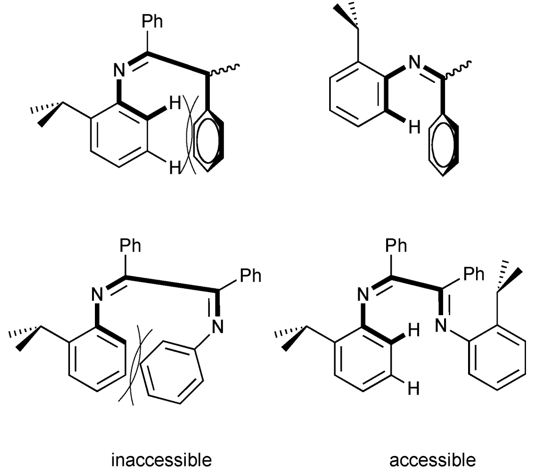
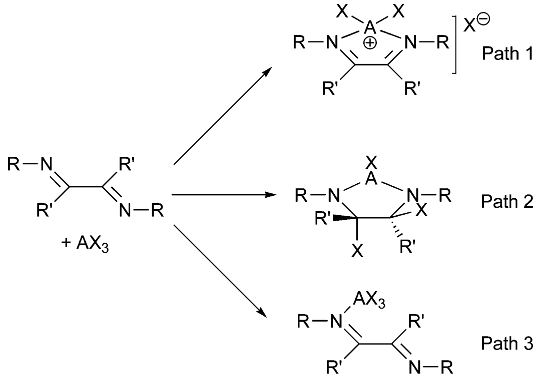


Chart 1 Steric interactions in possible C_s transient conformations for *E* and *Z* imines.



Scheme 1

expulsion of a halide from the co-ordination sphere, Scheme 1, path 1.[6a–e]

This results, in the case of boron, in a generation of diazaborolium salts. Use of a further mole of Lewis acid AX_3 can promote isolation of clean, crystalline products such as AX_4^- salts, as recently demonstrated crystallographically.[6i,24] In contrast, reaction of **1** with BCl_3 at high dilution in hexane resulted instead in highly diastereoselective addition of B–Cl across both C=N bonds to yield **3**, Fig. 2.[7] Such chloroboration of imines (path 2) is without precedent, though chloroboration of other unsaturated functions, such as isocyanates, isothiocyanates,[25] and alkynes[26] is well-established. We originally hypothesised that this reaction may have been caused by the reluctance of the boron atom to entertain four-co-ordination in the presence of such bulky aryl substituents, since it was the bulk on the aryls which distinguished **3** from the borolium formulations of prior workers.[6] However, the 2,6-diisopropylphenyl substituent has since been found in a very similar environment in a dichlorodiazaborolium salt isolated by Clyburne.[24] In that case, a planar, π-delocalized backbone on the diazabutadiene precluded the saturating attack of chloride, hence more conventional borolium behaviour was found. Furthermore, recent results from Weber's group suggest that the behaviour is *not* restricted to cases of extreme steric bulk, since C-chlorinated compounds were obtained from reaction of BCl_3 with N-mesityl analogues of **1**.[6i] Rather, the N-aryl substituent is the distinguishing factor, since such behaviour is not observed with N-alkyl-substituted diazadienes. All synthetic transformations are summarised in Scheme 2.

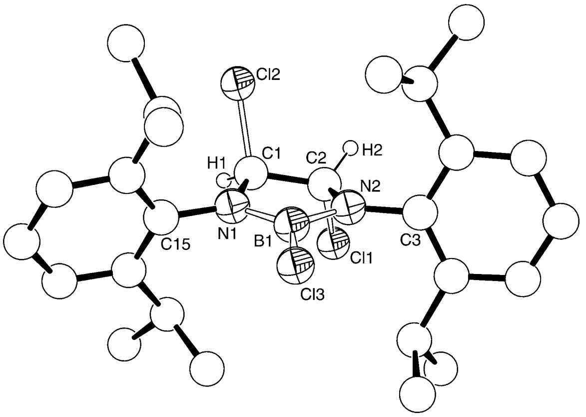


Fig. 2 Crystal and molecular structure of **3**. Previously communicated.[7] Bond lengths (Å): Cl(3)–B(1) 1.743(3); N(1)–B(1) 1.403(3); N(2)–B(1) 1.416(3); N(1)–C(1) 1.413(3); N(2)–C(2) 1.417(3); C(1)–C(2) 1.528(3); C(1)–Cl(2) 1.840(3); C(2)–Cl(1) 1.841(3). Bond Angles (°): B(1)–N(1)–C(1) 109.10(19); B(1)–N(1)–C(15) 128.9(2); C(1)–N(1)–C(15) 121.98(19); B(1)–N(2)–C(2) 108.82(19); B(1)–N(2)–C(3) 129.4(2); C(3)–N(2)–C(2) 121.78(19); N(1)–B(1)–N(2) 109.4(2); N(1)–B(1)–Cl(3) 125.5(2); N(2)–B(1)–Cl(3) 125.1(2); N(1)–C(1)–C(2) 105.45(19); N(1)–C(1)–Cl(2) 112.93(17); C(2)–C(1)–Cl(2) 107.26(16); N(2)–C(2)–C(1) 105.05(19); N(2)–C(2)–Cl(1) 112.85(17); N(2)–C(2)–Cl(1) 112.85(17); C(1)–C(2)–Cl(1) 107.51(17). Diazaborinane ring hydrogen atoms are shown, others are omitted.

