N-Functionalized Amino-aluminium and -boron Complexes: Intramolecular Aromatic Nitrogen-assisted Formation of Aminoboranes

Lutz M. Engelhardt,[a] Geraldine E. Jacobsen,[a] Peter C. Junk,[b] Colin L. Raston,[b]* and Allan H. White[a]

[a] *Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, W.A., 6009, Australia*

[b] *Division of Science and Technology, Griffith University, Nathan, Brisbane, 4111, Australia*

Reaction of 6-methyl-2-bis(trimethylsilyl)pyridine or 8-bis(trimethylsilyl)aminoquinoline with BCl_3 in hexane results in facile elimination of $ClSiMe_3$ affording an aminodichloroborane, (**2**) or (**5a**), then a novel aminobis(dichloroborane), (**3**) or (**6**); compounds (**3**) and (**5b**), prepared from a lithium reagent and $AlCl_3$, have been structurally authenticated using *X*-ray diffraction data.

Reactions of halogenoboranes with silylamines, notably hexamethyldisilazane[1] and tris(trimethylsilyl)amine,[2,3] yield aminoboranes through intermolecular elimination of chlorosilanes, usually under rather forcing conditions. We show that an aromatic nitrogen centre in close proximity to nitrogen bearing two $SiMe_3$ groups results in rapid elimination of one or two molecules of $ClSiMe_3$ in the presence of BCl_3, the final product being a novel aminobis(dichloroborane). In addition, we report the synthesis of an aminodichloroaluminium compound which also undergoes rapid elimination of $ClSiMe_3$ with BCl_3.

$NAr(SiMe_3)_2$ (Ar = 6-methyl-2-pyridyl) (**1a**)[4] rapidly yields the aminoborane (**2**) or aminodiborane (**3**) under mild conditions.† The ^{11}B NMR spectrum of (**3**) shows a chemical shift characteristic of three- and four-co-ordinate boron centres,[5] respectively δ 7.2 and 32.0 p.p.m. commensurate with the solid state structure (see below); that of compound (**2**), δ 7.5 p.p.m. is consistent with four-co-ordinate boron centres and thus molecules of this compound are assumed to possess a strained four-membered chelate ring.

Compound (**1b**) failed to undergo elimination under the same conditions as the isoelectronic compound (**1a**), although it reversibly binds BCl_3 to give a white solid, presumably a Lewis base adduct. This has mechanistic implications for the aforementioned elimination reactions, namely that the primary process is activation of BCl_3 by complexation of the aromatic nitrogen centre, which is a much stronger base than a silylated amine.[6] Such a proximity effect is reminiscent of intramolecular Lewis base assisted lithiation reactions.[7] The second elimination/activation could arise by competitive complexation between BCl_3 and the dichloroborane unit.

$NAr(SiMe_3)_2$ (Ar = 8-quinolyl) (**4**)[4] parallels the reaction of (**1**) with BCl_3, yielding the corresponding silylaminoborane (**5a**), and aminobis(dichloroborane) (**6**) under mild conditions. Compounds (**5a**) and (**6a**) are assumed to have similar structures to (**2**) and (**3**), albeit with less strained five-membered chelate rings, mainly on the basis of the similarity of the ^{11}B NMR resonances [δ 9.2 p.p.m. for (**5a**); δ 8.8 and 34.8 p.p.m. for (**6**)]. In addition, the structure of the aluminium compound (**5b**), isolobal with (**5a**), has been established using *X*-ray diffraction data (see below), clearly establishing the chelating prowess of the ligand. Access to compound (**5b**) involved treating a lithium reagent with $AlCl_3$; there was no reaction between (**4**) and $AlCl_3$ even under more forcing conditions than those in the synthesis of (**2**) and (**5a**), in contrast to the reaction of $AlCl_3$ with *N,N,N'*-tris(trimethylsilyl)benzamide.[8] Compound (**5b**) undergoes $ClSiMe_3$ elimination with BCl_3 yielding a yellow, sparingly soluble powder, devoid of trimethylsilyl groups (IR), but of variable composition. The hindered amino ligand in (**5**), and also (**2**), is relatively new, previous studies being restricted to lithium complexes.[4]

