Structural Analyses of Borane and Chloroborane Adducts of 1,3,5-Dithiaza-, -Dioxaza-, -Thiadiaza-, and -Triazacyclohexanes and Their Rearrangement Products, Boracyclohexanes

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Structural and conformational studies performed by ^{1}H-, ^{11}B-, ^{13}C-, two-dimensional, and variable-temperature NMR spectroscopy of borane and chloroborane adducts of 1,3,5-heterocyclohexanes and their rearrangement products, boracyclohexanes, are reported. *N*-Methyl derivatives gave equatorial *N*-borane adducts whereas the *N*-isopropyl derivatives produced the axial borane compounds. Rearrangement reactions of the adducts gave the first examples of chloroboracyclohexanes bearing boron and nitrogen atoms as stable stereogenic centers. $BClH_2$ and BCl_2H adducts were found to be more stable towards ring rearrangement than the corresponding *N*-BH_3 analogs.

Introduction

We have been systematically studying the synthesis and particularly the coordination behavior of 1,3,5-heterocyclohexanes bearing heteroatoms such as O, S, and N, which are rich in lone pairs and good ligands for Lewis acids.[1] Reactions with boron[1a,1b,1e−1f] and lithium[1g] compounds were investigated because these reagents function as coordination probes conveniently studied by NMR techniques.

Herein, we report extended studies of chloroboranes, which are more acidic reagents which could give stronger coordination bonds and more stable adducts, and of new families of heterocycles: 1,3,5-thiadiazacyclohexanes and 1,3,5-dioxazacyclohexanes. Because these heterocycles are difficult to prepare, few examples of them were known,[2] but fortunately we have recently established suitable reaction conditions for their preparation.[1h]

Results and Discussion

Herein, we present the study of the reactions of BH_3·THF and various chloroborane·DMS with the heterocycles 3,5-dialkyl-1,3,5-thiadiazacyclohexane (**1**, **2**,[1h,2] and **3**[1h]), 5-alkyl-1,3,5-dioxazacyclohexane (**4** and **5**[1h]), 5-alkyl-1,3,5-dithiazacyclohexane (**6**, **7**,[1d] and **8**[1g]), and 1,3,5-trimethyl-1,3,5-triazacyclohexane[1f] (**9**) (Figure 1).

Acid−base studies with BH_3 as the Lewis acid partner, showed that the potential basicity decreases in the order N > S > O. Therefore, we would expect mono(*N*-BX_3) derivatives to form from the reactions of **1**−**9** with BH_3 or chloroborane compounds, and that two or even three borane molecules would coordinate to heterocycles **1**−**3** and **9**. Also,

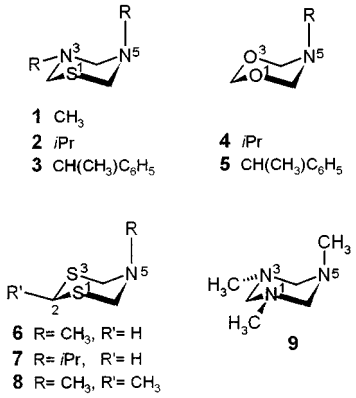

Figure 1

we were interested to find out if coordination would freeze the conformations of the heterocycles. NMR studies of heterocycles **1**−**7** and **9** showed that they are in ring- and nitrogen-conformational equilibrium at room temp. (400-MHz ^{1}H NMR), whereas compound **8** has a preferred chair conformation with the 2-methyl group in the equatorial and the *N*-methyl group in the axial position.[1g]

When heated, *N*-BH_3 adducts of 1,3,5-dithiazacyclohexanes rearrange into boracyclohexanes by exchange of boron and carbon atoms[1b] (Scheme 1). The stability of these boraheterocycles depends on the size of the *N*-alkyl group: Those with bulky groups are rapidly converted into *N*-(BH_3)-dimethylalkylamine complexes.[1b] This rearrangement was not found for 1,3,5-triazacyclohexanes. Therefore, we wanted to investigate if these rearrangements occur for other heterocyclohexanes or with the more reactive chloroboranes, if the more acidic boron atom in the resulting chloroborate allows better coordination and a more stable ring, if the chlorine atom could have a preferred position in a frozen ring and thus result, stereoselectively, in a stereogenic boron atom. In addition, we wanted to study the influence of the chlorine atom on the reactivity and NMR data and on the conformational behavior.