In the original communication,[7] we erroneously interpreted the multiple isopropyl methine resonances in the ^1H NMR spectrum of **3** as being due to restricted aryl rotation, whereby one isopropyl group on the same side of the diazaborolidine ring as the chlorine substituent gave rise to one signal, while the isopropyl from the other side of the same phenyl ring gave rise to the other signal. It is now clear that two inequivalent phenyl groups, both with chemically equivalent 2- and 6-isopropyl groups, produce the observed spectrum. That is to say, in solution in solvents more polar than the hexane from which the crystals were isolated, elimination of HCl occurs. This strange hypothesis was proved by isolation of crystals of **4** from an NMR tube $CDCl_3$ sample of **3**. Furthermore, crystals of compound **4**, the spontaneously reduced diazaborole, were directly preparable by combination of **1** with BCl_3 in the more polar solvent dichloromethane (Fig. 3). This also explains the anomalous chemical shift of the 'diazaborolidine' ring hydrogen, since after dissolution for NMR analysis it is in fact an alkenyl hydrogen from a diazaborole. We have no data to inform mechanistic speculation on this curious reaction. We note, however, that the C–Cl bonds in **3** are amongst the longest known (Fig. 1), and that the transoid disposition of the chlorines makes 1,2-elimination of HCl a favourable process. While the compound **4** is among the first diazaboroles to possess halo substitution on the ring,[6i] there is an interesting parallel to be drawn between the reactivity of **1** with BCl_3 and that of DAB ligands with PCl_3, which can also result in ring C-monochlorination.[27] Further close comparisons can be drawn with recently published work from the group of Weber, which described the variety of products obtained from reaction of BCl_3 with mesityl and xylyl analogues of **1**.[6i] His findings have many parallels with our own, including isolation of spontaneously reduced, mono-C-chlorinated diazaboroles, among a variety of other products.[6i]

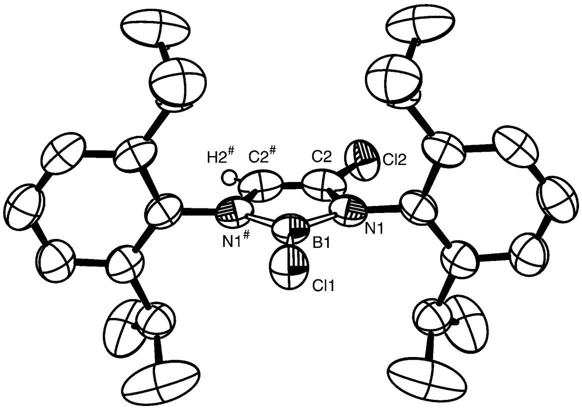
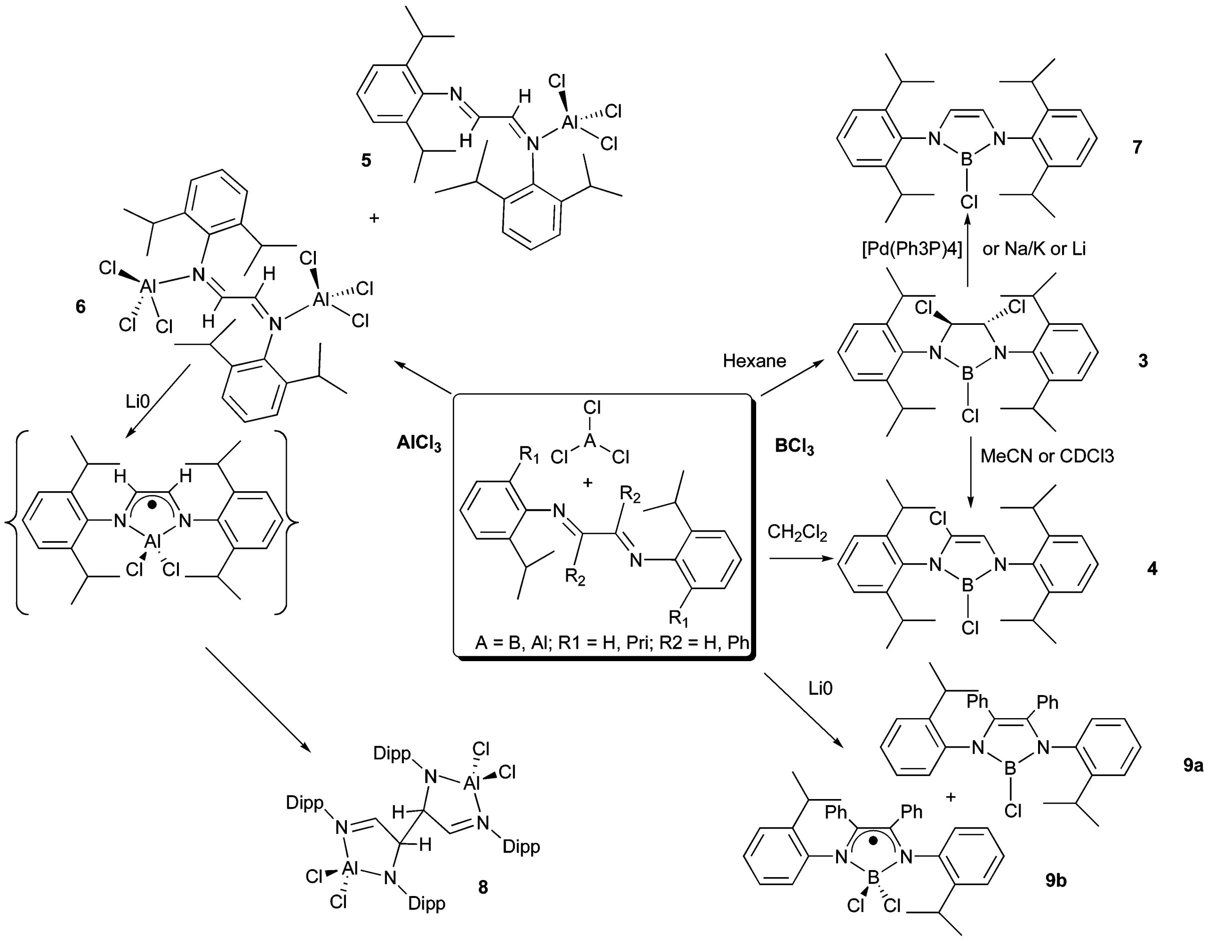


Fig. 3 Crystal and molecular structure of **4**. A crystallographic plane lies along B1–Cl1. Symmetry-equivalent atoms are denoted by #. There is substitutional disorder on C2: the C2-substituent is 50% Cl, 50% H. The Cl2 only is shown on C2, the H2# only on C2#. Other hydrogen atoms are omitted. Thermal ellipsoids are drawn at 50% probability level.

