Reactivity of Dithiazinanes towards BH_3, BD_3 and BF_3. New Heterocycles: 5,5-Dimethyl-1,3-dithia-5-azonia-4-boratacyclohexane and 6,6-Dideuterio-5-methyl-5-[D_1]methyl-1,3-dithia-5-azonia-4-boratacyclohexane. A Method for the Dimethylation and Monodeuteriomethylation of Primary Amines

Angelina Flores-Parra*, Gregorio Cadenas-Pliego, Luz Maria R. Martínez-Aguilera, M. Lourdes García-Nares and Rosalinda Contreras

Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, México, D. F. 07000, México

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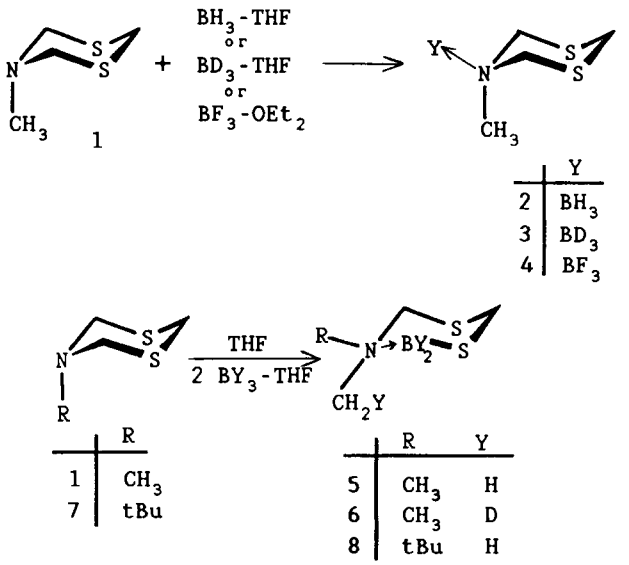
5-Methyl- and 5-*tert*-butyl-1,3,5-dithiazinane (**1** and **7**) react with BH_3 · THF, BD_3 · THF, and Et_2O · BF_3 to yield the *N*-coordinated adducts **2**–**4** (with BH_3, BD_3, and BF_3, respectively). The conformations and spectroscopic properties of the adducts are discussed. The reactions of **1** and **7** with BY_3 · THF lead to the six-membered boron heterocycles 5,5-dimethyl-1,3-dithia-5-azonia-4-boratacyclohexane (**5**), 4,4-dideuterio-5-methyl-5-[D_1]methyl-1,3-dithia-5-azonia-4-boratacyclohexane (**6**), and 5-*tert*-butyl-5-methyl-1,3-dithia-5-azonia-4-boratacyclohexane (**8**). Compounds **2** and **5** are isolobal isomers. The reaction of BH_3 or BD_3 with **7** affords, after heating, *tert*-butyldimethylamine–borane (**9**) and *tert*-butyldi([D_1]methyl)-amine–trideuterioborane (**11**), respectively. The dithiazinane derivatives may be used in organic synthesis for the dimethylation of primary amines and the preparation of alkyldimethylamines with monodeuterated methyl groups.

We are currently studying the use of borane as a probe for the basic properties of Lewis bases[1] and for locking nitrogen configurations in acyclic amines[2] or in nitrogen heterocycles of five-[3] and six-membered rings[4]. We are also interested in the preparation of boron heterocycles[5,6]. In continuation of these studies, we have investigated the reaction of boron reagents with 1,3,5-dithiazinanes as they are excellent models for adducts formation, as well as for conformational analysis and boron heterocycle synthesis.