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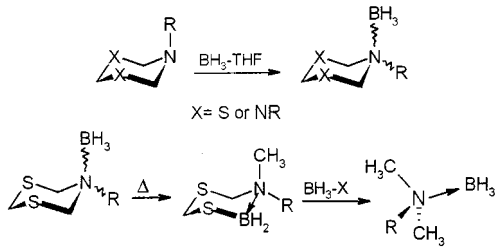

Scheme 1. Rearrangement of the BH_3 adducts

Borane Adducts

NMR spectroscopy showed that the equimolar reaction of thiadiazacyclohexane **1** with BH_3·THF resulted in monoadduct **10**, whereas an excess of borane led to bis(borane) **11** (Figure 2). The ^{13}C-NMR spectrum of compound **1**, at −90°C in [D_8]THF (100.53 MHz), did not indicate a preferred conformation, as the CH_3 and SCH_2N resonances were averaged, indicating that $\Delta G^{\neq}$ for the ring inversion is very low. In contrast, **10** and **11** are present in frozen conformations, because the CH_2 groups have geminal coupling patterns. Their *N*-BH_3 groups are in equatorial positions as shown by the position of the *N*-CH_3 group in the ^{13}C spectrum at δ ≈ 45;[1e] this conformation is also supported by an X-ray diffraction structure.[1i] The bis(borane) **11** is an analog of the reported compound **12**.[1f] In solution, adduct **10** is slowly transformed into **11** and the free heterocycle. ^{1}H-NMR data are summarized in Table 1.

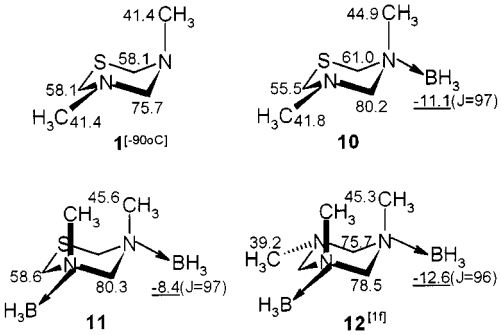

Figure 2. ^{11}B- and ^{13}C-NMR chemical shifts of **10**−**12**

The reaction of equimolar amounts of BH_3·THF and 3,5-diisopropyl-1,3,5-thiadiazacyclohexane (**2**) afforded the stable *N*-borane **13** with the two isopropyl groups in equatorial positions and the BH_3 group in the axial position (Figure 3). Compound **13** is more stable than **14**,[1b] which could be observed only at low temperature. In the presence of an excess of BH_3·THF, **13** rapidly rearranged into **31** (vide infra, Figure 8), whereas the triisopropyltriazacyclohexane **15**[1f] gave a small amount of the bisadduct **16**.[1f] The reaction of BH_3·THF with the dioxazacyclohexane **4** also yielded an *N*-borane, **17**, as shown by NMR spectroscopy at room temp. The stability of the borane adducts is shown by the order of the ease of rearrangemen: **14** > **17** > **13** > **15**.

The room-temp. NMR spectra of **13**−**17** (Figure 3) show that the ring conformation is preferentially that of a chair with the bulky isopropyl groups in equatorial positions, as shown by the ^{13}C-δ values for CH (δ ≈ 54; for the axial position δ ≈ 46).[1e] These heterocycles provide examples of axial BH_3 groups. The frozen conformation of **13** that results from BH_3 addition makes the N atoms stereogenic centers and the C−CH_3 groups diasterotopic. The signal of CH_3 groups of the isopropyl group attached to the coordinated nitrogen atom appear at δ = 15.9 and 15.7, whereas those of the ones attached to the free nitrogen atom appear at δ = 18.8 and 18.4. In the free ligand **2** the signals of all the CH_3 groups appear at δ = 20.1.