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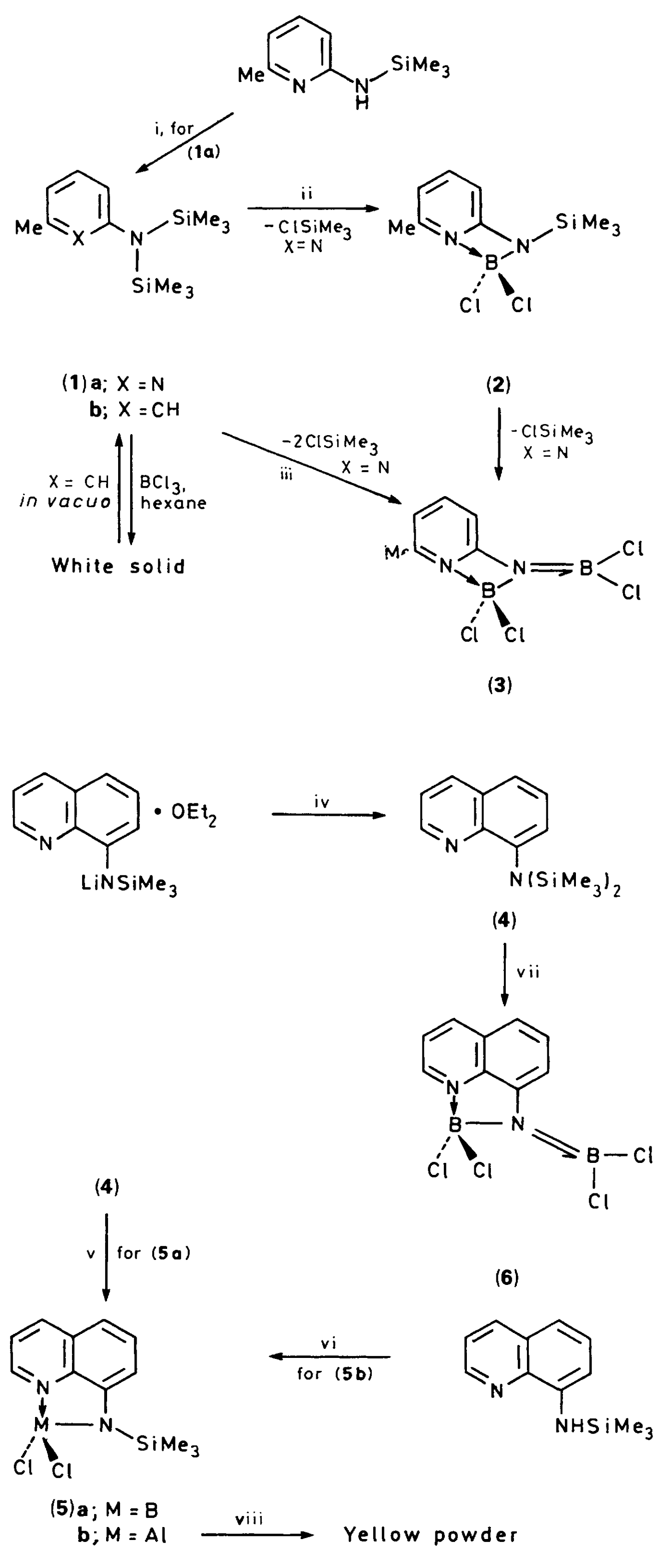
† *Spectroscopic data* (^1H NMR, 300 MHz in C_6D_6; ^{11}B NMR, 96 MHz, ref. $BF_3{\cdot}OEt_2$): (**1a**), oil, b.p. 42—44 °C (1 mmHg); ^1H NMR, δ 0.24 (18H, s, $SiMe_3$), 2.28 (3H, s, CMe), and 6.4—7.1 (3H, m, pyridyl); *m/z* 252. (**2**), m.p. 81—83 °C (decomp.); ^1H NMR, δ 0.29 (9H, s, $SiMe_3$), 1.99 (3H, s, CMe), and 5.5—6.8 (3H, m, pyridyl); ^{11}B NMR, δ 7.2 p.p.m.; *m/z* 261. (**3**), sublim. 120—140 °C (10^{-2} mmHg); ^1H NMR, δ 1.87 (3H, s, CMe), and 5.6—6.6 (3H, m, pyridyl); ^{11}B NMR, δ 7.5 (s) p.p.m.; *m/z* 268. (**4**), b.p. 88—89 °C (4 mmHg); ^1H NMR, δ 0.20 (18H, s, $SiMe_3$) and 6.7—7.7 (6H, m, quinolyl); *m/z* 288. (**5a**), m.p. 141—144 °C (decomp.); ^1H NMR, δ 0.02 (9H, s, $SiMe_3$) and 5.6—7.6 (6H, m, quinolyl); ^{11}B NMR, δ 9.2 (s) p.p.m.; IR, ν (B–Cl) 560 cm^{-1}; *m/z* 297. (**5b**), Sublim. 150 °C (0.1 mmHg); ^1H NMR, δ 0.41 (9H, s, $SiMe_3$) and 6.2—7.6 (6H, m, quinolyl); IR, $\nu_{(Al-Cl)}$ 512 and 560 cm^{-1}; *m/z* 314. (**6**), m.p. 195 °C (decomp.); ^{11}B NMR, δ 8.8 (s) and 34.8 p.p.m. (s); IR, $\nu_{(B-Cl)}$ 560, 717, 740, and 780 cm^{-1}. (**7**), m.p. 131 °C (decomp.); ^{11}B NMR, δ 1.7 p.p.m. (s); IR, $\nu_{(Al-Cl)}$ 505 and 540; $\nu_{(B-Cl)}$ 730 and 780 cm^{-1}.