Chloro substitution has a minimal effect on metrical parameters (see Table 1), but does offer a path for further synthetic elaboration of the ligand. Indeed, in Weber's case, some C=C coupled bis(diazadienyl) complexes were isolated as byproducts.[6i] We find similar, but not identical, behaviour for aluminium, *vide infra*.

$AlCl_3$ behaves quite differently from BCl_3 towards **1**, mirroring more closely the behaviour of BF_3 with the less bulky mesityl analogues of **1** as reported by Weber.[6d] Among the mixture of products from 1 : 1 reactions of $AlCl_3$ with **1**, simple adducts **5** were found, *i.e.*, path 3. Crystals of both *E*/*E* (**5a**) and *E*/*Z* (**5b**) isomers were isolated. The structure of the adduct **5a** can be found in the ESI; that of **5b** is presented in Fig. 4.

Adduct **5a** bears the closest resemblance to that of the free ligand **1**, which also crystallizes in an *E*/*E* conformation.[28] It is the less



Scheme 2

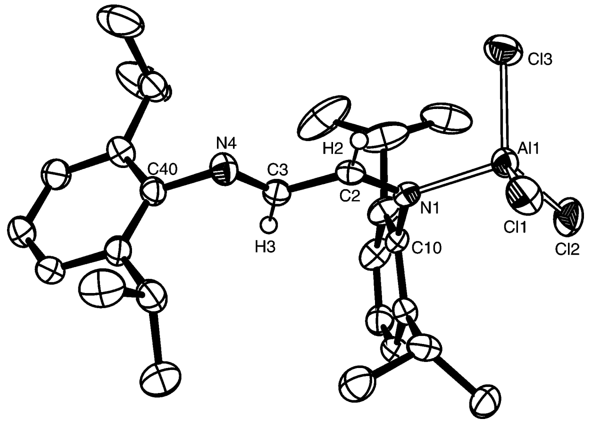


Fig. 4 Crystal and molecular structure of *E*/*Z* isomer **5b**. Diazabutadiene hydrogens H2 and H3 are shown, others are omitted.

densely packed of the two isomers of **5**. Adduct **5b** has isomerized at the co-ordinated nitrogen (*E*/*Z*), but otherwise is similar: Both have a non-crystallographic plane of symmetry running through Al1 and Cl2 as well as N1, C2, C3, N4, C10 and C40. The aryls are almost orthogonal to this diazabutadiene conjugated plane (aryl–diazabutadiene plane angles of 88.3 and 89.5° in **5a**, for example). Co-ordination of AlCl$_3$ to the diazadiene **1** in either conformation had a negligible effect on conjugation, the ligand bond lengths being closely similar to those found for the free ligand **1**. Bond lengths to the co-ordination nitrogen N1 increase slightly, as expected for an atom with increased co-ordination number. The geometry around Al1 is that of a compressed tetrahedron, the Cl–Al–Cl angles being systematically several degrees larger than the Cl–Al–N ones (Table 1). This is common to related adducts of AlCl$_3$ with single monodentate nitrogen ligands.[29]

When a further molar equivalent of AlCl$_3$ co-ordinated, generating circumstances where abstraction of chloride by one molecule of AlCl$_3$ might have caused cyclization as found for related boron systems,[6d,24] instead the 2 : 1 adduct **6** was produced (Fig. 5), again mirroring Weber's results with BF$_3$. This is in stark contrast to the situation for BCl$_3$, and, less surprisingly, in contrast to the findings of Jones and co-workers for AlI$_3$.[30] For both BF$_3$ and AlCl$_3$, the bonds resisting cleavage are between atoms of the same period. It remains possible that other non-crystalline products which contain diazadiene metallacycles exist in the complex mixtures produced by these reactions. Indeed, Weber's recent results on xylyl and mesityl analogues of **1** with BCl$_3$ display a wide array of reactivity, depending on temperature and reaction solvent, including cases where adducts analogous to **5** were postulated as low-temperature intermediates.[6i]

The configuration at both imine bonds in **6** is *Z*. It seems probable that this minimises steric conflict between the AlCl$_3$ and diisopropylphenyl moieties. It does not favour formation

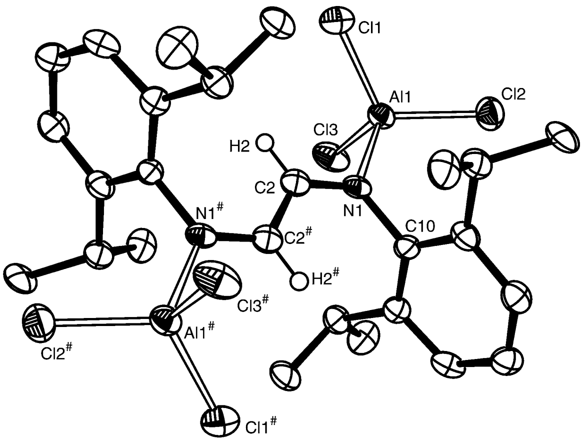


Fig. 5 Crystal and molecular structure of **6**. The asymmetric unit comprises one half-molecule; symmetry-equivalent atoms are labelled with #. Diazabutadiene hydrogens are shown, others are omitted. Thermal ellipsoids are drawn at 50% probability level.

