

Borane-stabilized Boranediyls (Borylenes): Neutral *nido*-1-Borane-2,3,4,5,6-pentamethyl-2,3,4,5,6-pentacarbahexaboranes(6)

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Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 70th birthday

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The reaction of $(C_5Me_5)_2Si$ or $(C_5Me_5)SiMe_3$ with B_2Cl_4 leads to the adducts $(C_5Me_5)B \rightarrow BCl_2SiCl_3$ (**5a**) or $(C_5Me_5)B \rightarrow BCl_3$ (**5b**), in which the Lewis acids stabilize the boranediyl frag-

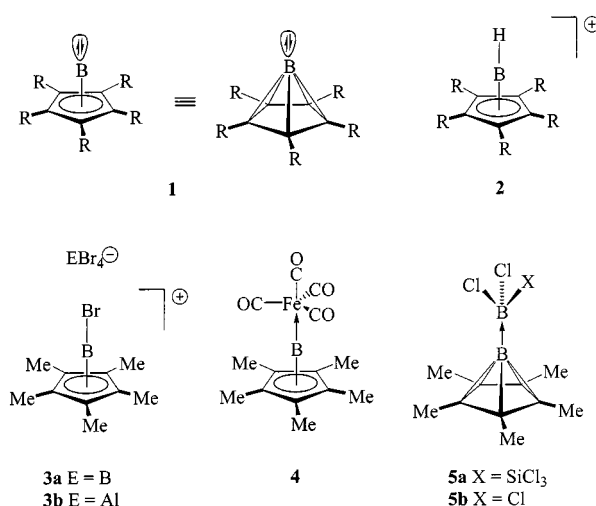
ments. Spectroscopic data and X-ray structure analyses confirm the adducts.

Introduction

In contrast to the heavier analogs of $[(\eta^5-C_5Me_5)E:]_n$, $E = Al$,^[1] Ga ,^[2] In ,^[3] Tl ,^[4] derivatives of $(\eta^5-cyclopentadienyl)boranediyl$ **1** with a lone electron pair at boron are unknown. Protonation of hypothetical **1** could lead to the cation $[(\eta^5-C_5R_5)BH]^+$ (**2**) and formal addition of the bromonium ion Br^+ to the cation $[(\eta^5-C_5Me_5)B-Br]^+$, first obtained by Jutzi et al.^[5] in the reaction of $Me_5C_5-GeMe_3$ with an excess of BBr_3 leading to **3a**. Schnöckel et al.^[6] observed the formation of **3b** from the reaction of $[(C_5Me_5)Al]_4$ with BBr_3 and confirmed the proposed structure of the cation^[5] as well as the calculated orientation of the substituents in **2** ($R = H$) towards the apical boron atom^[7] by a crystal structure analysis. Very recently, Cowley et al.^[8] prepared the tetracarbonyliron-pentamethylcyclopentadienylboranediyl complex **4** and reported a theoretical study on free and $Fe(CO)_4$ -complexed borylenes.^[9a] The related alanediy compound $(C_5Me_5)Al-B(C_6F_5)_3$ has been synthesized.^[9b] Compounds of the types **1–4** and the neutral polyhedron derivatives **5a,b** presented here are best described as *nido* clusters^[10] with six skeletal atoms held together by $2n + 4 = 16$ skeletal electrons. We here present a new approach to stabilize the hypothetical boranediyl **1** ($R = Me$) as a Lewis base with the Lewis acids $Cl_3Si-BCl_2$ and BCl_3 .

Results and Discussion

When $(\eta^5-C_5Me_5)_2Si$ ^[11] is treated with B_2Cl_4 at $-110^\circ C$ in pentane a red-brown suspension forms, which on warm-

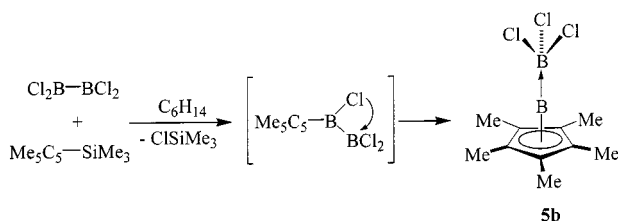


ing to room temperature results in a yellow solution and a colorless solid, which turns violet on longer standing or on contact with air. The mass spectra of the crude product indicate the presence of two compounds (see Experimental Section), recrystallization from hot toluene yields **5a**.^[12] Its EI and CI mass spectra do not show the M^+ peak; however, the $[M_2 - Cl]^+$ ion is seen in low intensity at $m/z = 689$. Besides the base peak in the CI spectrum at $m/z = 327$ $[M^+ - Cl]$ the only other fragment is found at $m/z = 227$ $[B_2SiCl_5]^+$ which is the base peak in the EI MS.

