First Trichloroaluminum Adducts of Silyliminoborenes

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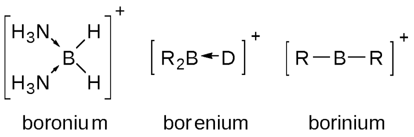
The reactions between the fluoroboranes $[(Me_3Si)_2N]_2BF$ or $(Me_3Si)_2N$–BF–$N(CMe_3)SiMe_3$ and $AlCl_3$ in diethyl ether afforded the first tri- and disilylated aminoiminoborenes, which were isolated and structurally confirmed as $AlCl_3$ adducts, $Me_3Si(AlCl_3)N{=}B{=}N(R)SiMe_3$, [R = $SiMe_3$ (**1**), CMe_3 (**2**)]. Density functional theory calculations of **1** and **2** were performed to understand the regioselectivity of the adduct formation.

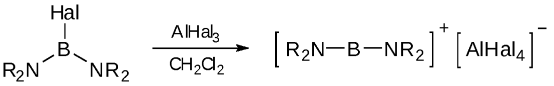
Key words: Aminoiminoborene, Silyliminoborene, Aluminum Halide Adducts, Crystal Structure, Density Functional Theory

Introduction

Boron chemistry is characterized by neutral and ionic species with tri- and tetracoordinated boron atoms. While boronium cations have been known for a long time, the first borenium and borinium cations were reported around 1980. In these compounds the boron atom is tetra-, tri- and dicoordinated, respectively [1].



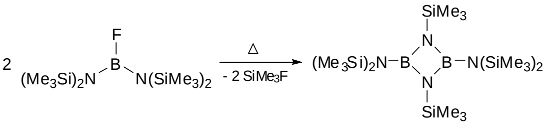
The most widely used method for generating salts containing Lewis-acidic borenium and borinium ions is the boron-halogen bond heterolysis. $BHal_3$, $AlCl_3$, $AlBr_3$, and $GaCl_3$ are the preferred reagents for this reaction [1b, c, d] (Eq. 1) which resembles the one applied for the synthesis of phosphenium ions [2] or $AlCl_3$ adducts of iminosilenes [3].



(1)

The B–Hal bond cleavage becomes more difficult with increasing bond strength in the series $X = F > Cl > Br > I$ [1d]. Nevertheless, bis(amino)-fluoroboranes have been successfully used to prepare borinium cations, *e. g.* $(Me_3Si)_2N{=}B{=}N(SiMe_3)_2{}^+$ $BBr_4{}^-$ [1b].

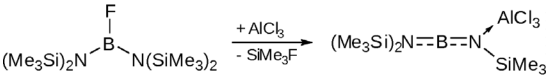
The first molecular iminoborenes with divalent boron atoms were synthesized by halosilane elimination reactions from the corresponding aminoboranes [1a]. Since iminoborenes are thermodynamically unstable with respect to oligomerization, they can only be isolated by kinetic control through bulky substituents [1a, 4]. Metastable iminoborenes form *e. g.* cyclic dimers [1a] like $[(Me_3Si)_2N$–B–$NSiMe_3]_2$, containing a B_2N_2 four-membered ring, generated by heating of $(Me_3Si)_2N$–BF–$N(SiMe_3)_2$ (Eq. 2) [5].



(2)

Results and Discussion

With the $AlCl_3$ adducts of iminosilenes in hands, prepared from lithiated aminofluorosilanes and free iminosilenes [3, 6], we investigated the reaction of $(Me_3Si)_2N$–BF–$N(SiMe_3)_2$ with $AlCl_3$ and isolated the $AlCl_3$ adduct of bis(trimethylsilyl)amino-trimethylsilyliminoborene (**1**) (Eq. 3) and not the corresponding borinium ion-containing salt $(Me_3Si)_2N{=}B{=}N(SiMe_3)_2{}^+$ $AlX_4{}^-$ possibly anticipated from Eq. 1.



1 (3)

Compound **1** is the first silylsubstituted iminoborene as well as the first alane adduct of an iminoborene that could be investigated by X-ray diffraction. It can be obtained as a crystalline solid, which is completely inert to dimerization or decomposition if stored under dry nitrogen gas.

The molecular structure of **1** (Fig. 1) shows well separated $(Me_3Si)_2N{=}B{=}N(AlCl_3)SiMe_3$ monomers [7], which is ideal for the comparison of the solid state structural features with results from quantum-chemical calculations (B3LYP/6-311+G(2d,p)) [8]. The theoretically determined bond lengths are depicted in parentheses in the caption of Fig. 1. The B–N bond lengths are 132.2(3) pm to the imino and 133.8(3) pm to the amino nitrogen atom. This tendency is comparable to the bonding situation in the adducts of carboaminoiminoborenes with gallium and indium trichloride [9] (131.7(4)/134.4(4) pm; 131.2(2)/134.5(2) pm) or pentacarbonyl chromium [10] (129.5(6)/136.8(6) pm) [11]. The alane coordination of the imine nitrogen lone pair prevents the formation of an aminoiminoborine (N–B≡N) in which different B–N bond lengths suggest formal single and triple B–N bonds (139.2(5) *vs.* 125.3(5) pm) [12].