The heterocycle **1** has five lone pairs of electrons and is especially interesting for the synthesis of adducts with Lewis acids. This dithiazinane is in a ring conformational equilibrium with an inversion energy of $\Delta G^* = 46.0 \pm 1.2$ kJ/mol[7]. Due to the anomeric effect both chair conformations have the methyl group in an axial position. We have recently prepared a N · BH_3 derivative of **1**[4]. In this paper we report on two other boron adducts of the dithiazinane **1**, N · BD_3 **3** and N · BF_3 **4** (Scheme 1). Compound **3** has been prepared in order to follow the ring-opening mechanism as commented below and the formation of N · BF_3 adduct **4** to explore the preference of BF_3 for the sulfur or nitrogen atoms. Of the three new examples of boron heterocycles, **5** and **6** have been obtained by the reaction of compound **1** with BH_3 · THF and BD_3 · THF, respectively, in refluxing THF, whilst **8** is formed from borane and compound **7** at −70°C (Scheme 1). Six-membered heterocyclic boron compounds are known, in which the combination of heteroatoms[8] is different from those reported in this paper. When dithiazinane **7** is heated with an excess of BH_3 or BD_3 in refluxing THF, dimethylamine adduct **9** or its dideuterated analog **11** are obtained.

Scheme 1



Results and Discussion

Synthesis of the N · BD_3 Adduct 3

An excess of B_2D_6, bubbled through a THF solution of dithiazine **1**, leads quantitatively to **3** as a pure stable solid. Similarly, **2** is obtained with BH_3 · THF. Only one BH_3 molecule is coordinated regardless of the dithiazinane-borane stoichiometric relationship used. Compounds **3** and **2** occur in a preferred conformation as revealed by the ^{1}H- and ^{13}C-NMR spectra: the Lewis acid enters selectively in the equatorial position of the nitrogen atom (Scheme 1).

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The frozen conformation makes it possible to study the electronic effects on the equatorial and axial hydrogen atoms. Compound **3** is still frozen when heated to 45°C in $CDCl_3$, and its ^{1}H-NMR spectrum implies that the activation energy for ring inversion must be above 65 kJ/mol. The ^{11}B-NMR spectrum of **3** shows a broad signal ($\delta = -8.6$), whereas that of the normal BH_3 adduct **2** exhibits a quartet ($\delta = -8.0$, $J_{B\text{-}H} = 98$ Hz).

Synthesis of the N · BF_3 Adduct 4

The reaction of the dithiazinane **1** with an excess of $Et_2O \cdot BF_3$ in chloroform produces the N · BF_3 adduct **4** ($\delta = -0.1$, q, $J_{B\text{-}F} = 13$ Hz). Only one molecule of BF_3 is coordinated to the dithiazinane, with no evidence in the NMR spectra of a S · BF_3 coordination. The coupling pattern of the ^{1}H-NMR spectrum at 27°C indicates that the ring has a preferred chair conformation. The excess of BF_3 required for the formation of **4** might be due to a weaker N–B bond than in **2** and **3**. This is further supported by the formation of the THF · BF_3 adduct[9] when **4** is dissolved in THF.

Synthesis of Boron Heterocycles

a) Reaction of 5-Methyl-1,3,5-dithiazinane (1) with Borane–THF

The addition of two equivalents of BH_3 · THF to dithiazinane **1** and heating of the reaction mixture for two hours gives cleanly the boradithiazinane **5** in quantitative yield. This is a stable compound (m.p. 41°C) under dry nitrogen. The ^{11}B-NMR spectrum exhibits a triplet [$\delta = -3.3$ ($J_{B\text{-}H} = 107$ Hz)] characteristic of a S · BH_2 function coordinated to a nitrogen atom[10]. While at room temperature the ^{13}C-NMR spectrum shows three absorptions, at −55°C four signals are observed, two *N*-methyl groups at $\delta = 44.34$ (eq) and 53.14 (ax) and two other signals for the methylene groups, indicating that the ring is no longer in conformational equilibrium at this temperature. The ^{1}H-NMR (270 MHz) spectrum at −55°C shows the four coupled methylene protons. The activation energy for the ring inversion has been calculated from the variable temperature NMR spectra to be 51.4 ± 0.4 (^{1}H) and 51.2 ± 0.4 (^{13}C) kJ/mol. This value is higher than that of the free dithiazinane **1** (46.0 ± 0.8 kJ/mol)[7]. The frozen molecule does not have a plane of symmetry, and two enantiomers are possible. Compound **5** is an isolobal isomer[11] of the *N*-borane adduct **2**. The compounds differ only in the position of the boron and one carbon atom and show very similar ^{13}C-NMR spectral data (Figure 1). In contrast to compound **2**, that is in a preferred conformation at room temperature, the heterocycle **5** is in conformational equilibrium. The ^{1}H-NMR spectrum of **5** (Figure 2) shows that the equatorial proton at 2-H is coupled to both the equatorial proton at 4-H and the equatorial hydride at the boron atom with approximately the same W coupling constants ($^W J_{H,H}$) of 2.0 Hz. Compound **2** has the same coupling constant of 2.0 Hz between the equatorial 2-H and the equatorial protons 4-H and 6-H.