The 1H NMR spectrum exhibits one signal at $\delta = 2.25$ for the methyl groups indicative of a pentahapto structure, which is confirmed by two ^{13}C resonances at $\delta = 113.1$ (C_5) and $\delta = 4.2$ (CH_3). In the ^{11}B NMR spectrum two signals at $\delta = -6.2$ (sp^3 boron) and $\delta = -51.7$ (apical boron) are in agreement with a $C_5B \rightarrow B$ pyramidal arrangement. At room temperature, because of the partially relaxed scalar $^{11}B-^{11}B$ coupling, only the two inner lines of the 1:1:1:1 pattern are observed. At elevated temperatures ($55^\circ C$), due to the slower quadrupolar relaxation of the ^{11}B nuclei, the two outer lines appear as shoulders. The more precise value for

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 Scheme 1. Formation of **5b**

the coupling constant $^1J(^{11}\text{B}, ^{11}\text{B})$ is measured for the resonance of the apical ^{11}B nucleus (125 ± 3 Hz).

These data support the formation of the borane-stabilized boranediyl adduct **5a**, which is confirmed by a crystal structure analysis.

A much simpler transfer of a C_5Me_5 group to a diborane(4) molecule occurs with $\text{Me}_5\text{C}_5\text{-SiMe}_3$ (Scheme 1). The reaction of equimolar amounts of $\text{Me}_5\text{C}_5\text{-SiMe}_3$ and B_2Cl_4 in hexane at low temperature leads to a colorless solid which is thermally stable up to 280°C . Its NMR and mass spectra confirm the formation of **5b**: one signal at $\delta_{\text{H}} = 2.21$ indicates pentahapto bonding of the C_5Me_5 group and two high-field signals prove the presence of one sp^3 hybridized ($\delta_{\text{B}} = 2.8$) and one *apex* boron atom ($\delta_{\text{B}} = -53.0$). The two different ^{11}B nuclei couple as described for **5a** [$^1J(^{11}\text{B}, ^{11}\text{B}) = 121 \pm 5$ Hz]. The CI mass spectrum exhibits the base peak $[\text{M} - \text{Cl}]^+$ ($m/z = 227$) and the $[\text{M}_2 - \text{Cl}]^+$ peak ($m/z = 491$). The EI spectrum shows the base peak $[\text{M} - \text{Cl}]^+$ and the molecular-ion peak M^+ ($m/z = 262$) with the isotopic pattern expected for $\text{C}_{10}\text{H}_{15}\text{B}_2\text{Cl}_3$. Compound **5b** is only slightly sensitive to moisture but is decomposed in CH_2Cl_2 by gaseous HCl .

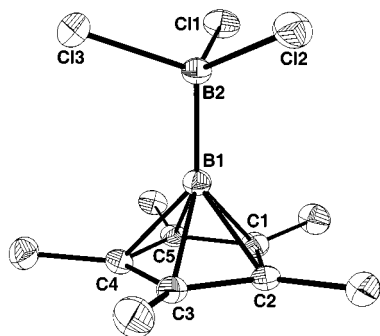


Figure 1. Molecular structure of **5b** in the crystal; selected bond lengths [Å] and angles $^\circ$ (values for **5a** given in brackets): B1–C_{5 plane} 1.260(3) [1.289(6)], B1–C_{ring} 1.747–1.756(3), av. 1.752 [1.752–1.773(8), av. 1.762], B1–B2 1.681(3) [1.686(7)]; X_{C5}–B1–B2 179.4 [176.7], B1–B2–Cl 110.0–110.5(1) [B1–B2–Si1 116.1(3); B1–B2–Cl1 110.1(4); B1–B2–Cl2 108.1(3)]; the methyl groups are bent out of the C₅ plane towards B1 by 5.6–7.2 (av. 6.4) in **5b** and by 3.3–5.2 (av. 4.5) in **5a**; hydrogens are omitted for clarity.

The ORTEP plot in Figure 1 shows the molecular structure of **5b**,^[13] selected bond lengths and angles of **5a** and **5b** are listed in the legend. Both structures are very similar, the structure determination of **5b** being more accurate. Any small differences are caused by the presence of the SiCl_3 group. The average C–B bond length (1.75 Å) is identical to that in $[(\eta^5\text{-Me}_5\text{C}_5\text{B-SiCl}_2(\eta^1\text{-C}_5\text{Me}_5))]^+[\text{Cl}_3\text{B}(\eta^1\text{-C}_5\text{Me}_5)]^-$ ^[14] and lies between the values for **3b** (1.68 Å)

and **4** (1.81 Å). The larger B–C distance in **4**^[8] indicates a weaker bonding between boron and the C_5Me_5 ring, which is probably due to a less positive charge at the boranediyl moiety **1** (R = Me). In **5a, b** the $(\text{C}_5\text{Me}_5)\text{B}$ unit is attached to XBCl_2 with a B–B distance of 1.69 Å for **5a** and 1.68 Å for **5b**, which is in the range for a normal 2c–2e bond. The bulky SiCl_3 group causes a slight deviation of 3.3° from the expected linear B–B–X_{C5} arrangement (X_{C5} being the center of the C₅ ring) found for **5b**. The methyl groups of the C_5Me_5 ring are bent out of the C₅ plane towards the *apical* boron atom with an average angle of 4.6° (**5a**) and 6.4° (**5b**). Such a behavior was predicted theoretically^[7] and has been verified experimentally in **3b** (3.9°) and in $[(\eta^5\text{-Me}_5\text{C}_5\text{B-SiCl}_2(\eta^1\text{-C}_5\text{Me}_5))]^+[\text{Cl}_3\text{B}(\eta^1\text{-C}_5\text{Me}_5)]^-$ (4.2°).^[13]

The formation of **5a** may be rationalized by the assumption that the postulated oxidative addition product $(\text{C}_5\text{Me}_5)_2\text{Si}(\text{Cl})\text{-B}(\text{Cl})\text{-BCl}_2$ undergoes intra- and intermolecular substituent exchanges and a rearrangement occurs as proposed for **5b**.