of metallacycles. However, rapid *E*/*Z* equilibration has been previously noted in aryl imines, and is not seriously inhibited by complexation with group 13 Lewis acids.[23]

NMR spectra of the crystalline products from a 1 : 1 reaction of **1** with $AlCl_3$ showed **5** and **6** in an approximate 1 : 0.8 ratio. Two isomers of **5** were not detectable. It was clear from the pair of doublets for the aldimine hydrogens at 9.1 and 7.6 ppm that the major component was **5**. There was also doubling of all other peaks. The minor component exhibited a single aldimine hydrogen resonance at 8.7 ppm, shifted from the analogous peak in free ligand **1** at 8.0 ppm. This, and corresponding single groups of resonances from the isopropyl groups, suggested the presence of **6** in samples of **5**. The peaks assigned to **6** increased when a further molar equivalent of $AlCl_3$ was used in the synthesis, strengthening confidence in assignments, but pure bulk samples of neither **5** nor **6** proved isolable.

For the bulkier ligand **2**, reaction with BCl_3 is presumed to proceed along path 1, given that the increased bulk on the diazadiene carbon atoms would be expected to prevent the attack of chloride. Only insoluble powders were obtained, which provided neither satisfactory analysis figures nor readily interpretable spectra, so samples of the presumed borolium salt were used directly in attempted reductions without full characterization.

Reaction chemistry 2: reduction

If **3** is reacted with $[Pd(PPh_3)_4]$, Na–K alloy or Li sand, C-dechlorination to produce the diazaborole **7** occurs, as for analogous, less bulky systems.[6] Thus, a C-chlorinated or C-unchlorinated diazaborole is available by either spontaneous HCl ejection or chemical reaction with a variety of reductants, respectively. The cleanest product was obtained using the Pd reductant. Interestingly, Pd/C was used in the earliest preparations of diazaboroles by dehydrogenation of diazaborolines.[31] Where alkali reductants were employed, some contamination with **4** was evident. In confirmation of the results of Weber, in no case was further reduction to B(II) or B(I) species achieved *via* chlorides.[6a–e] Weber has accessed B(II) compounds *via* reduction of chalcogenides,[6f] and Morris has reduced chlorides of analogous tetrazaboroles to diborane(4) derivatives with Na–Hg.[32] While this manuscript was in preparation, it was reported by Nozaki that use of BBr_3 in place of BCl_3 allows full reduction to B(I) with Li naphthalide, even for prototype diazadiene **1**.[5] Some early attempts by us to use 4,4′-bis-Bu^t-biphenyl as a catalyst of lithium reduction were plagued with problems of contamination with the lithium biphenyl, while Nozaki was able to remove the less-soluble excess lithium naphthalenide by filtration.[5]

The structure of **7** is shown in Fig. 6. It has metrical parameters in accordance with those of other N,N′-diaryl-diazaboroles,[6d,g,i] the shortening of all the bonds within the diazaborole ring upon reduction of **3** to form **7** being evident. The planarity of the diazaborole ring is not shared by N,N′-dialkyl analogues.[6c]

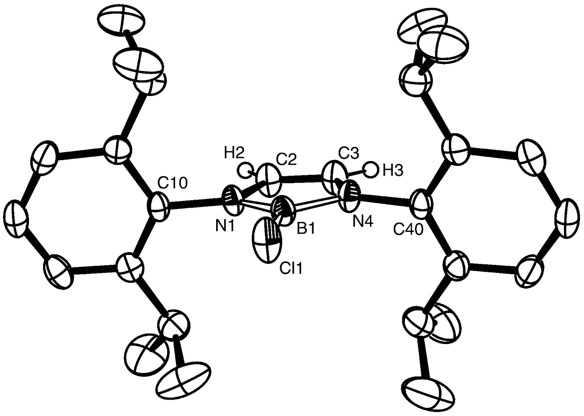


Fig. 6 Crystal and molecular structure of diazaborole **7**. Diazaborole ring hydrogens are shown, others are omitted.

Lithium reduction of **6** proceeded slowly, but after three weeks of stirring, refrigeration produced a small yield of complex **8**, Fig. 7.

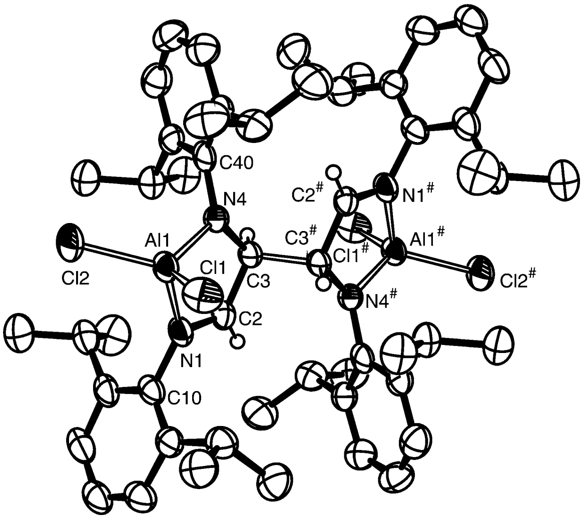


Fig. 7 Crystal and molecular structure of **8**. Amido-imine ring hydrogens are shown, others are omitted. The asymmetric unit comprises one half-molecule; symmetry-equivalent atoms are labelled with #. Thermal ellipsoids are drawn at 50% probability level.

