A New Lithium 5-Methyl-1,3-dithia-5-azacyclohex-2-ylborate−5-Borane and Two Dimeric 5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium Compounds − Stereochemistry and Reactivity

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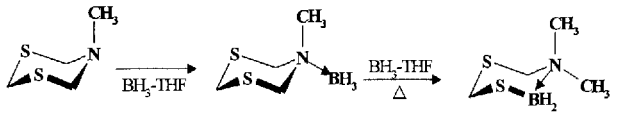
Syntheses of the dimers of axial 5-methyl-2-dithiazinyllithium (**4**) and equatorial 5-methyl-2-dithiazinyllithium−5-borane (**5**), and lithium 5-methyl-2-dithiazinanylborate−5-borane (**6**) are reported. Compounds **4**, **5**, and **6** are configurationally and conformationally stable. The ^{1}H-, ^{13}C-, ^{11}B-, and ^{7}Li-NMR study of the reactions of **4** and **5** with BH_3−$S(CH_3)_2$, BH_3−THF, and CH_3I is presented.

We have previously reported that dithiazine **1**, which is a molecule with five lone pairs available for coordination, reacts with borane−THF to give a stable N−BH_3 adduct **2** which has a preferred conformation with the BH_3 group equatorial; the sulfur atoms do not coordinate to BH_3[1−3]. Heating transforms the heterocycle **2** into the boradithiazine **3**[2] (Scheme 1). We have decided to add a new lone pair to dithiazines **1** and **2**, through the synthesis of a carbanion at C-2, and to explore the competition for coordination to Lewis acids. Herein, two 2-dithiazinyllithium compounds (**4** and **5**) are reported, and their reactions with borane and methyl iodide are investigated.

Scheme 1



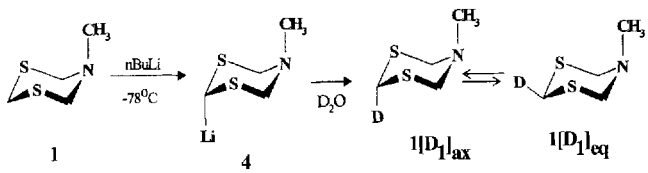
1 2 3

Results and Discussion

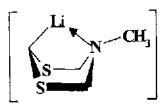
Synthesis of 2-Dithiazinyllithium Heterocycles 4 and 5

A) *5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium* (**4**): One of us has earlier reported on the synthesis of **4**[4]. It was prepared from the reaction of heterocycle **1** with butyllithium in THF. The carbanion is stable enough to allow determination of its structure by NMR; its resists solvent evaporation and dissolution in dry [D_8]THF. The ^{1}H-NMR spectrum showed the presence of a pure compound. Evidence of the covalent lithium−carbon atom bond is provided in the ^{1}H-coupled ^{13}C-NMR spectrum, by the shift of the C-2 resonance to lower frequencies ($\Delta\delta$ = 3.0 ppm) which appears as a doublet (δ = 31.3, J_{CH} = 130 Hz; in the parent compound C-2 is a triplet, J_{C-H} = 151), the smaller coupling constant C−H for C-2 in compound **4** is a consequence of the donor character of the lithium ion. In the ^{1}H-NMR spectrum 2-H gives rise to a singlet (δ = 3.36). The ^{1}H-, ^{13}C-, and ^{15}N-chemical shift data for NCH_3 in **4** are similar to those of **1**, this indicates the axial position of the methyl group and the absence of a lithium coordination to the nitrogen atom, for example, in a boat conformation (Scheme 2). The ^{7}Li-NMR spectrum (δ = −0.16, $w_{1/2}$ = 8.4 Hz, [D_8]THF) is characteristic of alkyllithium compound (δ^7Li of BuLi is 0.63, [D_8]THF, sharp line)[5]. Methylation and deuteration at C-2 give additional evidence of the lithium bonding. Addition of D_2O provides the monodeuterated compounds at C-2 (**1**[D_1]$_{ax}$ and **1**[D_1]$_{eq}$).