Scheme 1. *Reagents and conditions*: i, LiBu^n (1 equiv.) at 0 °C, then 25 °C, 15 min, then ClSiMe$_3$ (1 equiv.) 7 days, 79%; ii, BCl$_3$ (1 equiv.), hexane, −78 °C, 30 min, 66%; iii, BCl$_3$ (4 equiv.), hexane, 0 °C, 7 days, 21%; iv, ClSiMe$_3$ (1.1 equiv.), OEt$_2$, 0 °C, then room temp., 4 days, 87%; v, BCl$_3$ (1 equiv.), hexane, 97%; vi, 8-trimethylsilylaminoquinoline[4] (in OEt$_2$ at 0 °C) + LiBu^n (1.1 equiv.) (in hexane), add to AlCl$_3$ (1 equiv.) in OEt$_2$ at 0 °C, then room temp. overnight; vii, BCl$_3$ (3.5 equiv.), hexane, 0 °C, then 24 h, room temp., 94%; viii, (**5b**) in hexane, BCl$_3$ (5.5 equiv.).

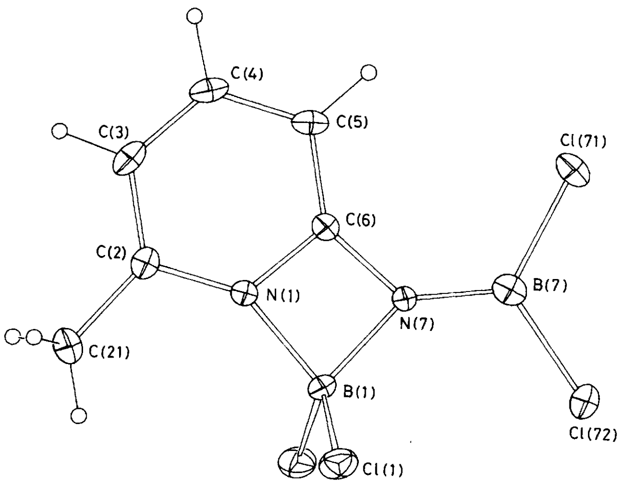


Figure 1. Molecular projection of compound (**3**) showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°): B(1)–N(1) 1.587(7), B(1)–Cl(1) 1.808(3), B(1)–N(7) 1.574(7), C(6)–N(7) 1.387(7), B(7)–N(7) 1.371(8), B(7)–Cl(71,72) 1.758(7), 1.759(7); Cl(1)–B(1)–Cl(1′) 114.0(7), Cl(1)–B(1)–N(1) 113.7(2), Cl(1)–B(1)–N(7) 114.7(2), N(1)–B(1)–N(7) 82.3(3), B(1)–N(1)–C(2) 146.0(4), B(1)–N(1)–C(6) 89.8(4), B(1)–N(7)–C(6) 89.1(4), B(1)–N(7)–B(7) 137.7(5), C(6)–N(7)–B(7) 133.2(5), N(7)–B(7)–Cl(71) 119.1(5), N(7)–B(7)–Cl(72) 122.8(5), Cl(71)–B(7)–Cl(72) 118.1(4).

