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Imine chloroboration: reaction of boron trichloride with a bulky diazadiene gives not a diazaborolium salt, but a 2,4,5 trichloro-1,3,2-diazaborolidine†

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Reaction of *N,N′*-bis(2,6-diisopropylphenyl)-1,4-diazadiene with BCl_3 in hexane gave the crystalline product of double chloroboration, *N,N′*-bis(2,6-diisopropylphenyl)2,4,5-trichloro-1,3,2-diazaborolidine, which was characterised by single crystal X-ray diffraction, microanalysis and multinuclear NMR spectroscopy.

Hydroboration has become one of the principal vehicles of functional group interconversion. Additions of B–H across all manner of unsaturated bonds, including C=O and C=N, are extremely well documented.[1] Haloboranes, conversely, are best known as Lewis acids and ether cleavage agents, where the mode of reactivity is insertion into a single bond,[2] as opposed to addition across a multiple bond. Addition of a haloborane reagent across a multiple bond, 'haloboration', is less widely studied; though isolated reports of such reactivity began in the mid-20th century, covering alkynes, aldehydes and isocyanates,[3] only recently through the work of Suzuki and coworkers has the synthetic utility of the reaction type been systematically probed, concentrating on the bromoboration of alkynes.[4] Chloroboration of alkenes has also been recently identified as the mechanism for the living cationic polymerisation of isobutene.[5] During the attempted synthesis of a very bulky diazaborolium salt, it was discovered that the compound produced was the product of a double B–Cl addition across two aldimine C=N bonds, the first case, to our knowledge, of imine haloboration. In our attempts to explore novel metal boryl chemistry, it became necessary to prepare extremely bulky diazaborolium salts. These species have been known for some time to be available *via* the addition of boron halides to diazadiene ligands.[6] Interest in the area has recently been revived,[7] spurred by the isolation of stable carbenes by Arduengo *et al.*[8] However, during all of these syntheses, which were in most cases directed at further reduction of the putative diazaborolium halides to produce 6π pseudoaromatic diazaborole compounds, no diffraction data were collected on the diazaborolium compounds.

Reaction† of $(2,6\text{-}\mathrm{Pr^i}_2C_6H_3NCH)_2$ with BCl_3 in hexane produced an orange powder, **1a**. This was isolated by filtration and from the filtrate, diffraction quality crystals of **1b** were grown. Both the orange powder **1a** and the crystals **1b** showed the same microanalysis, corresponding to the 1:1 product, and had identical NMR spectra in $CDCl_3$. The spectra appeared consistent with the expected diazaborolium formulation $[(2,6\text{-}\mathrm{Pr^i}_2C_6H_3NCH)_2BCl_2]^+Cl^-$, save for the fact that the 'diazaborolium' ring CH protons resonated at 6.9 ppm, slightly upfield of where they are normally found (8–9 ppm)[6,7] in the ^1H NMR spectrum, and the ^{11}B NMR signal was slightly shifted from its expected position, and much broader than expected for a pseudo-tetrahedral boron site. More puzzling was the observance of two distinct isopropyl methine resonances. This was indicative not only of extremely slowed aryl ring rotation, but also of a lack of an approximate plane of symmetry in the molecule in any conformation.

The reason for the spectral anomalies became clear upon solution of the X-ray diffraction data:‡ The crystalline compound is not an ionic salt **1a**, but the neutral diazaborolidine molecule **1b** (see Fig. 1 and Scheme 1), the result of a double chloroboration of the diazadiene. Only a single chloride remains

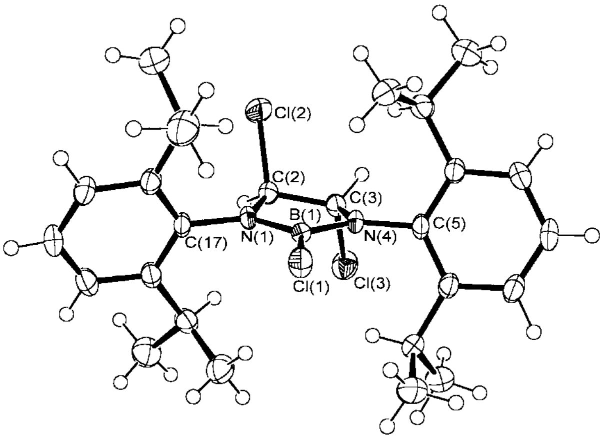
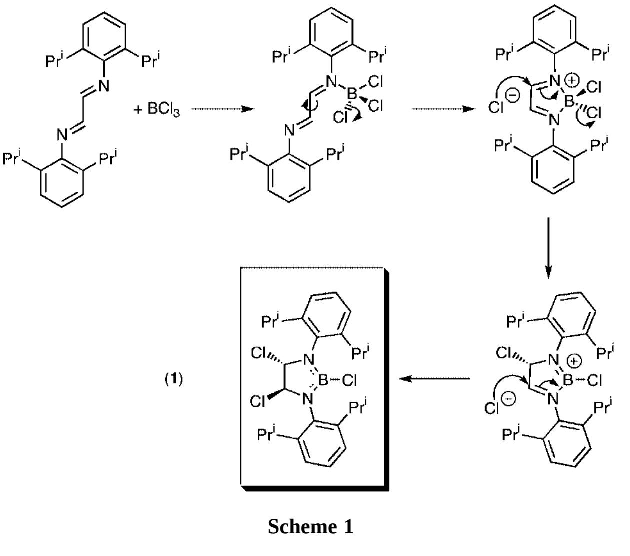