Scheme 2



1 4 1[D_1]$_{ax}$ 1[D_1]$_{eq}$



Compound **4** was found in a preferred chair conformation as denoted by the different resonances of equatorial and axial hydrogen atoms in its ^{1}H-NMR spectrum at room temperature. The configuration of C-2 was deduced by comparison of the NMR data of **4** with those of the frozen dithiazine **1** (−90°C, 270 MHz, [D_8]THF)[1,3] and compound **5** (Figure 1). The lithium ion principally affects the chemical shifts of the C-2 and 2-H signals; in the equatorial position its electronic donor effect is stronger than in axial

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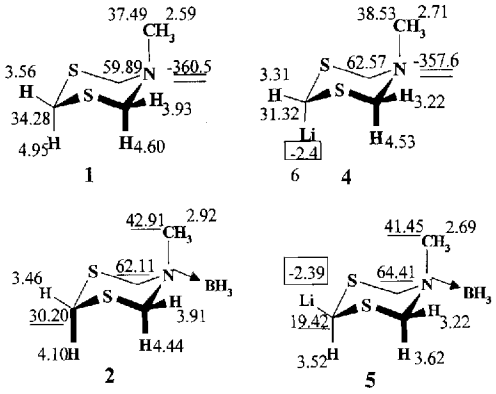
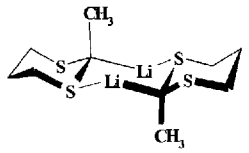
position (compound **5**[6]). The NMR spectra of the isolated compound **4** show the presence of tetrahydrofuran coordinated to the lithium ion, OCH_2 and OCD_2 (from the deuterated solvent) groups are slightly shifted to high field (^{13}C $\Delta\delta = 0.2$).

Figure 1. ^1H-, ^{13}C- (−), ^7Li- (□) and ^{15}N- (=)-NMR data of compounds **1**, **2**, **4** and **5**



A peak at 281.30 in the mass spectrum shows the presence of a dimer [$M^+ - H$], the monomeric compound is also observed ($C_4NS_2LiH_8$: 141.15). The dimeric structure is supported by the report of an X-ray diffraction study of a similar dimeric lithium compound[7] (Figure 2).

Figure 2. Reported structure of the dimer of 5-methyl-1,3-dithiocyclohexane found by an X-ray diffraction study; the lithium ions are also coordinated to *N,N,N',N'*-tetramethylethylenediamine[7]



An explanation of the stability of the axial lithium group in compound **4** is that it forms a stable dimer as demonstrated by the molecular mechanic calcualtions[8] [E = 10.7 kcal]. The isomeric dimer, with the lithium ion in equatorial position, has a similar calculated energy [E = 11.9 kcal] (Figure 3).

In order to check the structure of compound **4** we decided to synthesize the 1,3-dithiocyclohex-2-yllithium from butyllithium and 1,3-dithiocyclohexane. It was earlier reported that this compound is in a preferred conformation with the lithium ion in the equatorial position, its dimeric nature was not mentioned[9,10]. The ^1H-NMR spectrum was uncorrectly assigned in ref.[10]. We have performed 2D-$^{13}C/^1H$-HETCOR and $^1H/^1H$-COSY experiments in order to unequivocally assign the spectra. The shifts of the axial and equatorial 4-H and 6-H signals in 1,3-dithiocyclohex-2-yllithium were compared with those of an anchored 2-substituted 1,3-dithiocyclohexane[11]. We have found the same trends as in compound **5** indicating the equatorial preference of the lithium ion in both compounds (Figure 4).