The formation of **5** may be explained by an intramolecular rearrangement of **2**, but since an excess of BH_3 is required,

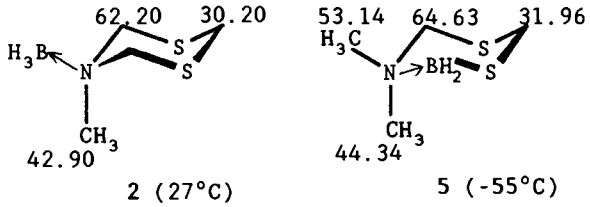


Figure 1. ^{13}C-NMR data of compounds **2** and **5** (δ values)

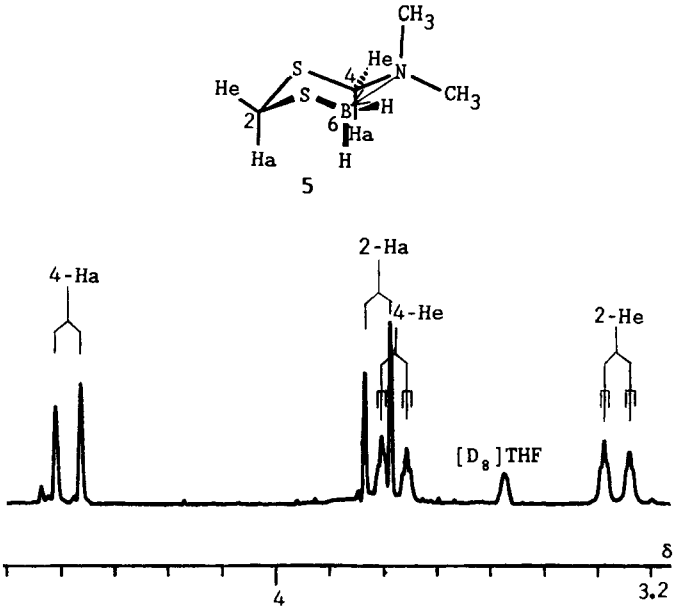
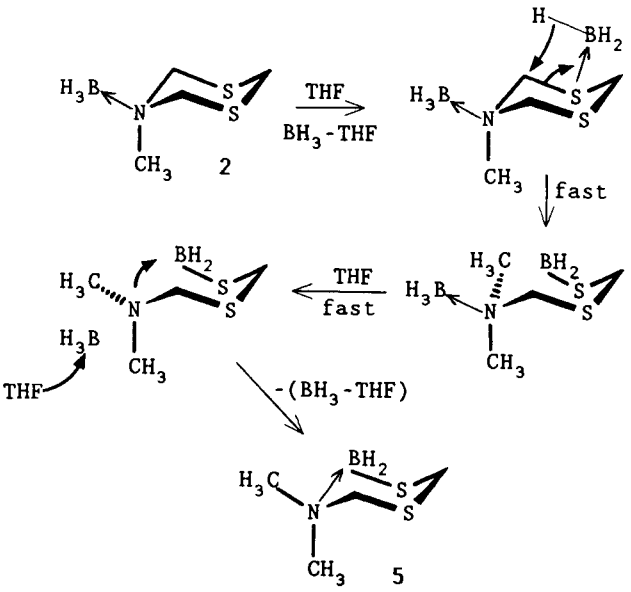