While reduction succeeds in closing the diazaaluminolium ring, the open-shell $AlCl_2$ complex of a hemi-reduced diazabutadiene appears to be unstable. This is surprising in view of the fact that an

AlI_2 complex of the same diazabutadiene radical anion has been spectroscopically and crystallographically characterized.[30] In the case of $AlCl_2$, the open-shell species undergoes C–C coupling to produce the linked, closed-shell complex **8**. The coupling happens in such a way as to generate *meso* diamides. The crystallographic centre of the $P\bar{1}$ space group lies at the midpoint of the C3–C3$^{\#}$ bond. This coupling serves to localise the π-system, such that the ligand is now best described as a bis(α-amino-imine). The two nitrogen–aluminium interactions, which might be termed covalent and dative, are distinguished by differing bond lengths, 1.82 and 1.95 Å, respectively. A notable feature is the pyramidalization of the amido-nitrogen. N1 lies 0.197 Å above the plane defined by its three substituents. Most amidoaluminum complexes have the amido groups in bridging positions; we recently published data which allows a close comparison, a β-amidoalane with a terminal amide where the organic substituent on the amide was identical (2,6 diisopropylphenyl), and the aluminium was co-ordinated also by a neutral imine donor and two hydride or chloride ligands. In that case, the pyramidalization was greatly reduced (distance of N above plane defined by its three substituents: 0.013 Å).[33] The pyramidalization in **8** may therefore be the consequence of steric repulsion between the two halves of the dimeric species, since the distortion observed maximised this separation. Its NMR spectra were very broad, suggesting the presence of paramagnetism in the sample. No NMR data have been reported for the similar AlI_2 complex.[30]

This coupling of diazabutadienes has been seen before in zinc chemistry,[34] and recently in a pyridyl imine on gallium,[35] but this is the first observation of the behaviour involving the very bulky ligand **1**. The bulk would have been expected to help to stabilize the radical, as it did for **1**·AlI_2.[30] The differing sterics of Cl *vs.* I would appear to be too remote from the site of coupling to have a bearing on the relative stability of open and closed-shell species. Quantum-chemical computations were employed to probe the electronic aspects of this difference. These indicated that substitution of iodide for chloride had a negligible effect on spin density on the carbon atoms involved in the coupling (see ESI§). The electronic structure calculations confirmed the established view of such compounds as AlX_2^+ complexes of ligand-based radical anions.[36] The remaining possibilities are (i) that there is a negligible energy difference between C–C coupled closed shell and radical complexes, and better packing in the solid state favours the formation of the closed shell dimeric species **8** while in solution it is in equilibrium with open-shell monomer, or (ii), that differing synthetic routes (the iodide case was a product of *in situ* reduction with Al powder)[30] caused the chloride and iodide reactions to follow different courses. We favour the former explanation, since we recently showed in a related adduct of a similarly bulky diketiminate-ketone complex that a solution-promoted bond scission equilibrium was operating on a C–C bond of length 1.64 Å.[9] The C3–C3$^{\#}$ length is shorter than this, but at 1.58 Å, is still a long C–C bond. Furthermore, such solution equilibria have been well-established in the case of zinc-diazadiene radicals.[33]

While the presumed intermediate radical complex proved elusive for aluminium due to C–C coupling, and our attempts to characterise it spectroscopically were frustrated by sample decomposition and low yields, phenyl substituents on the diazabutadiene carbons prevented any such path for the diazaborolium salt derived from ligand **2**. When it was reduced with lithium sand, the reaction proceeded as far as diazaborole **9a**, but crystals showed shadow positions above and below the single remaining chlorine substituent whose 14-line regular multiplet solution phase X-band EPR spectrum indicates approximately equal couplings to two ^{14}N, one ^{11}B and two ^{35}Cl atoms. This indicated that approximately 11% of lattice points in the crystal were occupied not with the closed shell diazaborole **9a**, but with the less-reduced open-shell **9b**, a neutral complex of a diazadiene radical anion with (BCl_2) cation. Both **9a** and **9b** are shown as a composite structure in Fig. 8. The compound possesses a crystallographic C_2 axis along the B(1)–Cl(1a) bond vector. This dictates an *anti* arrangement of isopropyl groups. The imine-aryls lie at an angle of 72.5° with respect to the central diazachloroborole plane indicating limited delocalization, but the C-aryls lie at an angle of 44.4° to the central plane, suggesting some stabilization of spin density through partial π-delocalization from the diazadiene. While the open shell **9b** might be expected to exhibit longer C–C and shorter C–N bonds than the more fully reduced **9a**, there is no evidence of split sites, or even of distorted ellipsoids, for C(2). The changes are so slight as to be undetectable. The bond lengths found are comparable with those from other known diazaboroles.[6] Fortunately, the presence of some paramagnetism in the sample, while allowing EPR to be observed for **9b**, did not hamper the observation of NMR data for **9a**. This revealed, when recorded immediately after dissolution, major peaks assigned to the *anti* conformation exhibited in the crystal, and some additional small peaks assigned to a *syn* conformation of isopropyl groups. On standing for 100 min, the populations of both conformations became essentially equal, and remained constant thereafter, indicating a negligible energy difference between them in the solution state, and a relatively slow fluxion, with no exchange broadening.

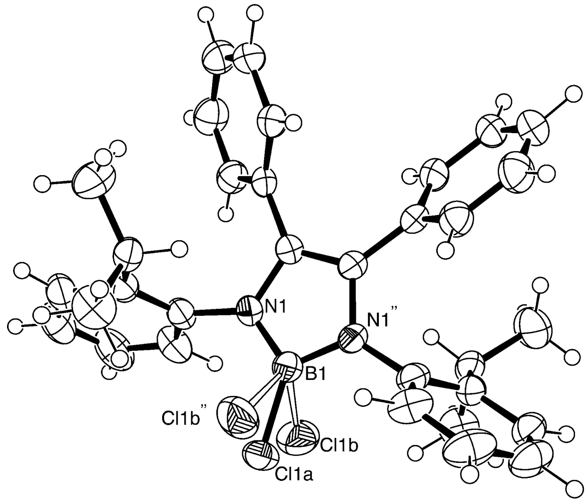


Fig. 8 Crystal and molecular structure of **9a**/**b**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted.