Fig. 1 Crystal and molecular structure of **1b**. Selected bond lengths (Å) and angles (°): B(1)–N(1) 1.403(3), B(1)–N(4) 1.416, B(1)–Cl(1) 1.743(3), N(1)–C(2) 1.413(3), N(1)–C(17) 1.445(3), N(4)–C(3) 1.417(3), N(4)–C(5) 1.433(3), Cl(3)–C(3) 1.841(3), Cl(2)–C(2) 1.840(3), C(2)–C(3) 1.528(3); N(1)–B(1)–N(4) 109.4(2), N(1)–B(1)–Cl(1) 125.5(2), N(4)–B(1)–Cl(1) 125.1(2), B(1)–N(1)–C(2) 109.10(19), B(1)–N(1)–C(17) 128.9(2), C(2)–N(1)–C(17) 121.98(19), B(1)–N(4)–C(3) 108.82(19), B(1)–N(4)–C(5) 129.4(2), C(3)–N(4)–C(5) 121.78(19), N(1)–C(2)–C(3) 105.45(19), N(1)–C(2)–Cl(2) 112.93(17), C(3)–C(2)–Cl(2) 107.26(16), N(4)–C(3)–C(2) 105.05(19), N(4)–C(3)–Cl(3) 112.85(17), C(2)–C(3)–Cl(3) 107.51(17).



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental details and characterisation data for **1**. See http://www.rsc.org/suppdata/cc/b1/b101580j/

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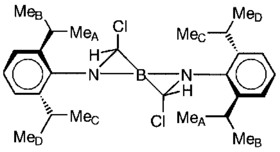

Scheme 2

bound to boron, completing the trigonal-planar geometry around that atom. The other two chlorides have added to the carbons of the diazadiene fragment, in an *anti* configuration, generating two chiral centres. Structurally **1b** bears close similarities with previously reported diazaborolidines of which there are two characterised by single-crystal X-ray diffraction [$(MeNCH_2)_2BMe$ and $(EtNCH_2)_2BMe$],[9] and one by gas-phase electron diffraction [$(MeNCH_2)_2BCl$].[10] All exhibit a puckered ring with slight pyramidalization at nitrogen, and one methylene group lying above, and one below, the mean ring plane. However, in **1b**, each nitrogen is rigorously planar, due to the bulky aromatic substituent. These aryl rings are slightly skewed from orthogonality (+14.4 and −14.3°) with the diazaborolidine ring by repulsions from the chlorides. This generates a C_2-symmetric environment about the boron (Scheme 2).

The IR spectrum of **1a** showed an absorption in the region 1580–1590 cm^{-1} indicative of a boron-coordinated imine,[6,7] whereas that of the crystals **1b** contained no such band. Furthermore, **1a** and **1b** were established to be different materials by powder X-ray diffraction. This identified **1a** as the expected diazaborolium salt, even though NMR spectroscopy in $CDCl_3$ showed it to be identical to **1b**. This leads to the conclusion that conversion of the initially formed diazaborolium salt to **1b** is completed in that solvent. The alternative possibility that in $CDCl_3$ the chlorides in **1b** dissociate from the carbons is excluded by the observation of distinct signals for the isopropyl methine resonances, directly ascribable to the reduction in symmetry generated by the addition of the chlorides above and below the diazaborolium ring plane (Scheme 1). Similar behaviour was observed in CD_3CN.

The fact that **1b** is indistinguishable by elemental analysis from the diazaborolium formulation, and the previous lack of diffraction data, offered the possibility that this unexpected reactivity had been missed in previous literature, but careful re-examination of published data showed that the diazaborolium formulation was amply supported by conductivity, IR and ^1H and ^{11}B NMR data.[6,7] The chloroboration reaction is therefore exclusive to **1**. Since previously reported examples include close analogues of **1**, including one case[7] which is identical save for the substitution of methyl groups in the aryl 2- and 6-positions for the isopropyl groups in **1**, the key to the reactivity appears to lie in the increased bulk. It may be that the boron atom cannot sustain four-coordination in the presence of the two diisopropylphenyl groups. In hexane solvent, the nucleophilicity of chloride, once ejected from the coordination sphere of the boron atom, would be high. Allying this to the fact that boron halides in their role as Lewis acids are often employed in order to encourage attack by nucleophiles at *ipso* carbon atoms, including such roles for imine additions[11] leads to a tentative mechanism such as that shown in Scheme 1. That the reaction proceeds to completion in the more polar solvents deuterochloroform and deuteroacetonitrile, more facilitative of ionization, further supports a description of the reactivity as a double 1,3-nucleophilic rearrangement.