Chloroborane Adducts

We prepared the chloroborane adducts of 1,3,5-heterocyclohexanes **18**−**22** and **24**−**29**. The reaction of a commercial mixture of BH_2Cl, $BHCl_2$, and BH_3 (in the ratio 90:8:2, respectively), in DMS, with compounds **6** and **8** produced, in the same ratio, the corresponding adducts **18**−**21** (Figure 4). Upon coordination, the ring of adducts **18**−**21** adopted a preferred conformation with the *N*-methyl group in the axial position as indicated by their ^{13}C-δ values in the range δ = 37.7−40.2 (Table 2). To analyze the trends in the NMR spectra, the data of compounds **18**−**21** were compared to those of the BCl_3 (**22**) and BH_3 (**23**[1b]) adducts of **6**. In the ^{1}H as well as the ^{11}B spectra, the resonances of the CH_2 groups close to the N−B bond are systematically shifted to higher frequencies with an increasing number of chlorine atoms. The coupling constants ^1J(B−H) increase in the same order.

We found that chloroborane adducts are more stable to ring rearrangement than the corresponding *N*-BH_3 analogs, making them useful for the observation and study of coordination compounds of heterocycles with bulky groups. For example, we obtained adduct **24**, derived from 3-isopropyl-1,3,5-dioxazacyclohexane (Table 1, Figure 5). It is moderately stable and could be observed by NMR, but we were not able to detect the corresponding BCl_2H adduct. The *N*-BH_3 adducts of **3** and **5** could not be observed because they are rapidly reduced to the corresponding dimethylamineborane.

Heterocycle **1** has two N sites for borane coordination and readily formed monoadduct **25** and bis(monochloroborane) adduct **26**. Both are stable compounds with the *N*-chloroborane group in the equatorial position as the preferred conformation. In contrast, only one example of an *N*-BCl_3 adduct of a 1,3,5-thiadiazacyclohexane was prepared, **27**, which is a weak complex that decomposes on vacuum evaporation of the solvent. According to its ^{13}C-NMR spectrum, the BCl_3 adopts an axial position (Figure 5). An interesting observation was that BCl_3 adducts of the studied heterocycles are less stable than adducts with at least one B−H bond. This can be explained by the stabilization resulting from interaction between the hydrides on B and the protons on C, as discussed in the next paper.[1i]

The *N*-BH_2Cl monoadduct **28** and bisadduct **29** of 1,3,5-triazacyclohexane (**9**) were obtained. The BH_2Cl groups oc-

Table 1. ^{1}H-NMR data (400 MHz in $CDCl_3$ at 25°C or in [D_8]THF at low temperature; for atomic numbering see Figure 1)

Compd.	R^2 or 2-H_{eq}/2-H_{ax}	4-H_{eq}/4-H_{ax}	6-H_{eq}/6-H_{ax}	N^1−R	N^3-R	N^5-R
1 (−90°C)	3.82/4.57	3.53/3.93	3.82/4.57		2.56	2.56
2 (−95°C)	3.92/4.15	4.76/4.24	3.92/4.15		3.13	3.13
3	4.20/4.58	4.21/4.04	4.20/4.58		3.73	3.73
4 (−80°C)	5.12/5.04	4.68	4.68			3.42
5 (−60°C)	5.11/5.16	4.13/4.59	4.98/4.83			4.63
6 (−80°C)	3.56/4.60	3.93/4.95	3.93/4.95			2.59
7 (−90°C)	3.68/4.65	4.29/4.80	4.29/4.80			3.73
8 (27°C)	1.46/4.24	4.09/4.67	4.09/4.67			2.56
9 (−90°C)	3.86/3.18	3.86/3.18	3.86/3.18	2.83	2.83	2.83
10	3.60/4.14	3.55/4.23	3.66/3.81		2.65	2.61
11	3.54/3.85	3.97/3.71	3.54/3.85		2.47	2.47
12[1f]	3.69/2.59	3.54/3.12	3.54/3.12	2.30	2.79	2.79
13	4.14	4.08/3.51	3.82/3.96		2.99	4.33
15[1f]	3.75/3.07	4.02/3.16	4.02/3.16	2.81	2.81	4.19
16[1f]	4.25/3.64	4.43/4.08	4.43/4.08	3.02	3.89	3.89
17	5.16/4.88	4.80/4.44	4.80/4.44			4.06
24	4.93	4.53/4.28	4.53/4.28			4.37
25	3.66/4.22	3.34/4.32	3.73/4.00		2.61	2.73
28	2.90/2.76	3.74/3.33	3.74/3.33	2.37	2.37	2.92
30[1f]	3.65/3.36	3.73/4.03	3.65/3.36	2.30	2.30	2.47
33	1.39/4.41	3.45/4.94		2.79	2.72	
34	1.40/4.22	3.73/5.12		3.10	2.95	
38 (25°C)	2.65/4.05	3.93/4.30		2.80		2.71