Figure 2. ^{1}H-NMR (270 MHz) spectrum of compound **5** showing the coupling pattern

along with the fact that heating of **2** yields an equimolar mixture of **1** and **5**, an intermolecular reaction must occur. Therefore, we propose the reaction path described in Scheme 2. It can be assumed that the excess of borane gives rise to

Scheme 2. Proposed mechanism for the formation of the boron heterocycle **5**



the formation of a S · BH_3 adduct (this species has been observed at low temperature in the reaction of **7** with BH_3, vide infra) which promotes cleavage of the S–C bond with the generation of a S–BH_2 bond, and migration of a hydride to the methylene to give a N–CH_3 group. Ring formation by tetrahydrofuran-assisted borane elimination allows the stabilization of the BH_2 group by nitrogen coordination and formation of a very stable cyclic compound that remains unchanged when heated at the THF reflux temperature with an excess of borane for 12 h.

The hydride migration from the boron to the carbon atom has been checked by heating compound **3** in an excess of BD_3 · THF. The resulting deuterated heterocyclic **6** has been found, as expected, to display properties similar to those of the boron hydride **5**. When the molecule is studied at −55 °C in the ^{13}C-NMR spectrum (67.80 MHz) in the proton-decoupled mode, two frozen diastereoisomers (each representing a pair of enantiomers) are detected, one with an equatorial monodeuterated methyl group (**6e**: δ = 52.74, t, $J_{C,D}$ = 22.0 Hz) and another with the monodeuterated methyl in an axial position (**6a**: δ = 43.93, t, $J_{C,D}$ = 22.0 Hz; ΔG^* = 50.95 ± 0.9 kJ/mol, calculated from the ^{13}C-NMR spectra, Figure 3). Again, the formation of the pure heterocycle **6** proceeds quantitatively.

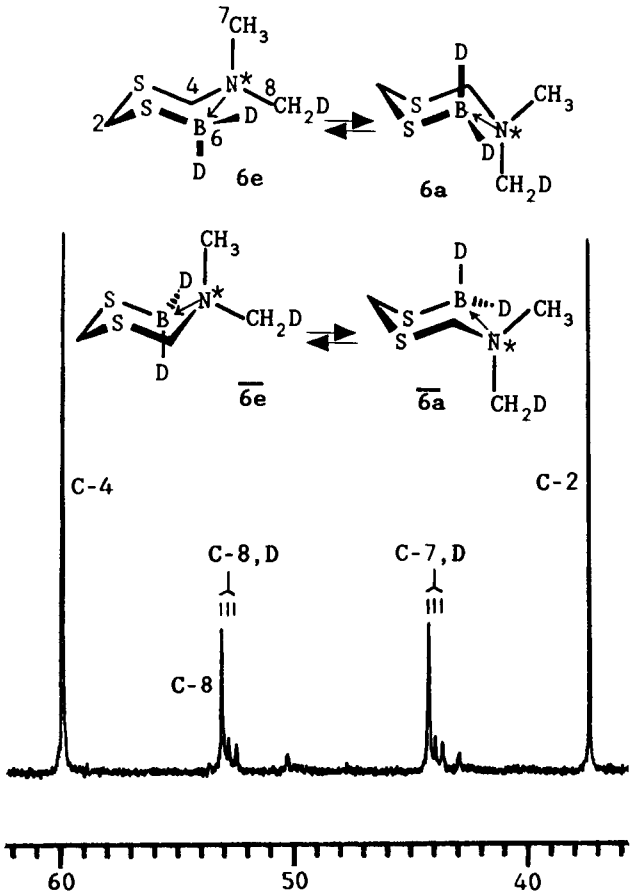


Figure 3. ^{13}C-NMR (86.55 MHz) spectrum (δ scale) of frozen deuterated diastereoisomers **6a** and **6e**. CH_2D axial and equatorial groups appear as triplets (δ = 43.93, $J_{C,D}$ = 22 Hz for **6a**; 52.74, $J_{C,D}$ = 22 Hz for **6e**)