B) *5-Methyl-1,3-dithia-5-azacyclohex-2-yllithium−5-Borane* (**5**): The reaction of the BH_3 adduct **2** with *n*BuLi proceeds cleanly to give the corresponding carbanion without affecting the N−borane group. The stereochemistry of **5** was deduced from the ^1H- and ^{13}C-NMR data (Figure 1). The C-2 signal is a doublet in the ^1H-coupled ^{13}C spectrum (δ = 19.4, J = 133), the 2-H gives rise to a singlet (δ = 3.52). The reaction afforded only one isomer in a fixed conformation with the lithium ion in the equatorial position, coordinated THF is detected in the NMR spectra. Compound **5** shows a signal at $\delta = -2.39$ in the ^7Li-NMR spectrum ($w_{1/2}$ = 8.4 Hz, [D_8]THF). The mass spectrum presents a peak at 284.50 for the dimer [$M^+ - B_2H_4$], another peak at 155.45 is attributed to the monomer $C_4NS_2BLiH_{11}$. Addition of D_2O provides two compounds monodeuterated at C-2 (**2**[D_1]$_{eq}$, **2**[D_1]$_{ax}$) with anchored conformation in a ratio 60:40 (Scheme 3).

Reactions of 2-Dithiazinyllithium Compounds with Borane and Methyl Iodide

A) *2-Dithiazinyllithium* **4**: The reaction of compound **4** with one equivalent of $BH_3-S(CH_3)_2$ gave regioselectively the N−BH_3 adduct **5**, under these conditions the borane adduct does not react with the anionic position C-2 (Scheme 3), while reaction of compound **4** with two equivalents of BH_3−THF afforded a mixture of dithiazinyllithium−5-borane **5**, lithium 2-dithiazinylborate−5-borane **6** and lithium 2-dithiazinylborate **7** (Scheme 4). Compound **4** reacts with one equivalent of CH_3I to give the product 2,5-dimethyl-1,3-dithia-5-azacyclohexane (**8**) which, by reaction with borane−THF, afforded the 2,5-dimethyl-1,3-dithia-5-azacyclohexane−5-borane (**9**). The reaction of **4** with an excess of methyl iodide produced the 2,5,5-trimethyl-1,3,5-dithiazinium iodide **10**.

B) *2-Dithiazinyllithium−5-Borane* **5**: The reaction of **5** with CH_3I at 40°C leads to an exchange of an endocyclic carbon versus an exocyclic boron atom to yield 2,5,5-trimethyldithia-5-azonia-4-boratacyclohexane (**11**). It has a stereogenic center at C-2 and prefers the conformation shown in Scheme 5. The reaction of compound **5** with one equivalent of $BH_3-S(CH_3)_2$ produces, as the main product, the lithium 2-dithiazinylborate **6**, which presents in the ^{11}B-NMR spectrum a quadruplet at $\delta = -29.7$ (J_{B-H} = 80 Hz, $CDCl_3$) of the 2-BH_3 group, and a broad signal at $\delta = -8.0$ of the N−BH_3 group. The ^7Li-NMR shows a signal at $\delta = -1.35$ ($w_{1/2}$ = 33.6 Hz). In this reaction some trimethylamine−borane is produced by reductive cleavage of the ring.

Conclusions

Two stable dimeric covalent organolithium compounds, 5-methyl-1,3,5-dithiazinyllithium **4** and 5-methyl-1,3,5-dithiazinyllithium−5-borane **5**, were prepared which showed a preferred chair conformation with two different configurations at the carbanion center. Compounds **4** and **5** have the lithium ion in axial and equatorial positions, respectively. The lithium 5-methyl-1,3,5-dithiazinylborate−5-borane **6** was obtained which is also in a fixed conformation with both borane groups in equatorial positions. Reaction of **4** with one equivalent of $BH_3-S(CH_3)_2$ afforded

Figure 3. a) Stable structures of the dimer of **4** and b) its equatorial lithium isomer, found by molecular-mechanics calculations[8]