Returning to **9b**, similar diazadiene radical anion complexes are known for Al alkyls[37] and iodides,[30,36] Ga iodides and bromides,[30,35,36,38] and In chlorides,[35,36,39] but we find $AlCl_3$ behaviour with diazadiene **1** to be different from all the above, and from BCl_3 behaviour. In addition, stable radical $(DAD)_2M$ complexes have long been known for M = Al and Ga,[40] and

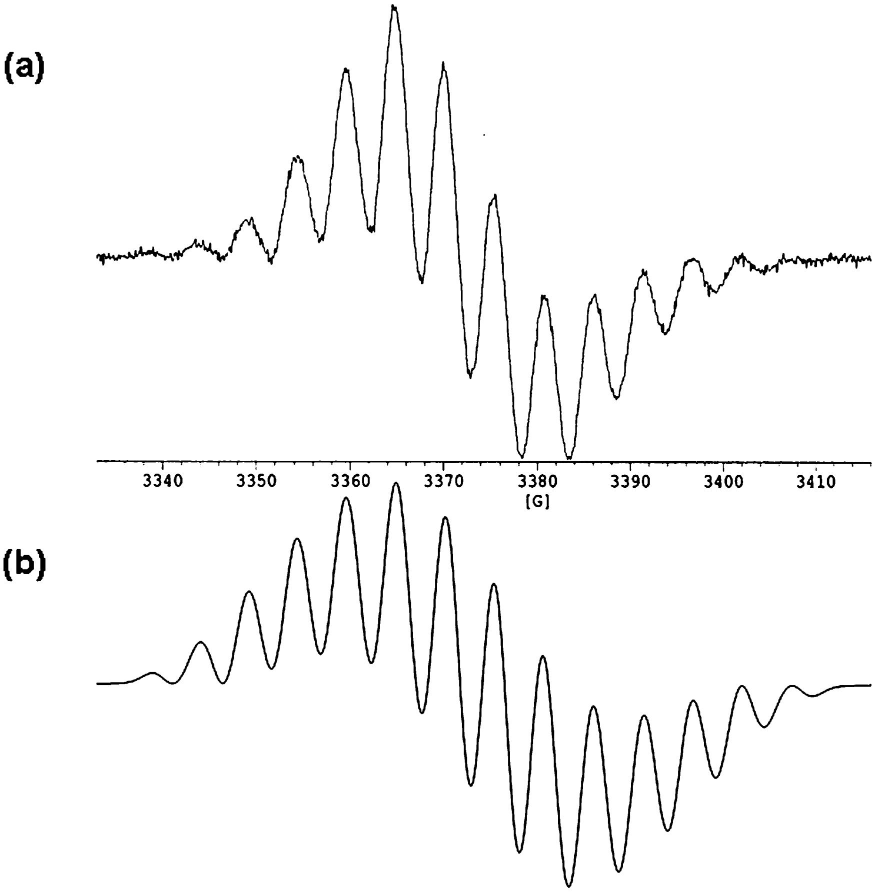


Fig. 9 (a) 1st derivative plot of the EPR spectrum of the fluid solution of **9b** in $CDCl_3$ at 293 K. (b) SIMFONIA simulation using coupling constants $a_{11\text{-B}} = 4.0$, $a_{10\text{-B}} = 1.34$, $a_{14\text{-N}} = 5.5$; $a_{35\text{-Cl}} = 4.5$; $a_{37\text{-Cl}} = 4.0$ G, Gaussian–Lorentzian parameter 0.7, and linewidth 2.4 G.

for M = Li, Mg and Zn,[41] but this is the first case of which we are aware of a stable diazadiene radical anion complex of boron. Heretofore, only computational data has been available.[42] These heavier analogues have been well-studied by EPR and ENDOR spectroscopies,[36] and instructive comparisons can be drawn with the data presented in Fig. 9. Computation of accurate *a*-values is notoriously difficult,[43] and this proved to be the case for **9b**: Unrestricted density functional-computed *a*-values for B, N, and Cl at b3lyp using 6-311G(d,p) basis were 6, 3 and 4 G, respectively. In particular, the value of 3 G for a_N in what is essentially a complex of a diazadiene radical seems small,[36,37] in common with more recent computational work on similar systems.[43] The generally regular features of the spectrum, where each peak is separated by around 5 G, suggest that all coupling constants converge close to this value. Indeed, in Ga and Al complexes of similar diazadiene radicals, values of 5 to 6 G have been observed for a_N.[36] The slightly sinusoidal envelope of the spectrum, and the deviation of intensities from the theoretical 1 : 5 : 15 : 33 : 57 : 81 : 96 : 96 : 81 : 57 : 33 : 15 : 5 : 1 ratio, suggests that some of the *a*-values deviate slightly from 5 G, but the breadth of the signals, partly due to minor isotopomers from ^{10}B ($I = 3$) and ^{37}Cl ($I = 3/2$) and numerous small, unresolved a_H couplings (all $a_H < 0.7$ G by computation), means that reasonable fits can be obtained for a range of values, and the only conclusion that can drawn with certainty is that two N, two Cl and one B nuclei couple to the unpaired spin density, all with values around 5 ± 1 G for the major isotopes. Such modest agreement with gas-phase *ab initio* computation is not unexpected, given the presence of different conformers in solution, and the room-temperature solution phase of the spectral data collection. Inclusion of the small couplings from the aryl hydrogens failed to improve the fit. Of interest is the fact that chlorine couplings could be observed, in contrast to the case with [**1**·$InCl_2$·thf] and [(**1**·InCl)$_2$].[39] This is presumably due to the closer proximity of the chlorine nuclei to the concentration of unpaired spin density on the diazadiene fragment in **9b**, and the greater Cl–N and Cl–B overlap than for the indium case. Notwithstanding the modest agreement with experiment, a plot of the total Unrestricted Density functional spin density is shown in Fig. 10a. A plot of the SOMO is shown in Fig. 10b. From this it is clear that the unpaired electron density is concentrated on the diazadiene fragment, in common with complexes of **1**, though significant delocalization from the diazadiene into the C-phenyls is evident, while negligible amounts reside on the near-orthogonal N-phenyls. The large α-spin density on nitrogen polarizes the boron spin density to be β; there is minimal contribution to the SOMO from boron. However, the significant α-spin on the chlorines can be attributed to the contribution of their p-orbitals to the π-SOMO *via* hyperconjugative donation of B–Cl σ-bonding elecron density, principally from a Cl 3p orbital, mixing with the partially occupied diazadiene π-system. Thus, spin-density on the chlorines appears to reside in a p-type orbital directed along the B–Cl bond vector.