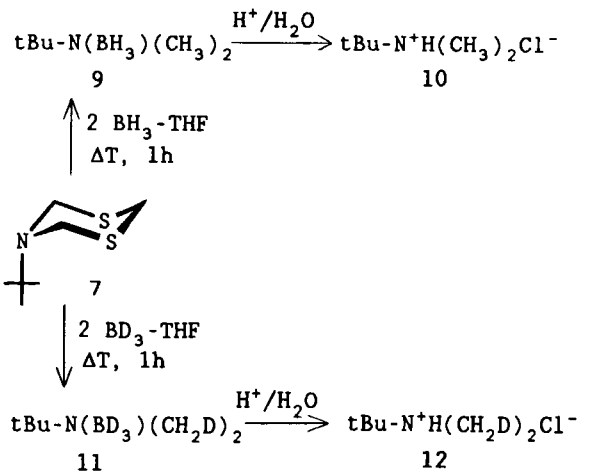
b) Reaction of 5-*tert*-Butyl-1,3,5-dithiazinane (7) with Borane–THF

Despite the bulky substituent on the nitrogen atom, compound **7** forms a conformational equilibrium. The analysis made by Katritzky[7] shows that the ring inversion energy is 38.9 ± 1.6 kJ/mol and that the *tert*-butyl group is locked in an axial position. At room temperature the reaction of the heterocycle **7** with borane is very fast, and it is not possible to isolate any borane adduct. However, the reaction can be followed by ^{11}B-NMR spectrometry when borane is allowed to react with **7** at −70 °C. In the spectrum recorded at −70 °C in [D_8]THF, a broad signal at δ = −22 is observed together with a triplet at −7.2 (J_{B-H} = 110 Hz). The first resonance is characteristic of a S · BH_3 complex[8i,j] and the second is assigned to **8**. At −60 °C, the signal at δ = −7.2 increases (80%) and the other diminishes. The ^{13}C-NMR spectrum of the solution at the same temperature shows free dithiazinane and another set of resonances attributed to the heterocycle **8**. When the solution is heated to room temperature the ^{11}B-NMR signal due to **8** disappears to give rise to the generation of two novel signals: a triplet at δ = −18.0 (J_{B-H} = 125 Hz) attributed to a sulfur-boron derivative and a quartet at δ = −11.8 (J_{B-H} = 97 Hz) of *tert*-butyldimethylamine–borane (**9**)[12]. Compound **8** contains a chiral nitrogen atom; from the ^{13}C-NMR data[13] it is deduced that the methyl group is in an axial position. The reactivity of **7** as well as that of **8** is attributed to the steric strain at the quaternized nitrogen atom. The N–borane adduct of compound **7** is not observed due to the steric effect produced by the *tert*-butyl substituent favoring the sulfur-borane interaction and migration of the methyl group to the nitrogen atom. The boron heterocycle **8** is a fleeting species that undergoes ring cleavage to the amine–borane complex **9**. The sulfur part of the molecule forms a precipitate that contains a boron, carbon, and sulfur derivative which has not been completely identified.

Synthesis of Dimethylamines

The reaction of two equivalents of borane with compound **7** for 1 h in refluxing THF affords the amine adduct **9**. The

Scheme 3



same reaction with $BD_3 \cdot THF$ yields the $N \cdot BD_3$ adduct **11**. Treatment of the reaction mixtures with hydrochloric acid allows the isolation of the amines **10** and **12** as hydrochlorides in good yield (Scheme 3). Treatment of the bulky dithiazinane with $BH_3 \cdot THF$ or $BD_3 \cdot THF$ is an excellent synthetic method to attach two methyl groups or two monodeuterated methyl groups to a nitrogen atom of a bulky primary amine. This method may be especially relevant to perform dimethylation of expensive or scarce amines[14,15]. Selective deuterations are very important[16] and often difficult to perform[17].