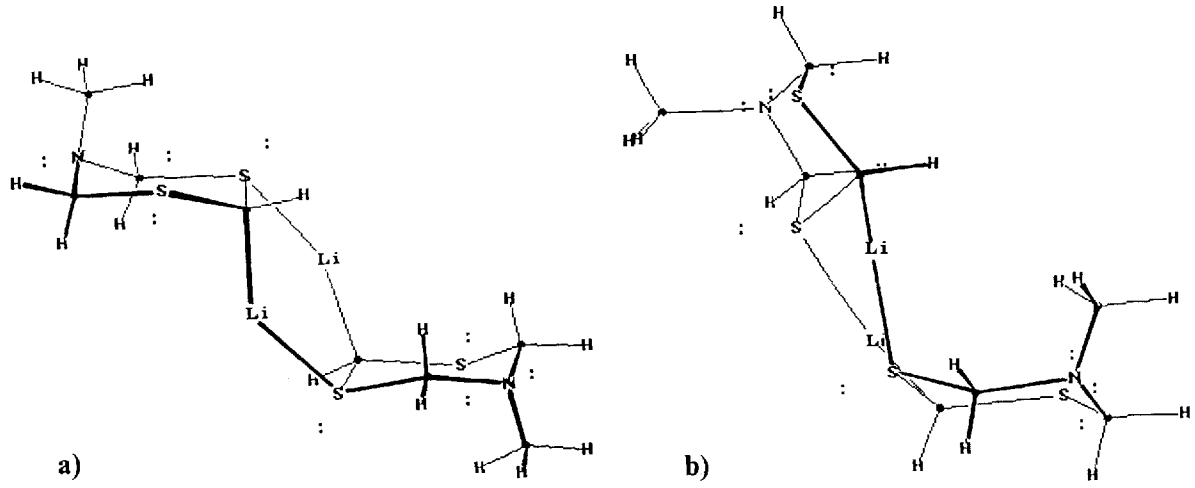
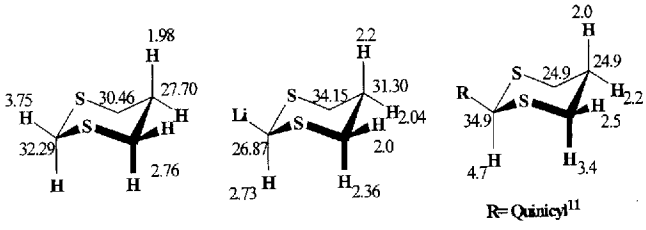
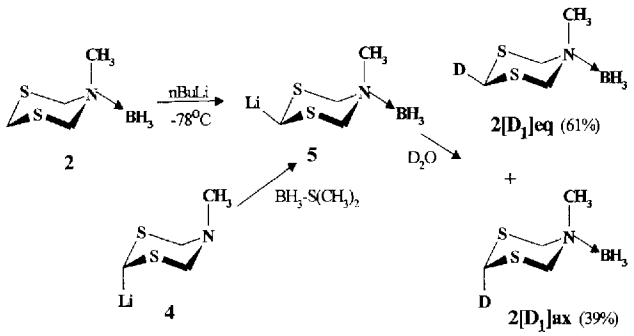


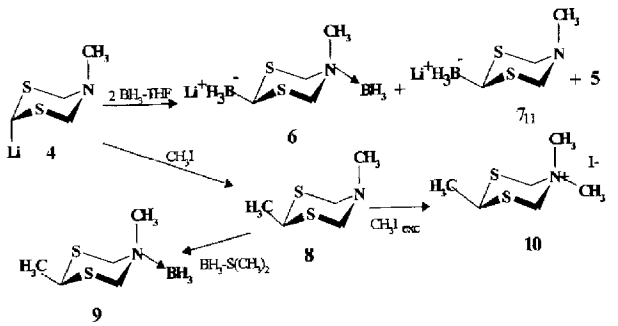
Figure 4. ^{1}H- and ^{13}C-NMR data of 1,3-dizhiocyclohexane, its lithium and 2-alkyl derivative



Scheme 3

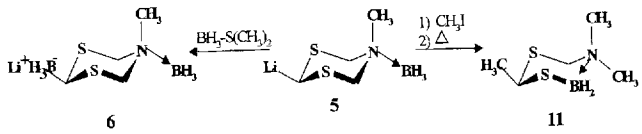


Scheme 4



exclusively compound **5**. With an excess of borane, compound **6** was also observed. The reported compounds may

Scheme 5



be classified in two isolobal groups, one including **1**–**4** and **5**, and another **6**, **9**, **7**, and **11**.