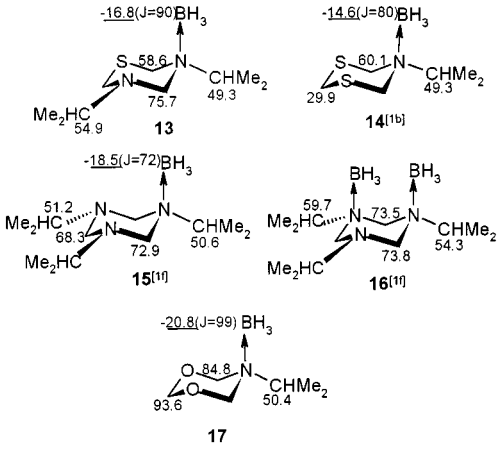

Figure 3. Borane adducts of *N*-isopropyl heterocycles; ^{11}B-NMR data are shown, the boron signal of **16** is masked by that of **15**

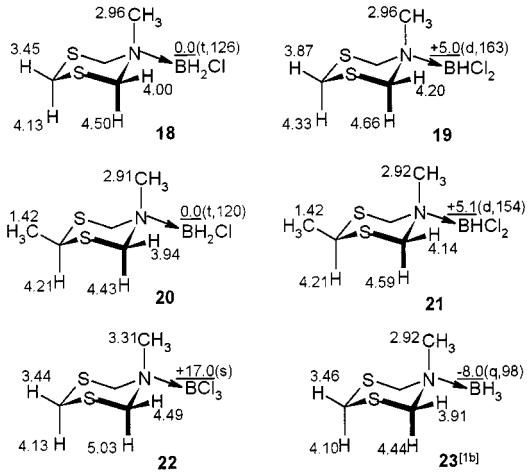

Figure 4. ^{11}B- and ^{1}H-NMR data of **18**−**23**

Table 2. ^{13}C-NMR data (100.5 MHz, in $CDCl_3$ at 25°C or [D_8]THF at low temperature; for atomic numbering see Figure 1; * = quaternary nitrogen atom)

Compd.	C-2	C-4	C-6	N^*−R
1 (−90°C)	58.1	75.7	58.1	41.4
2 (−95°C)	54.1	69.3	54.1	50.3
3	59.2	70.1	59.6	54.6
4 (−20°C)	95.4	81.3	81.3	50.5
5 (−60°C)	95.2	80.2	81.3	56.0
6 (−90°C)	34.3	59.9	59.9	37.5
7 (−80°C)	34.3	56.9	56.9	45.8
8	44.3	60.3	60.3	37.0
9 (−100°C)	80.7	75.9	75.9	39.7,[b] 41.4[a]
18	30.9	60.0	60.0	40.2
19	30.7	59.1	59.1	38.3
20	42.5	61.0	61.0	39.5
21	42.0	59.7	59.7	37.7
22	30.3	58.9	58.9	38.6
23	30.2	62.2	62.2	42.9
32eq (−65°C)	30.2	62.2		44.5*,[a] 47.7*[b]
32ax (−65°C)	29.9	63.9		43.8*,[a] 52.6*[b]
37 (−55°C)	32.0	64.6		44.3*,[a] 53.1*[b]

[a] Axial position. − [b] Equatorial position.

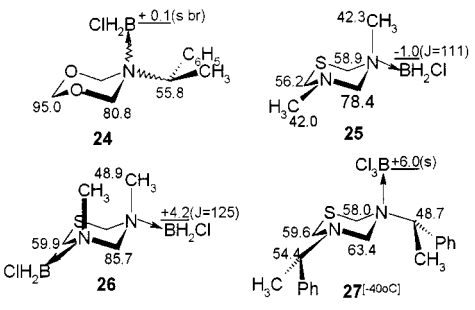

Figure 5. ^{11}B- and ^{13}C-NMR chemical shifts and the preferred conformations of **24**, **25**, **26**, and **27**

cupy equatorial positions and the ring is not fluxional. The ^{13}C chemical shifts of **28** and **30**[1f] were similar, and those of **29** and **12** were also similar[1f] (Figures 2, 6).