Experimental

^1H-, ^{13}C- and ^{11}B-NMR: Jeol 270-GXS spectrometer at 270, 67.80, and 86.55 MHz, respectively. ^1H- and ^{13}C-NMR chemical shifts were referenced to TMS and ^{11}B-NMR shifts to $Et_2O \cdot BF_3$. — IR: Nicolet MX-1-FT infrared FT spectrometer. — Melting points: Gallenkamp apparatus, uncorrected. — Anhydrous solvents were prepared according to the usual laboratory methods. All reactions were carried out in an inert atmosphere in oven-dried glassware. Compounds **1** and **7** were prepared as described in ref.[18] — Some deviations have been found in the mycroanalyses which were attributed to the presence of small quantities of boric acid produced from some borane hydrolysis.

5-Methyl-1,3,5-dithiazinane—5-Borane (1/1) (**2**)[4]: A solution of compound **1** (0.50 g, 3.7 mmol) in anhydrous THF (40 ml) was cooled to −78 °C under dry nitrogen, and a solution of 2.4 M $BH_3 \cdot THF$ (1.54 ml, 3.70 mol) was added dropwise. The reaction mixture was stirred for 1 h, and then the solvent was evaporated in vacuo to leave compound **2** as a white solid (0.53 g, 97%), m.p. 233 °C. — ^1H NMR (270 MHz, $CDCl_3$): δ = 1.70 (q, J = 94.6 Hz, 4H, BH_3), 2.92 (s, 3H, $[CH_3]_{ax}$), 3.46 (td, J = 2.0, 13.9 Hz, 1H, 2-H_{eq}), 3.91 (dd, J = 2.0, 13.9 Hz, 2H, 4-H_{eq} and 6-H_{eq}), 4.10 (d, J = 13.9 Hz, 1H, 2-H_{ax}), 4.44 (d, J = 13.9 Hz, 1H, 6-H_{ax}). — ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 30.20 (C-2), 42.90 (C-7), 62.20 (C-4, -6). — ^{11}B NMR (86.55 MHz, $CDCl_3$): δ = −8.0 (q, J = 98 Hz).

$C_4H_{12}BNS_2[B(OH)_3]_{1/8}$ (156.8) Calcd. C 30.63 H 7.71 N 8.93
Found C 30.69 H 7.90 N 8.17

5-Methyl-1,3,5-dithiazinane—Trideuterioboron (1/1) (**3**) was prepared according to the same procedure as employed for the synthesis of **2**, using $BD_3 \cdot THF$ formed by bubbling B_2D_6 (prepared from $NaBD_4$ and BF_3[19]) through the solution. Compound **3** was obtained as a white solid (0.53 g, 97%), m.p. 237 °C. — ^1H NMR (270 MHz, $CDCl_3$): δ = 2.91 (s, 3H, $[CH_3]_{ax}$), 3.46 (td, J = 2.0, 13.9 Hz, 1H, 2-H_{eq}), 3.91 (dd, J = 2.0, 14.6 Hz, 2H, 4-H_{eq} and 6-H_{eq}), 4.11 (d, J = 13.9 Hz, 1H, 2-H_{ax}), 4.44 (d, J = 14.6 Hz, 1H, 6-H_{ax}). — ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 30.21 (C-2), 42.91 (C-7), 62.11 (C-4, -6). — ^{11}B NMR (86.55 MHz, $CDCl_3$): δ = −8.6 (s, br).