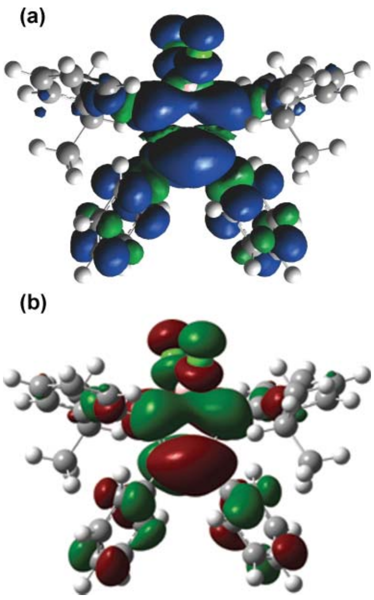


Fig. 10 (a) Plot of total spin density from an Unrestricted B3LYP/6-311G (d,p) geometry optimised density functional computation on **9b**; α-spin denoted as dark blue, β-spin as dark green. Atom colours: chlorine: light green; carbon: grey; hydrogen: white; boron: pink; nitrogen: light blue. (**b**) Plot of SOMO, atom colours as above, α-orbital red–brown, β-orbital green.

Conclusion

BCl_3 cyclizes **1** through a chloroborated intermediate **3**, isolable from hexane, to give in more polar solvents a spontaneously dehyrochlorinated diazaborole **4**. In contrast, reaction of $AlCl_3$ with **1** forms only acyclic mono- or di-adducts **5a/b** and **6**. Such preformed M(III) chloride complexes of diazadiene ligands do not lead to M(I) or M(II) species in the cases investigated. Reduction of boron diazadienes proceeded further than those of aluminium analogues, under similar conditions: Alkali metal reductions of **3** give mixtures of **4** and diazaborole **7**. Pd(0) reduction cleanly gave diazaborole **7**. Reduction of **6** gave a low yield of closed shell C–C coupled dimer **8** of the putative diazadiene radical anion-$AlCl_2$ complex monomer. Reduction of **2**/BCl_3, in which additional phenyl groups on the diazadiene carbon atoms hinder such radical coupling, gave predominantly diazaborole **2**·BCl **9a**, contaminated with **2**·BCl_2 **9b**, the first such stable radical diazadiene complex of boron. Thus, high degrees of *ortho*-aryl bulk on the N-substituents of the diazadiene promote varying and unusual chemistry, including the first documented case of chloroboration of an imine bond, the first example of C–C coupling of a diazadiene radical bearing 2,6-diisopropylphenyl substituents, and the first spectroscopic and structural data on a stable diazabutadiene radical complex of boron, such species having first been observed in heavier group 13 element compounds.

Acknowledgements

We gratefully acknowledge Mr John Friend of the EPSRC National Service for EPR spectroscopy for data collection and processing, Dr Robert Manning and Mr Martyn Peers for synthetic assistance, and the Nuffield Foundation, the EPSRC and Creators Ltd for financial support (JEW).