Like in the aminoiminoborine, the N–B–N backbone in **1** is approximately linear (179.0(2)°), and the R_2NB atoms at both nitrogen atoms are each almost perfectly in a common plane (sum of the angles at N1 = N2 = 360°; mean deviation from plane: 0.8 pm). The two planes enclose an angle of 89.3° which resembles the situation in allenes. The deviation from linearity of the N–B–N unit results exclusively from the sterical demand of the trimethylsilyl groups since the B3LYP geometry optimization with SiH_3 instead of the $SiMe_3$ groups yielded a perfectly C_s symmetrical molecule.

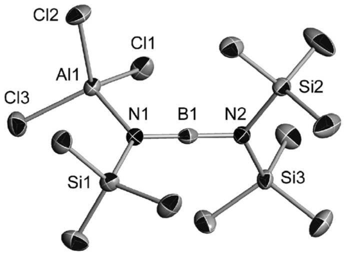
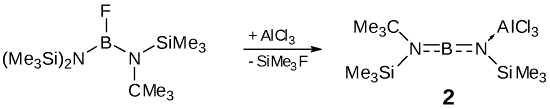


Fig. 1. Molecular structure, principal distances (pm) and angles (deg) of **1**: B1–N1 132.2(3) (131.7), B1–N2 133.8(3) (134.6), Al1–N1 188.5(2) (193.7), Al1–Cl1 213.3(1) (214.6), Al1–Cl2 213.0(1) (216.1), Al1–Cl3 211.1(1) (213.9), N1–Si1 178.6(2) (180.4), N2–Si2 180.5(2) (182.2), N2–Si3 180.1(2) (181.8); N(1)–B(1)–N(2) 179.0(2). (Hydrogen atoms omitted for clarity; theoretically calculated distances in parentheses).

The Al–N bond length (188.5(2) pm) is short in comparison to the sum of the covalent radii (195 pm [13]) as well as to that in $AlCl_3$ adducts with neighboring $SiMe_3$ groups of the imine [14] (190.2(2) pm) and amine [15] type (193.9(3) pm).



2 (4)

The isolation of **1** encouraged us to attempt the reaction of $(Me_3Si)(Me_3C)N{-}BF{-}N(SiMe_3)_2$ with trichloroalane (Eq. 4) in order to study the effect of the asymmetrical substitution. In a preparation similar to that decribed for **1**, we obtained the [*tert*-butyl (trimethylsilyl)amino]-trimethylsilyliminoborene aluminum trichloride adduct **2**. The crystal structure analysis supported by the NMR data of **2** proved the abstraction of the trimethylsilyl group from the symmetrically substituted nitrogen atom. It is well known in amine chemistry that a silyl substituted nitrogen atom loses donor strength and basicity compared to the carbon analogs [16]. This effect is not fully understood, because numerous studies on substituent effects show the higher inductive effect of a silyl group [17]. Surprisingly, the disilylated nitrogen atom in **2** shows a higher Lewis-basic character in comparison to the one in the $N(CMe_3)(SiMe_3)$ group. This has been proven by a natural bond orbital (NBO) analysis [18], which yielded natural charges of $-1.60\ e$ at $N(Si_2)$ and $-1.21\ e$ at N(SiC). Moreover, the adduct **2** is thermodynamically favored by $\Delta G = 0.9\ \mathrm{kcal\,mol^{-1}}$ (from B3LYP/6-311+G(2d,p)). The mechanism for the formation of **1** and **2** most probably consists of two steps: the addition of the Lewis acid to one of the planar amino groups followed by the rate-determining elimination of Me_3SiF *via* a four-membered ring transition state. The quantum-chemical investigation of the potential energy surface for this reaction is currently performed in our laboratory.

The molecular structure of **2** shows bond lengths (B1–N1: 133(1) pm; B1–N2: 135(1) pm; Al1–N1: 188.6(2) pm) similar to those of **1**. However, a detailed bond analysis is prevented by a $SiMe_3/CMe_3$ disorder (64 : 36) in the crystals.

The ^{11}B NMR signal can be related to the electron density at the boron atom [1a,c]. The chemical shift of **1** (38.6 ppm) is 6.7 ppm further downfield compared to **2** indicating a decreased electron density at the boron atom due to the additional silyl substituent. The ^{27}Al chemical shifts for **1** (102.8 ppm) and **2** (103.1 ppm) indicate more shielding than in the aluminum trichloride trimethylamine adduct (108.9 ppm), but resemble the shift observed in the carboaminoiminoborene adduct (103.6 ppm) [9]. This explains nicely the shorter Al–N bond lengths in the title compounds with their increased nitrogen donor strength compared to that in other $AlCl_3$ adducts.

Additional experiments are under way to further extend the application of this novel synthetic route to stabilized silylated aminoiminoborenes.