$C_4H_9D_3BNS_2[B(OH)_3]_{1/5}$ (164.45) Calcd. C 29.21 H 7.34 N 8.52
Found C 29.06 H 7.69 N 7.86

5-Methyl-1,3,5-dithiazinane—Boron Trifluoride (1/1)(**4**): A solution of **1** (0.50 g, 3.7 mmol) in anhydrous $CHCl_3$ (40 ml) was cooled to 0 °C under dry nitrogen and boron trifluoride—ether (1.35 ml, 11.1 mmol) was added dropwise. The reaction mixture was stirred for 1 h, then the solvent was evaporated in vacuo to leave **4** as a viscous liquid (0.50 g, 82%). — ^1H NMR (270 MHz, $[D_8]THF$): δ = 1.70 (q, J = 94.6 Hz, 4H, BH_3), 2.96 (s, 3H, $[CH_3]_{ax}$), 3.49 (td, J = 1.6, 13.9 Hz, 1H, 2-H_{eq}), 3.98 (dd, J = 1.6, 13.9 Hz, 2H, 4-H_{eq} and 6-H_{eq}), 4.30 (d, J = 13.9 Hz, 1H, 2-H_{ax}), 4.69 (d, J = 13.9 Hz, 1H, 6-H_{ax}). — ^{13}C NMR (68.80 MHz, $[D_8]THF$): δ = 29.68 (C-2), 35.74 (C-7), 56.09 (C-4, -6). — ^{11}B NMR (86.55 MHz, $[D_8]THF$): δ = −0.1 (q, J = 13 Hz). — By NMR spectrometry **4** appears as a pure compound, although the nitrogen analysis was not correct, may be due it to some interference from F or S.

$C_4H_9BF_3NS_2$ (203.1) Calcd. C 23.66 H 4.46 N 6.90
Found C 23.55 H 5.41 N 3.21

5,5-Dimethyl-1,3-dithia-5-azonia-4-boratacyclohexane (**5**): To a solution of **1** (1.0 g, 7.4 mmol) in anhydrous THF (60 ml) a solution of 2.4 M $BH_3 \cdot THF$ (6.17 ml, 14.80 mmol) was added, and the reaction mixture was stirred at room temp. for 10 min. It was then refluxed for 2 h, and the solvent was evaporated in vacuo. Compound **5** was obtained as a solid (1.08 g, 98%), m.p. 41 °C. — ^1H NMR (270 MHz, $[D_8]THF$, −55 °C): δ = 2.63 (s, 3H, $[CH_3]_{eq}$), 2.89 (s, 3H, $[CH_3]_{ax}$), 3.36 (td, J = 2.0, 12.9 Hz, 1H, 2-H_{eq}), 3.78 (td, J = 2.0, 12.5 Hz, 1H, 4-H_{eq}), 3.81 (d, J = 12.9 Hz, 1H, 2-H_{ax}), 4.38 (d, J = 12.5 Hz, 1H, 6-H_{ax}). — ^{13}C NMR (68.80 MHz, $[D_8]THF$, −55 °C): δ = 31.96 (C-2), 44.34 (C-7), 53.14 (C-8), 64.63 (C-4). — ^{11}B NMR (86.55 MHz, $[D_8]THF$): δ = −3.3 (q, J = 107 Hz).

$C_4H_{12}BNS_2[B(OH)_3]_{1/15}$ (153.2) Calcd. C 31.36 H 7.89 N 9.14
Found C 31.41 H 7.65 N 9.15

4,4-Dideuterio-5-methyl-5-[D_1]methyl-1,3-dithia-5-azonia-4-boratacyclohexane (**6**) was prepared as described for **5** by using $BD_3 \cdot THF$. It was obtained as a white solid (0.55 g, 97%), m.p. 43 °C. — ^1H NMR (270 MHz, $[D_8]THF$, −55 °C): δ = 2.63 (s, 3H, $[CH_3]_{eq}$), 2.88 (s, 3H, $[CH_3]_{ax}$), 3.37 (td, J = 1.0, 12.5 Hz, 1H, 2-H_{eq}), 3.78 (td, J = 1.0, 12.5 Hz, 1H, 4-H_{eq}), 3.81 (d, J = 12.5 Hz, 1H, 2-H_{ax}), 4.38 (d, J = 12.5 Hz, 1H, 6-H_{ax}). — ^{13}C NMR (68.80 MHz, $[D_8]THF$, −55 °C): δ = 31.96 (C-2), 44.34 (C-7), 53.14 (C-8), 64.63 (C-4). — ^{11}B NMR (86.55 MHz, $[D_8]THF$): δ = −3.3 (q, J = 107 Hz).