References

1 A. J. Arduengo, III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
2 E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9758; E. S. Schmidt, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 2001, 505.
3 R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 3844.
4 A. Sunderman, M. Reiher and W. W. Schoeller, *Eur. J. Inorg. Chem.*, 1998, 305; N. Metzler-Nolte, *New J. Chem.*, 1998, 793.
5 Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113.
6 (*a*) L. Weber and G. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 1; (*b*) G. Schmid and J. Schulze, *Chem. Ber.*, 1977, **110**, 2744; (*c*) G. Schmid, M. Polk and R. Boese, *Inorg. Chem.*, 1990, **29**, 442; (*d*) L. Weber, E. Dobbert, R. Boese, M. T. Kirchner and D. Bläser, *Eur. J. Inorg. Chem.*, 1998, 1145; (*e*) L. Weber, M. Schneider, R. Boese and D. Bläser, *J. Chem. Soc., Dalton Trans.*, 2001, 378; (*f*) L. Weber, M. Schnieder and P. Lönneke, *J. Chem. Soc., Dalton Trans.*, 2001, 3459; (*g*) L. Weber, A. Rausch, H. B. Wartig, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 2002, 2438; (*h*) L. Weber, I. Domke, A. Rausch, A. Chrostowska and A. Dargelos, *Dalton Trans.*, 2004, 2188; (*i*) L. Weber, J. Förster, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 2006, 5048.
7 F. S. Mair, R. Manning, R. G. Pritchard and J. E. Warren, *Chem. Commun.*, 2001, 1136.
8 H. tom Dieck, M. Svoboda and T. Greiser, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1981, **36**, 823.
9 D. T. Carey, E. K. Cope-Eatough, E. Vilaplana-Mafé, F. S. Mair, R. G. Pritchard, J. E. Warren and R. J. Woods, *Dalton Trans.*, 2003, 1083.
10 R. Carlson, U. Larsson and L. Hansson, *Acta Chim. Scand.*, 1992, **46**, 1211.
11 K. YvonW. Jeitschko and E. Par,*LAZY PULVERIX, Software for the calculation of theoretical powder diffraction patterns from single crystal data*.
12 G. Ferguson, R. McCrindle, A. J. McAlees and M. Parvez, *Acta Crystallogr., Sect. B.*, 1982, **B38**, 2679.
13 *COLLECT, Data collection software*, Bruker-Nonius B.V., Delft, The Netherlands, 1999.
14 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, 307.
15 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **A51**, 33.
16 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
17 *SHELXL-97, Software for crystal structure refinement*, G. Sheldrick, University of Göttingen, Germany, 1997.
18 *GAUSSIAN 98, Revision A.7, Software for quantum chemical computation*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
19 W. Clegg, S. J. Coles, E. K. Cope and F. S. Mair, *Angew. Chem., Int. Ed.*, 1998, **37**, 796–798; H. Hamaki, N. Takeda, T. Yamasaki, T. Sasamori and N. Tokito, *J. Organomet. Chem.*, 2007, **692**, 44.
20 R. van Belzen, R. A. Klein, W. J. J. Smeets, A. L. Spek, R. Benedix and C. J. Elsevier, *Recl. Trav. Chim. Pays-Bas*, 1996, **115**, 275.
21 F. Sannicolò, *J. Org. Chem.*, 1983, **48**, 2924.
22 W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.
23 J. E. Johnson, N. M. Morales, A. M. Gorczyca, D. D. Doliver and M. A. McAllister, *J. Org. Chem.*, 2001, **66**, 7979; J. M. Blackwell, W. E. Piers, M. Parvez and R. McDonald, *Organometallics*, 2002, **21**, 1400.
24 H. A. Jenkins, C. L. Dumaresque, D. Vidovic and J. A. C. Clyburne, *Can. J. Chem.*, 2002, **80**, 1398.
25 M. F. Lappert and B. Prokai, *J. Chem. Soc.*, 1963, 4223.
26 A. Suzuki, *Rev. Heteroat. Chem.*, 1997, **17**, 271, and refs therein.

27 A. M. Kibardin, I. A. Litvinov, V. A. Naumov, Yu. T. Struchkov, T. V. Gryaznova, Yu. B. Mikhailov and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, 1988, **298**, 369.

28 T. V. Laine, M. Klinga, A. Maaninen, E. Aitola and M. Leskela, *Acta Chem. Scand.*, 1999, **53**, 968.

29 U. Klingebiel, M. Noltemeyer, H. G. Schmidt and D. Schmidt-Base, *Chem. Ber.*, 1997, **130**, 753.

30 R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 1196.

31 J. S. Merriam and K. Niedenzu, *J. Organomet. Chem.*, 1973, **51**, C1.

32 B. Hessett, J. B. Leach, J. H. Morris and P. G. Perkins, *J. Chem. Soc. A*, 1972, 131.

33 D. T. Carey, F. S. Mair, R. G. Pritchard, J. E. Warren and R. J. Woods, *Dalton Trans.*, 2003, 3792.

34 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606; G. van Koten, J. T. B. H. Jastrzebski and K. Vrieze, *J. Organomet. Chem.*, 1983, **250**, 49; E. Wissing, E. Rijnberg, P. A. van der Schaaf, K. van Gorp, J. Boersma and G. van Koten, *Organometallics*, 1994, **13**, 2609; E. Wissing, S. von der Linden, E. Rijnberg, J. Boersma, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1994, **13**, 2602.

35 R. J. Baker, C. Jones, M. Kloth and D. P. Mills, *New J. Chem.*, 2004, **28**, 207.

36 R. J. Baker, R. D. Farley, C. Jones, D. P. Mills, M. Kloth and D. M. Murphy, *Chem.–Eur. J.*, 2005, **11**, 2972.

37 H. Schumann, M. Hummert, A. N. Lukoyanov and I. L. Fedushkin, *Organometallics*, 2005, **24**, 3891.

38 T. Pott, P. Jutzi, W. Kaim, W. W. Schoeller, B. Neumann, A. Stammler, H.-G. Stammler and M. Wanner, *Organometallics*, 2002, **21**, 3169.

39 R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *Chem. Commun.*, 2002, 1196.

40 F. G. N. Cloke, C. I. Dalby, M. J. Henderson, P. B. Hitchcock, C. H. L. Kenna, R. N. Lamb and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1990, 1394; F. G. N. Cloke, C. I. Dalby, P. J. Daff and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 1991, 181; F. G. N. Cloke, G. R. Hanson, M. J. Henderson, P. B. Hitchcock and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1989, 1002; M. J. Henderson, C. H. L. Kennard, C. L. Raston and G. Smith, *J. Chem. Soc., Chem. Commun.*, 1990, 1203.

41 M. G. Gardiner, G. R. Hanson, M. J. Henderson, F. C. Lee and C. L. Raston, *Inorg. Chem.*, 1994, **33**, 2456; P. J. Bailey, C. M. Dick, S. Fabre, S. Parsons and L. J. Yellowlees, *Dalton Trans.*, 2006, 1602.

42 W. W. Schoeller and S. Grigoleit, *J. Chem. Soc., Dalton Trans.*, 2002, 405.

43 T. Chivers, D. J. Eisler, C. Fedorchuk, G. Schatte, H. M. Tuononen and R. T. Boeré, *Chem. Commun.*, 2005, 3930; H. M. Tuononen and A. F. Armstrong, *Dalton Trans.*, 2006, 1885; H. M. Tuononen, T. Chivers, A. F. Armstrong, C. Fedorchuk and R. T. Boeré, *J. Organomet. Chem.*, 2007, **692**, 2705.