Experimental Section

General: ^{1}H, ^{7}Li, ^{11}B, ^{13}C, and ^{15}N NMR: Jeol 270 GXS spectrometer at 270, 104.88, 86.55, 67.80, and 27.25 MHz, respectively; ^{1}H- and ^{13}C-NMR chemical shifts were referenced to TMS, δ^7Li to $LiClO_4$ (D_2O infinited dilution), δ^{11}B to Et_2O-BF_3 and δ^{15}N to neat CH_3NO_2. – Anhydrous solvents were prepared according to the usual laboratory methods. All reactions were carried out in an inert atmosphere in oven-dried glassware. – Mass spectra were recorded with a Hewlett-Packard 5989 mass spectrometer. – Melting points are uncorrected.

5-Methyl-1,3,5-dithiazine **1**: Compound **1** was prepared as described in ref.[12]. – ^{1}H NMR (90.05 MHz, $CDCl_3$): δ = 4.39 (br. s, 4H, 2 × 4-H and 2 × 6-H), 4.05 (br. s, 2H, 2-H), 2.61 (br. s, 3H, 7-H). – ^{1}H NMR (90.05 MHz, –80°C, [D$_8$]THF): δ = 2.59 (s, 3H, 7-H), 3.56 (dt, J = 13.3 and 2.6, 1H, 2-H_{eq}), 3.93 (dt, J = 12.7 and 2.6, 2H, 4-H_{eq} and 6-H_{ax}), 4.60 (d, J = 13.3, 1H, 2-H_{ax}), 4.95 (d, J = 12.7, 2H, 4-H_{ax} and 6-H_{ax}). – ^{13}C NMR (67.80 MHz, $CDCl_3$): δ = 34.28 (d, J = 151.0, C-2), 59.89 (d, J = 152.1, C-4 and C-6), 37.49 (q, J = 135.5, C-7). – ^{15}N NMR (27.25 MHz, $CDCl_3$): δ = –360.5 (s).

5-Methyl-1,3,5-dithiazin-2-yllithium **4**[4]: A solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled at –78°C under dry nitrogen, and 0.81 ml of a solution of *n*BuLi/hexane (1.0 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for 30 min and then the solvent was evaporated in vacuo to –5°C to leave compound **4** as a white solid. – ^{1}H NMR (270 MHz, [D$_8$]THF): δ = 2.71 (s, 3H, N[CH_3]$_{ax}$), 3.22 (d, J = 12.1, 2H, 4-H_{eq} and 6-H_{eq}), 3.31 (s, 1H, 2-H_{eq}), 4.53 (d, J = 12.1, 2H, 4-H_{ax} and 6-H_{ax}). – ^{13}C NMR (68.80 MHz, [D$_8$]THF): δ = 31.32 (d, J = 130, C-2), 38.43 (q, J = 133.3, N[CH_3]$_{ax}$), 62.57 (t,

J = 145.3, C-4 and C-6). – ^{7}Li NMR (104.88 MHz, [D$_8$]THF): δ = −2.46 (s). – ^{15}N NMR (27.25 MHz, [D$_8$]THF): δ = −357.6 (s). – MS (15 eV); *m/z* (%): 141.15 (1) [1/2 M$^+$], 281.30 (8) [M$^+$ − H].