Experimental Section

Starting materials: Bis[bis(trimethylsilyl)amino]fluoroborane (**I**), *tert*-butyl(trimethylsilyl)amino-bis(trimethylsilyl)amino-fluoroborane (**II**), aluminum trichloride. Reactions were carried out under dry nitrogen atmosphere.

*Bis(trimethylsilyl)amino-trimethylsilyliminoborene aluminum trichloride (**1**) and [tert-butyl(trimethylsilyl)amino]-trimethylsilyliminoborene aluminum trichloride (**2**)*

35.0 g (0.1 mol) of **I**, or 33.4 g (0.1 mol) of **II**, was added to 13.33 g (0.1 mol) of aluminum trichloride in 100 mL of diethyl ether at 0 °C. The solution was stirred at r. t. for 1 d. The solvent and the trimethylfluorosilane were removed *in vacuo* ($1.3 \cdot 10^{-2}$ mbar). After the recrystallization of the residue from diethyl ether **1** and **2** were obtained in 97 % yield.

(**1**): M. p. 117 °C. – ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.10 (s, 18 H, N(Si*Me*$_3$)$_2$), 0.30 (s, 9 H, AlNSi*Me*$_3$). – ^{11}B NMR (96.3 MHz, $CDCl_3$): δ = 38.6 (s). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 1.57 (N(Si*Me*$_3$)$_2$), 2.01 (AlNSi*Me*$_3$). – ^{27}Al NMR (78.2 MHz, $CDCl_3$): δ = 102.8 (s). – ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = 12.8 (AlN*Si*Me$_3$), 15.4 (N(*Si*Me$_3$)$_2$). – MS (EI, 70 eV): *m/z* (%) = 375 (95) [M–CH$_3$]$^+$, 355 (25) [M–Cl]$^+$.

(**2**): M. p. 176 °C. – ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.12 (s, 9 H, Me$_3$CNSi*Me*$_3$), 0.32 (s, 9 H, AlNSi*Me*$_3$), 1.07 (s, 9 H, C*Me*$_3$). – ^{11}B NMR (96.3 MHz, $CDCl_3$): δ = 31.9 (s). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 1.97 (Me$_3$CNSi*Me*$_3$), 1.99 (AlNSi*Me*$_3$), 32.28 (C*Me*$_3$), 58.35 (*C*Me$_3$). – ^{27}Al NMR (78.2 MHz, $CDCl_3$): δ = 103.1 (s). – ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = 11.3 (AlN*Si*Me$_3$), 13.3 (Me$_3$CN*Si*Me$_3$). – MS (EI, 70 eV): *m/z* (%) = 359 (100) [M–CH$_3$]$^+$, 339 (5) [M–Cl]$^+$.

X-Ray structure determination

The data were obtained from oil-coated shock-cooled crystals [19]. **1** and **2** were measured on a Bruker SMART-APEX II diffractometer with a D8 goniometer and graphite monochromator (MoK_α; λ = 71.073 pm) applying ω scans (0.3° scan width). The data were integrated with SAINT [20], and an empirical absorption correction with SADABS-2004/1 [21] was applied. The structures were solved by Direct Methods (SHELXS-97 [22]) and refined against F^2 with SHELXL-97 [23].

(**1**): $C_9H_{27}AlBCl_3N_2Si_3$, M = 391.74 g mol^{-1}, plate, $0.20 \times 0.15 \times 0.05$ mm^3, monoclinic, a = 952.89(4), b = 1647.13(7), c = 1438.82(6) pm, β = 107.551(1)°, V = 2.1532(2) nm^3, T = 100 K, space group Pn (no. 7), Z = 4, D_calcd = 1.208 g cm^{-3}, μ(MoK_α) = 0.624 cm^{-1}, $F(000)$ = 824 e, θ = 2.29 – 25.68°, $-11 \le h \le +11$, $0 \le k \le +20$, $-17 \le l \le +17$, 40635 reflections measured, 8159 unique (R_int = 0.026), 416 parameters refined, 189 restraints applied, g_1 = 0.036, g_2 = 0.230 [24], $R1$ = 0.023 ($I \ge 2\sigma(I)$) [25] and $wR2$ = 0.058 (all data) [26].

(**2**): $C_{10}H_{27}AlBCl_3N_2Si_2$, M = 375.66 g mol^{-1}, block, $0.20 \times 0.18 \times 0.10$ mm^3, monoclinic, a = 813.24(8), b = 1918.8(2), c = 1299.61(14) pm, β = 91.632(1)°, V = 2.0272(4) nm^3, T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, D_calcd = 1.231 g cm^{-3}, μ(MoK_α) = 0.604 cm^{-1}, $F(000)$ = 792 e, θ = 2.64 – 26.03°, $0 \le h \le +10$, $0 \le k \le +23$, $-15 \le l \le +16$, 19653 reflections measured, 3980 unique (R_int = 0.021), 266 parameters refined, 484 restraints applied, g_1 = 0.019, g_2 = 1.128 [24], $R1$ ($I \ge 2\sigma(I)$) = 0.028 [25] and $wR2$ = 0.067 (all data) [26].

CCDC 682843 (**1**) and 682844 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[24] $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$.

[25] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[26] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.