tert-Butyldimethylamine—Borane (1/1) (**9**): To a solution of **7** (250 mg, 1.42 mmol) in anhydrous THF (60 ml) a solution of 2.4 M $BH_3 \cdot THF$ was added (1.18 ml, 2.84 mmol) dropwise at room temp. The reaction mixture was stirred for 15 min and then refluxed for 2 h. A precipitate formed which was removed by filtration under nitrogen. Evaporation of the solvent afforded compound **9** contaminated with some sulfur derivate; it was only characterized by NMR spectrometry. — ^1H NMR (270 MHz, $CDCl_3$): δ = 1.50 (s, 9H, H_3C-C), 2.92 (s, 6H, H_3C-N). — ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 24.70 (H_3C-C), 38.81 (H_3C-N), 63.83 ($[H_3C]_3C-N$). — ^{11}B NMR (86.55 MHz): δ = −11.8 in $[D_8]THF$ or −12.4 in CD_2Cl_2 (q, J_{B-H} = 96.8 Hz).

tert-Butyldimethylamine Hydrochloride (**10**): To a solution of **7** (1.0 g, 5.65 mmol) in anhydrous THF (180 ml) a solution of 2.4 M $BH_3 \cdot THF$ (4.71 ml, 11.30 mmol) was added dropwise at room temp. The reaction mixture was stirred for 15 min and subsequently refluxed for 2 h. Then hydrochloric acid (1.2 ml, 37.3%) was added and the solution stirred for 10 min. The THF was evaporated and the remaining solid extracted with hot $CHCl_3$ and filtered. The filtrate was concentrated to 40 ml. Ethyl ether was added to precipitate hydrochloride **10**[20] (0.393 g, 51%), m.p. 217—220 °C. — ^1H NMR (270 MHz, $CDCl_3$): δ = 1.48 (s, 9H, H_3C-C), 2.76 (d, J = 5 Hz, 7H, H_3C-N and NH). — ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 24.39 (H_3C-C), 37.72 (H_3C-N), 61.67 ($[H_3C]_3C-N$).

tert-Butyldi([D_1]methyl)amine—Trideuterioborane (1/1) (**11**) was prepared according to the same procedure as applied to the synthesis of **9**, using $BD_3 \cdot THF$. — ^1H NMR (270 MHz, $CDCl_3$): δ = 1.52 (s, 9H, H_3C-C), 2.95 (s, 4H, DH_2C-N). — ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 24.91 (H_3C-C), 47.08 (t, $J_{C,D}$ = 22.0 Hz, DH_2C-N), 62.42 ($[H_3C]_3C-N$). — ^{11}B NMR (86.55 MHz, $CDCl_3$): δ = −12.9 (s, br).

tert-Butyldi([D_1]methyl)amine Hydrochloride (**12**) was prepared in the same manner as compound **10**, 55% yield. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.49 (s, 9H, H_3C-C), 2.75 (s, 5H, DH_2C-N and NH). – ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 24.49 (H_3C-C), 37.28 (t, $J_{C,D}$ = 22.0 Hz, DH_2C-N), 61.85 ($[H_3C]_3C-N$).

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[13] NMR data of heterocycle **8** at –60°C: ^{13}C NMR (67.8 MHz, [D_8]THF) δ = 29.90 (H_3C-C), 31.54 (C-2), 37.92 ($[CH_3]_{ax}$), 55.75 (H_3C-C-N), 58.13 (C-4). – ^{11}B NMR (86.55 MHz, [D_8]-THF): δ = –7.2 or (86.55 MHz, $CDCl_3$) –4.8 (t, J = 126 Hz).

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