2-Deuterio-5-methyl-1,3,5-dithiazine **1[D$_1$]**: To a solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) 0.5 ml of D$_2$O were added. The reaction mixture was stirred for 5 min and then the solvent was evaporated in vacuo. Compound **1[D$_1$]** is a yellow liquid (0.1 g, 100%). – $C_4H_8DNS_2[C_4H_8O]_{1/8}$ (145.27): calcd. C 37.20, H 7.63, N 9.64, S 44.14; found C 37.47, H 6.92, N 10.24, S 45.20. – ^{1}H NMR (270 MHz, [D$_8$]THF): δ = 2.61 (s, 3H, N[CH$_3$]$_{ax}$), 4.04 (s, 1H, 2-H), 4.40 (s, 4H, 2 × 4-H and 2 × 6-H). – ^{13}C NMR (68.80 MHz, [D$_8$]THF): δ = 34.02 (t, J_{CD} = 22.0, C-2), 37.53 ([CH$_3$]$_{ax}$), 59.81 (C-4 and C-6). – MS (20 eV) *m/z* (%): 44.00 (100), 42.00 (84), 57.15 (81), 135.15 (55), 136.15 (27).

Equatorial Isomer **1[D$_1$]$_{eq}$**: ^{1}H NMR (270 MHz, −80°C, [D$_8$]THF): δ = 2.59 (s, 3H, N[CH$_3$]$_{ax}$), 3.96 (d, J = 12.5, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.57 (s, 1H, 2-H$_{ax}$), 4.94 (d, J = 12.5, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

Axial Isomer **1[D$_1$]$_{ax}$**: ^{1}H NMR (270 MHz, −80°C, [D$_8$]THF): δ = 2.59 (s, 3H, N[CH$_3$]$_{ax}$), 3.60 (s, 1H, 2-H$_{ax}$), 3.96 (d, J = 12.5, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.94 (d, J = 12.5, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

5-Methyl-1,3,5-dithiazine−5-Borane **2**[3]: A solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled at −78°C under dry nitrogen and 0.24 ml of a solution of BH$_3$−THF (3.03 M, 0.74 mmol) was added. The reaction mixture was stirred for 30 min and then the solvent was evaporated in vacuo at −5°C to give compound **2**. – ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.92 (s, 3H, CH$_{3\ ax}$), 3.46 (dt, J = 13.9, 2.0; 1H, 2-H$_{eq}$), 3.91 (dd, J = 13.9, 2.0; 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.10 (d, J = 13.9, 1H, 2-H$_{ax}$), 4.44 (d, J = 139, 1H, 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 30.20 (ddt, J = 155.3, 147.6, 6.6, C-2), 42.91 (qt, J = 141.1, 5.5, N[CH$_3$]$_{ax}$), 62.11 (t, J = 154.6, C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): δ = −8.0 (q, J = 98).

5-Methyl-1,3,5-dithiazin-2-yllithium−5-Borane **5** was prepared by two methods: a) the same procedure as applied to the synthesis of **4**, using compound **2**, b) same procedure as applied to the synthesis of **2**, using compound **4**. – ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.69 (s, 3H, N[CH$_3$]$_{ax}$), 3.22 (d, J = 13.0, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 3.52 (s, 1H, 2-H$_{ax}$), 3.62 (d, J = 13.0, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 19.42 (d, J = 133.0, C-2), 41.45 (q, J = 140.0, N[CH$_3$]$_{ax}$), 64.41 (t, J = 152.6, C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): δ = −8.45 (br. s). – ^{7}Li NMR (104.88 MHz, CDCl$_3$): δ = −2.39 (s). – MS (15 eV) *m/z* (%): 155.45 (2) [1/2 M$^+$], 285.50 (1) [M$^+$ − B$_2$H$_4$].

2-Deuterio-5-methyl-1,3-dithia-5-azacyclohexane−5-Borane **2[D$_1$]**: To a solution of compound **5** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) 0.5 ml of D$_2$O was added. The reaction mixture was stirred for 5 min and then the solvent was evaporated in vacuo. A mixture of compounds **2[D$_1$]** with 10% of dithiazine **1** was obtained. – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 29.85 (t, J_{CD} = 24.3, C-2), 42.86 (N[CH$_3$]$_{ax}$), 62.05 (C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): δ = −8.18 (q, J = 100). – MS (20 eV) *m/z* (%): 44.15 (40), 57.15 (100), 89.20 (72), 136.30 (79), 137.30 (87), 150.30 (2).