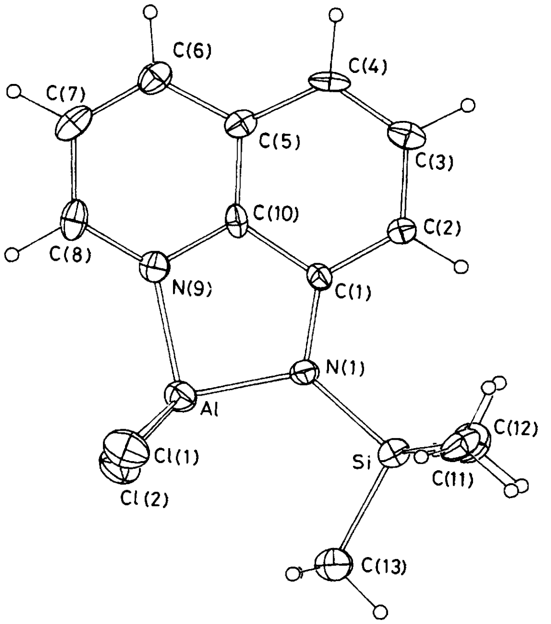


Figure 2. Structure of compound (**5a**). Selected bond distances (Å) and angles (°): Al–Cl(1) 2.122(5), Al–Cl(2) 2.109(5), Al–N(1) 1.816(8), Al–N(9) 1.935(8), N(1)–Si 1.749(8), N(1)–C(1) 1.42 (1); Cl(1)–Al–Cl(2) 109.5(2), Cl(1)–Al–N(1) 117.7(3), Cl–Al–N(9) 108.4(3), Cl(2)–Al–N(1) 118.1(3), Cl(2)–Al–N(9) 111.5(3), N(1)–Al–N(9) 89.7(3).

Results of the *X*-ray structure determinations‡ are presented in Figures 1 and 2. Molecules of (3) lie on crystallographic mirror planes; key structural features include a strained four-membered chelate ring with similar B–N distances within the ring, some 16% longer than the exocyclic B–N bond distance, which is short [1.371(8) Å][5] implying $N \rightleftharpoons B$ bonding, in contrast to only a 2.5% difference between the B–Cl distances for the two boron centres. The asymmetric unit in (**5b**) consists of discrete molecules. Noteworthy features are as follows. Firstly, the molecule is planar, except for the halogens and silicon substituents. Secondly, the difference in Al–N(aromatic), Al–N(amino) distances [1.935(8), 1.816(8) Å, *cf.* 1.882(3) Å in $PhC(NSiMe_3)_2AlCl_2$[8]], the Al–N(amino) distance being significantly lower than in the three-co-ordinate aminoaluminium compound, $[Al\{N(SiMe_3)_2\}_3]$, 1.78(2) Å.[9] Thirdly, the Si–N distance, 1.749(8) Å, is within the range for aminosilanes,[10] and is the same as in $[Al\{N(SiMe_3)_2\}_3]$ (1.75 Å).[9] However, it is longer than in an analogous Li(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)† complex of the same amino ligand, and of the amino ligand in (**2**), both 1.69 Å, reflecting lower ionic character in the aluminium compound.[11]

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‡ *Crystal data:* (T = 295 K; Syntex $P2_1$ diffractometer, crystals mounted in capillaries). Compound (3) $C_6H_6B_2Cl_4N_2$, M = 296.6, orthorhombic, space group *Pnam*, a = 15.665(5), b = 10.220(3), c = 7.015(2) Å, U = 1123.0(5) Å^3, $F(000)$ = 536; Z = 4, D_c = 1.59 g cm^{-3}, μ(Mo-K_α) = 10.0 cm^{-1}, A^* 1.25—1.40, specimen 0.3 × 0.3 × 0.28 mm, 1350 unique reflections, 798 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 55°; R = 0.041, R_w = 0.036. Compound (**5b**): $C_{12}H_{15}AlCl_2N_2Si$, M = 313.2, monoclinic, space group $P2_1/c$, a = 7.229(5), b = 15.391(6), c = 14.270(7) Å, β = 92.60(5)°, U = 1586(2) Å^3, $F(000)$ = 648; Z = 4, D_c = 1.31 g cm^{-3}, μ(Mo-K_α) = 5.2 cm^{-1}, no absorption correction, 1475 unique reflections, 653 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 40°; R = 0.048, R_w = 0.039. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.