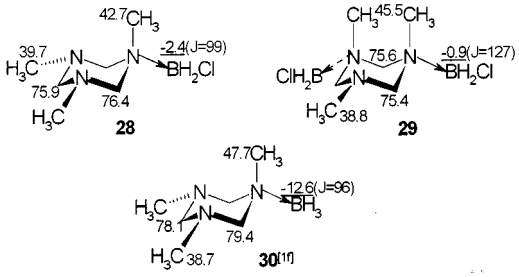

Figure 6. ^{11}B- and ^{13}C-NMR data and the preferred conformations of **28**, **29**, and **30**

1,3,5,6-Thiadiazaboracyclohexane (31)

Herein, we report the first example of a 1,3,5,6-thiadiazaboracyclohexane (**31**), quantitatively formed by reaction of 1,3,5-thiadiazacyclohexane (**2**) and an excess of BH_3·THF in $CHCl_3$ at room temp. The ^{11}B-NMR spectrum of **31** shows a triplet at $\delta = -5.3$, characteristic of an $S-BH_2\leftarrow N$ group. The ring appears nondynamic on the time scale of the ^1H-NMR spectrum at room temp (Figure 7).

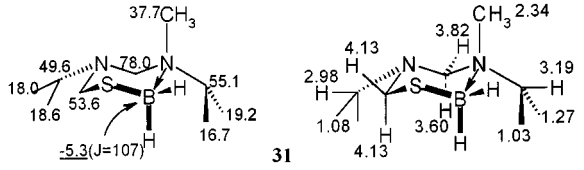

Figure 7. ^{13}C-, ^{11}B-, and ^1H-NMR chemical shifts of **31** at 25°C

1,3,5,6-Dithiazaboracyclohexanes 32−36

2-Chlorobora-1,3,5-dithiazacyclohexanes **32−36** were formed by allowing the 1,3,5-dithiazacyclohexanes **6−8** to react with excess BH_2Cl·DMS in $CHCl_3$. The resulting structures were assigned by HETCOR, COSY, and APT NMR experiments. The positions of the chlorine atoms were determined by their effects on the ^1H resonances of the neighboring protons and by comparison with the analogous BH_2 compounds. The boron atom becomes a stereogenic center and two isomers were indeed observed. At room temp. compound **32** is an equilibrium mixture of the two conformers shown in Figure 8. At −65°C, both conformers were observed in the ^{13}C- (Table 2) and ^{11}B-NMR spectra, for assignment a comparison with **37** was helpful. The conformer with the Cl atom in axial position was present in 70% abundance. At this temperature the $^1J(B-H)$ values of the two isomers differed significantly, with 161 Hz for equatorial B−H and 127 Hz for axial B−H, indicating frozen conformations.

Compound **8** with an excess of BH_2Cl produced the two diasteromers **33** and **34** in a 1:1 ratio (Figure 9). The ^1H- and ^{13}C-NMR data indicate that the chair conformation is the preferred one for both molecules at room temp., and the $C-CH_3$ group anchors the molecule. Here, the boron atom and C-2 are stereogenic centers.