Equatorial Isomer **2[D$_1$]$_{eq}$**: ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.92 (s, 3H, N[CH$_3$]$_{ax}$), 3.92 (d, J = 13.7, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.08 (s, 1H, 2-H$_{eq}$), 4.44 (d, J = 13.7, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

Axial Isomer **2[D$_1$]$_{ax}$**: ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.92 (s, 3H, N[CH$_3$]$_{ax}$), 3.92 (d, J = 13.7, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 3.45 (s, 1H, 2-H$_{ax}$), 4.44 (d, J = 13.7, 2H, 4-H$_{ax}$ and 6-H$_{ax}$).

2,5-Dimethyl-1,3,5-dithiazine−5-Borane **9**: Compound **9** was obtained by two methods: a) from anion **5** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) at −78°C, by treatment with CH$_3$I (0.23 ml, 3.7 mmol); or b) from compound **8** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) by adding 0.24 ml (3.03 M BH$_3$−THF, 0.74 mmol) at −78°C. The reaction mixture was stirred for 5 min, and the solvent was evaporated in vacuo. Compound **9** was obtained as a white solid; m.p. 190°C (dec.). – $C_5H_{14}BNS_2$ (163.11): calcd. C 36.81, H 8.65, N 8.59; found C 36.65, H 7.00, N 8.46. – ^{1}H NMR (270 MHz, CDCl$_3$): δ = 1.52 (d, J = 6.8, 3H, C[CH$_3$]$_{eq}$), 2.86 (s, 3H, N[CH$_3$]$_{ax}$), 3.93 (d, J = 41.1, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.22 (q, J = 6.8, 1H, 2-H$_{ax}$), 4.47 (d, J = 14.1, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 19.54 (q, J = 134.4, C[CH$_3$]$_{eq}$), 41.09 (d, J = 157.5, C-2), 42.55 (q, J = 140.0, N[CH$_3$]$_{ax}$), 63.02 (t, J = 154.2, C-4 and C-6). – ^{11}B NMR (86.55 MHz, CDCl$_3$): δ = −8.5 (q, J = 94.7).

2,5,5-Trimethyl-1,3-dithia-5-azonia-4-boratacyclohexane **11**: A solution of compound **9** (0.12 g, 0.74 mmol) in anhydrous THF (20 ml) was heated (40°C). The reaction mixture was stirred for 20 min and the solvent was evaporated in vacuo. Compound **11** was obtained as a white solid; m.p. 190°C (dec.). – $C_5H_{14}BNS_2$ (163.11): calcd. C 36.81, H 8.65, N 8.59; found C 36.52, H 6.91, N 8.79. – ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.65 (d, J = 6.8, 3H, C[CH$_3$]$_{eq}$), 2.71 (s, 3H, N[CH$_3$]$_{eq}$), 2.80 (s, 3H, N[CH$_3$]$_{ax}$), 3.93 (d, J = 12.7, 1H, 4-H$_{eq}$), 4.05 (q, J = 6.8, 1H, 2-H$_{ax}$), 4.30 (d, J = 12.7, 1H, 4-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 23.17 (q, J = 127.8, C[CH$_3$]$_{eq}$), 41.77 (d, J = 142.1, C-2), 44.92 (q, J = 140.0, N[CH$_3$]$_{ax}$), 51.07 (q, J = 139.9, N[CH$_3$]$_{eq}$), 63.70 (t, J = 152.6, C-4). – ^{11}B NMR (86.55 MHz, CDCl$_3$): δ = −3.60 (t, J = 113.7).