Experimental Section

nido-1-(Trichlorosilyl)dichloroborane-2,3,4,5,6-pentamethyl-2,3,4,5,6-pentacarbaheptaborane(6) 5a: To a solution of decamethylsilicocene (1.19 g, 3.97 mmol) in 40 mL of pentane was condensed B_2Cl_4 (650 mg, 3.97 mmol) at -110°C . A red-brown suspension immediately formed which, on warming to room temperature, became a yellow solution with a colorless precipitate (1.55 g). Its mass spectra indicated the presence of $(\text{C}_5\text{Me}_5)\text{B-BCl}_2\text{-SiCl}_2\text{C}_5\text{Me}_5$ ($m/z = 462$) and $(\text{C}_5\text{Me}_5)\text{B-BCl}_2\text{-Si}(\text{C}_5\text{Me}_5)_2\text{Cl}$ ($m/z = 562$) (or isomers). However, these products could not be isolated. The solid turned violet on contact with air or by storing under argon at room temperature for several weeks.^[12] The crude product (80 mg) was recrystallized from hot toluene to give **5a** (25 mg).

^1H NMR (CDCl_3 , 200 MHz): $\delta = 2.25$ (s, 15 H). – ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = -51.7$ (1 B, BC_5Me_5), -6.2 (1 B, sp^3B). – ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 9.2$ (CH_3), 113.1 (C_5). – CI-MS: m/z (%) = 689 (1.3) $[\text{M}_2^+ - \text{Cl}]$, 327 (100) $[\text{M}^+ - \text{Cl}]$, 227 (20) $[\text{B}_2\text{SiCl}_5^+]$. – EI-MS: m/z (%) = 327 (3) $[\text{M}^+ - \text{Cl}]$, 227 (100) $[\text{B}_2\text{SiCl}_5^+]$

nido-1-Trichloroborane-2,3,4,5,6-pentamethyl-2,3,4,5,6-pentacarbaheptaborane(6) 5b: A solution of B_2Cl_4 (600 mg, 3.57 mmol) in 60 mL of hexane was cooled to -100°C and $\text{Me}_5\text{C}_5\text{-SiMe}_3$ (744 mg, 3.57 mmol) dissolved in 5 mL of hexane was added dropwise to give a red solution. The reaction mixture was allowed to warm to room temperature overnight yielding a yellow solution and a colorless precipitate (**5b**, 496 mg, 53%).

^1H NMR (CDCl_3 , 200 MHz): $\delta = 2.21$ (s, 15 H). – ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = -53.0$ (1 B, BC_5Me_5), 2.8 (1 B, sp^3B). – ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 8.9$ (CH_3), 112.6 (C_5). – CI-MS: m/z (%) = 491 (63.0) $[\text{M}_2^+ - \text{Cl}]$, 227 (100) $[\text{M}^+ - \text{Cl}]$. – EI-MS: m/z (%) = 262 (0.7) $[\text{M}^+]$, 227 (100) $[\text{M}^+ - \text{Cl}]$

Crystal Structure Determinations: Data collection: Bruker AXS area detector (Mo-K_α $\lambda = 0.71073$ Å, -100°C); structures solved by direct methods, full-matrix least-squares refinement on F^2 .^[14]

5a: Orthorhombic, $\text{Pna}2_1$, $\text{C}_{10}\text{H}_{15}\text{B}_2\text{Cl}_5\text{Si-C}_7\text{H}_8$, $a = 26.863(2)$, $b = 9.0991(1)$, $c = 9.0991(1)$ Å, $V = 2224.1(5)$ Å³, $Z = 4$; 3126 unique reflections, non-hydrogen atoms anisotropic, hydrogen atoms in

calculated positions (riding), 236 parameters $R_1 = 0.041$ (observed reflections), $wR_2 = 0.090$ (all reflections). The crystals were twinned showing tetragonal symmetry.

5b: Orthorhombic, $Pna2_1$, $C_{10}H_{15}B_2Cl_3$, $a = 11.9805(8)$, $b = 14.2209(10)$, $c = 7.5215(5)$ Å, $V = 1281.5(2)$ Å³, $Z = 4$; 2713 unique reflections, non-hydrogen atoms anisotropic, hydrogen atoms isotropic, 209 parameters $R_1 = 0.030$ (observed reflections), $wR_2 = 0.070$ (all reflections).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140032 (**5a**) and CCDC-140427 (**5b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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