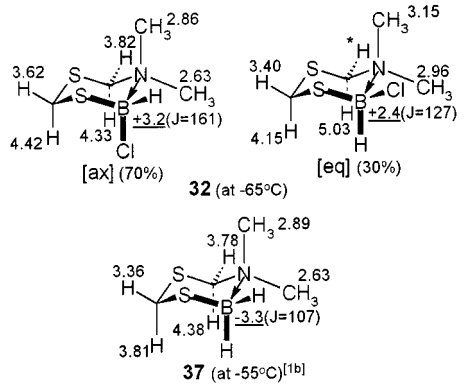

Figure 8. ^1H- and ^{11}B-NMR data of **32** and **37**

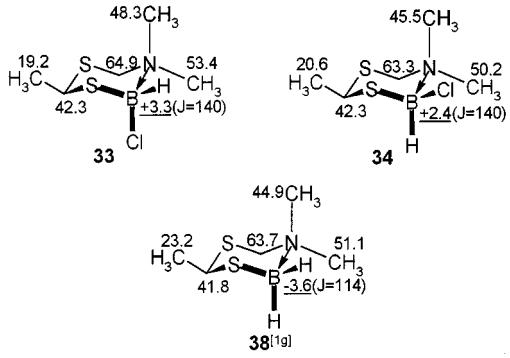

Figure 9. ^{13}C-NMR data of **33**, **34**, and **38** at 25°C

To see if a more bulky *N*-substituent will also function as an anchor for ring inversion, we treated the 1,3,5-dithiazacyclohexane **7** in equimolar amounts with the mixture of chloroboranes for 5 h at room temp. The reaction products were the cyclohexanes **35** (60%) and **36** (40%) (Figure 10). Both compounds were shown by their ^1H-NMR spectra to be nonfluxional, and their boron and nitrogen atoms are stereogenic centers. The equatorial position of the isopropyl groups was found by ^{13}C-NMR spectroscopy (CH at $\delta =$ 59.4 and 54.7 in **35** and **36**, respectively). An anomeric effect produced by the axial chlorine atom on the axial *N*-methyl group (which is deshielded) was observed for **33** and **35**.

Conclusions

The 1,3,5-heterocyclohexanes and borane or chloroborane form stable adducts which have frozen conformations as shown by the geminal coupling pattern of the CH_2 groups. The values of the coupling constants in the frozen free heterocycles vary according to the nature of the heteroatom (OCH_2O: 5.9; SCH_2S: ca. 13.3; NCH_2N: 8.0; SCH_2N: 10.5−13.5). The corresponding values in the adducts do not show systematic trends except for the triazacy-

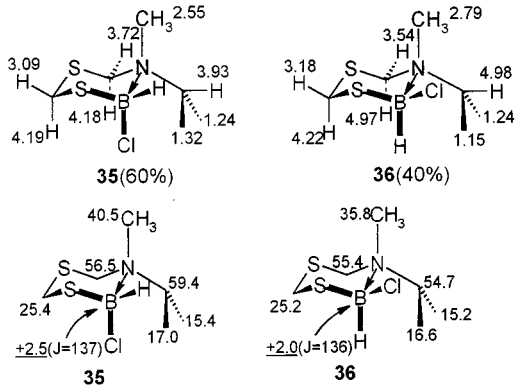

Figure 10. ^{13}C-, ^{11}B-, and ^{1}H-NMR chemical shifts of **35** and **36**

clohexanes and dithiazacyclohexanes where these values increase upon coordination [e.g., in **9** it increases from 8 Hz to 9.1 and 11.7 Hz, and in **6** (SCH_2N) it increases from 12.6 to 13.9−14.3 Hz, Table 3]. The frozen conformations are also deduced from the ^4J_w couplings between the equatorial protons, the values of which vary between 1.2 to 2.6 Hz. In **37** this coupling occurs between the equatorial C−H and B−H, with J = 2.0 Hz.

The configuration of the nitrogen atoms in borane and chloroborane adducts of triaza-, thiadiaza-, dithiaza-, and dioxazacyclohexanes is determined by the size of the *N*-substituents. The bulky isopropyl groups direct the borane units into the axial positions, while the methyl groups direct the boranes to the equatorial positions. ^1J(B−H) constants for axial BH_3 are smaller that the corresponding values for equatorial BH_3, which could be attributed to a weaker coordination of axial borane.

That the formation of adducts resulted in frozen ring conformations indicate that there is a hydride−proton interaction.[1i] This is supported by the result that BCl_3 did not give stable adducts. The use of excess borane and chloroboranes led to new boracyclohexanes. The chloroborata compounds are more stable because SBHCl is more acidic than the SBH_2 group.