Lithium 5-Methyl-1,3,5-dithiazin-2-ylborate−5-Borane **6**: A solution of compound **5** (0.11 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled to −78°C under dry nitrogen and 0.6 ml of a solution of BH$_3$−S(CH$_3$)$_2$ (1.33 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for 15 min, and the solvent was evaporated in vacuo at −5°C, to give compound **6** as a white solid. – ^{1}H NMR (270 MHz, CDCl$_3$): δ = 2.84 (s, 3H, N[CH$_3$]$_{ax}$), 3.46 (br. s, 1H, 2-H$_{ax}$), 3.75 (d, J = 13.8, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.32 (d, J = 13.8, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 36.20 (br. s, C-2), 42.12 (q, J = 139.0, N[CH$_3$]$_{ax}$). – ^{11}B NMR (86.55 MHz, CDCl$_3$): δ = −8.0 (br. s), −29.7 (q, J = 82.1). – ^{7}Li NMR (104.88 MHz, CDCl$_3$): δ = −2.87 (s).

2,5-Dimethyl-1,3,5-dithiazine **8**: A solution of compound **1** (0.10 g, 0.74 mmol) in anhydrous THF (20 ml) was cooled to −78°C under dry nitrogen, 0.81 ml of *n*BuLi/hexane (1.0 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for 30 min, and CH$_3$I (0.23 ml, 3.7 mmol) was added. The reaction was stirred and quenched after 20 min with 10 ml of water. Compound **8** was extracted from the reaction mixture with CH$_2$Cl$_2$ to give a yellow liquid (0.11 g, 100%). – $C_5H_{11}NS_2[H_2O]_2$ (185.31): calcd. C 32.41, H 8.15, N 7.55, S 34.60; found C 33.19, H 5.94, N 7.25, S 31.01. – ^{1}H NMR (270 MHz, CDCl$_3$): δ = 1.46 (d, J = 4.2, 3H, C[CH$_3$]$_{eq}$), 2.56 (s, 3H, N[CH$_3$]$_{ax}$), 4.09 (d, J = 12.6, 2H, 4-H$_{eq}$ and 6-H$_{eq}$), 4.24 (q, J = 4.2, 1H, 2-H$_{ax}$), 4.67 (d, J = 12.6, 2H, 4-H$_{ax}$ and 6-H$_{ax}$). – ^{13}C NMR (68.80 MHz, CDCl$_3$): δ = 22.64 (q, J = 129.4, C[CH$_3$]$_{eq}$), 37.02 (q, J = 135.2, N[CH$_3$]$_{ax}$), 44.43 (d, J = 153.1, C-2), 60.30 (t, J = 153.1, C-4 and C-6). – MS (20 eV) *m/z* (%): 44.05 (100), 42.00 (92), 57.05 (64), 149.20 (53).

2,5,5-Trimethyl-1,3,5-dithiazinium Iodide **10**: A solution of compound **4** (0.10, 0.74 mmol) in anhydrous THF (20 ml) was cooled to −78°C under dry nitrogen, 0.8 ml of *n*BuLi/hexane (1.0 M, 0.81 mmol) was added dropwise. The reaction mixture was stirred for

30 min and CH_3I (3.7 ml, 0.23 mmol) was added. The reaction was quenched with water (5 ml) and extracted with CH_2Cl_2. Compound **10** is a yellow liquid (0.17 g, 80%). – ^1H NMR (270 MHz, [D$_6$]DMSO): δ = 1.52 (br. s, 3H, C[CH_3]), 3.32 (s, 3H, N[CH_3]), 3.31 (s, 3H, N[CH_3]), 4.79 (br. s, 2H, 4-H_{eq} and 6-H_{eq}), 5.30 (br. s, 3H, 2-H_{ax}, 4-H_{ax} and 6-H_{ax}). – ^{13}C NMR (68.80 MHz, $CDCl_3$): δ = 19.03 (br. s, C[CH_3]), 39.40 (br. s, C-2), 44.01 (s, N[CH_3]$_{ax}$), 54.21 (br. s, N[NCH_3]$_{eq}$), 64.24 (br. s, C-4 and C-6).

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