A structural factor of particular note is the pronounced shortening in the diazaborolidine ring C–N bonds, which at a mean distance of 1.415(3) Å lie closer to the distances found in the pseudo-aromatic diazaboroles (mean of known values to date: 1.404 Å)[7,9] than to the more normal single bond values found in other known diazaborolidines (mean 1.459 Å).[9,10] The C–Cl distances in **1b** are conversely rather long at 1.84 Å, but are comparable to those in $(CHCl_2)_3N$ obtained by chlorination of triformamide;[12] the C–N and C–Cl distances in that case were 1.418(2) and 1.800(1) Å, respectively. It is a very rare situation because chloroamides are normally assumed to adopt an ionic form, *i.e.* the equilibrium shown in Scheme 3 lies to the left.[13] The analogy between this long-known behaviour and the newly discovered diazaborolium/diazaborolidine dichotomy is a strong one. In both cases, the molecular form would appear to retain a significant contribution from the ionic form in the ground-state equilibrium structure, as evidenced by the short C–N and long C–Cl bonds and rigorously planar nitrogen.[12] This type of behaviour has previously been termed single-bond–no-bond resonance.[14] No such behaviour is apparent in the much more common quaternary ammonium α-chloro-organonitrogen species.[14]

Scheme 3

An important distinction between the two cases discussed[12,13] above is that there is only one chloride on each carbon in **1**; as an isolable synthon for a mono-α-chloro secondary amine, **1** is unique. We intend to pursue this analogy in parallel with the reduction chemistry of the current system to access highly hindered diazaboroles. It is also apposite to reflect that the use of extreme steric bulk does not always merely pacify chemical reactivity, but in certain circumstances can engender new and unexpected directions of that reactivity.

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Notes and references

‡ *Crystal data* for **1b**: $C_{26}H_{36}BCl_3N_2$, M = 493.73, triclinic, space group $P\bar{1}$, a = 8.323(4), b = 9.8086(3), c = 17.35350(10) Å, α = 93.246(3), β = 90.208(2), γ = 115.0350(10)°, U = 1281.0(6) Å^3, Z = 2, D_c = 1.246 Mg m^{-3}, μ = 0.375 mm^{-1} (Mo-Kα, λ = 0.71073 Å), $F(000)$ = 524, T = 203 K. Nonius MACH 3 diffractometer, crystal size 0.4 × 0.3 × 0.3 mm, θ_{max} = 24.97°, 4812 reflections measured, 4475 unique. Final wR_2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$ = 0.1257 for all data, conventional R = 0.0445 for 3324 observed reflections. CCDC 160079. See http://www.rsc.org/suppdata/cc/b1/b101580j/ for crystallographic data in CIF or other electronic format.

1 H. C. Brown, *Hydroboration*, Benjamin, New York, 1962.

2 Y. Guindon, C. Yoakim and H. C. Morton, *Tetrahedron Lett.*, 1983, **24**, 2969; Y. Guindon, M. Therien, Y. Girard and C. Yoakim, *J. Org. Chem.*, 1987, **52**, 1680 and references therein. See also, J. March, *Advanced Organic Chemistry*, Wiley Interscience, New York, 4th edn., 1992, pp. 433–434.

3 M. F. Lappert, *Angew. Chem.*, 1960, **72**, 36; M. F. Lappert and B. Prokai, *J. Chem. Soc.*, 1963, 4223.

4 A. Suzuki, *Rev. Heteroat. Chem.*, 1997, **17**, 271, and references therein.

5 L. Balogh, L. F. Wang and R. Faust, *Macromolecules*,1994, **27**, 3453.

6 L. Weber and G. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 467; G. Schmid and J. Schulze, *Chem. Ber.*, 1977, **110**, 2744.

7 L. Weber, E. Dobbert, H.-G. Stammler, B. Neumann, R. Boese and D. Bläser, *Chem. Ber.*, 1997, **130**, 705; L. Weber, E. Dobbert, R. Boese, M. T. Kirchner and D. Bläser, *Eur. J. Inorg. Chem.*, 1998, 1145; L. Weber, M. Schnieder, R. Boese and D. Bläser, *J. Chem. Soc., Dalton Trans.*, 2001, 378.

8 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.

9 G. Schmid, M. Polk and R. Boese, *Inorg. Chem.*, 1990, **29**, 4421.

10 H. M. Seip, R. Seip and K. Niedenzu, *J. Mol. Struct.*, 1973, **17**, 361.

11 H. Yamada, T. Kawate, A. Nishida and M. Nakagawa, *J. Org. Chem.*, 1999, **64**, 8821.

12 E. Allenstein, W. Schwarz and E. Schrempf, *Z. Anorg. Allg. Chem.*, 1987, **546**, 107.

13 H. Eilingsfeld, M. Seefelder and H. Weidinger, *Angew. Chem.*, 1960, **72**, 836.

14 E. Anders, A. Opitz, K. Wermann, B. Wiedel, M. Walther, W. Imhof and H. Görls, *J. Org. Chem.*, 1999, **64**, 3113; Ch. Lambert and P. v. R. Schleyer, *Houben-Weil Carbanionen-Polare Organometall-Verbindungen*, Georg Thieme Verlag, Stuttgart, 1993, p. 1–98.