Experimental Section

^{1}H-, ^{13}C-, and ^{11}B-NMR spectra were recorded with Jeol spectrometers at frequencies of 270 and 400 MHz for protons; δ values are referenced to TMS, and to $BF_3{\cdot}OEt_2$ for ^{11}B-NMR spectra. − $BH_3{\cdot}$THF was prepared as described.[3] The $BH_{3-n}Cl_n{\cdot}S(CH_3)_2$ mixture was purchased from Aldrich Co. Anhydrous solvents were prepared according to usual laboratory methods. − All reactions were carried out in inert atmosphere with oven-dried glassware. − Adducts **10**, **11, 13**, **17**−**21**, **24**−**29**, and boracyclohexanes **31**−**36** were analyzed only by variable-temperature, and two-dimensional ^{1}H-, ^{13}C-, ^{11}B-NMR spectroscopy. Our attempts to isolate them from the mixture of adducts were unsuccessful because they are unstable. Therefore, we could not perform elemental analyses. However, their structures were derived by comparison to fully characterized similar compounds.[1]

Preparation of Mono-*N*-BH_3 Adducts 10, 13, and 17. − General Procedure: To a solution of the corresponding heterocyclohexane (0.25 g) in 20 mL of dry THF, was added a solution of $BH_3{\cdot}$THF (1.2 mmol) at −78°C. The mixture was stirred for 5 min, and then the solvent was removed under vacuum leaving behind a mixture of adducts as white solids which were analyzed by NMR spectroscopy (**10**, 80%; **13**, 85% and **17**, 80%).

Preparation of 3,5-Bis(borane)-3,5-dimethyl-1,3,5-thiadiazacyclohexane (11): To a stirred solution of **1** (0.25 g, 1.9 mmol) in 20 mL of dry THF, was added a solution of $BH_3{\cdot}$THF (2.0 mmol) at 25°C. After 10 min, more $BH_3{\cdot}$THF (4.1 mmol) was added and the reaction mixture was kept for 30 min at 50°C. The solvent was then removed under vacuum to give the adduct as a white solid. Compound **11** (80%, 0.24 g) was crystallized from $CHCl_3$. m.p. 40°C. − $C_5H_{18}B_2N_2S$ (132.23): calcd. C 37.56, H 11.34, N 17.52; found C 37.51, H 11.46, N 17.36.

Preparation of *N*-$BHCl_2$ and *N*-BH_2Cl Adducts 18−21, 24−26, 28, and 29. − General Procedure: To a stirred solution of the corresponding heterocyclohexane (**1**, **5**, **6**, **8**, or **9**) (0.25 g) in 20 mL of dry $CHCl_3$, was added at −60°C a solution of 1 or 2 equiv. of $BH_{3-n}Cl_n\ SMe_2$. The reaction mixture was stirred for 5 min. The solvents were then removed under vacuum to afford the *N*-$BHCl_2$ and *N*-BH_2Cl adducts: **19** and **21** (8%); **24** (50%); **25** (95%); **26** (85%); **28** (40%), and **29** (95%). − Adduct **18** was crystallized from $CHCl_3$ and obtained in 80% yield (0.27 g). − $C_4H_{11}BClNS_2$ (183.53): calcd. C 26.18, H 6.04, Cl 34.94, N 7.63; found C 26.69,

Table 3. ^2J(H−H) geminal coupling constants for CH_2 and ^4J_w(H−H) for equatorial CH groups; for atomic numbering see Figure 1

Compd.	2-H	4-H	6-H	^4J_w(H−H)	Compd.	2-H	4-H	6-H	^4J_w(H−H)
1 (−90°C)	12.4	13.5	12.4		**20**		12.1	12.1	
2 (−95°C)	10.5	13.5	10.5		**21**		14.1	14.1	
3	13.5	12.1	13.5		**22**	14.0	14.3	14.3	
4 (−80°C)	5.9				**23**	13.9	13.9	13.9	2.0
5 (−60°C)	5.9	10.6	11.4		**24**		11.0	11.0	
6 (−80°C)	13.3	12.7	12.7	2.6	**25**	13.2	13.2	13.2	2.6
7 (−90°C)	13.2	13.2	13.2		**28**	9.8	10.8	10.8	
8 (27°C)		12.6	12.6		**30**[1f]	11.6	13.8	13.8	1.8
9 (−90°C)	8.0	8.0	8.0		**31** (25°C)		7.0		
10	12.6	13.3	12.6	2.5	**32eq** (−65°C)	13.2	12.8		
11	14.1	13.6	14.1		**32ax** (−65°C)	13.5	12.1		
12[1f]	9.1	11.0	11.0	1.7	**33**		12.8		
13		12.5	11.5		**34**		13.1		
15[1f]	7.8	11.0	11.0	1.7	**35**	13.1	13.2		
16[1f]	12.8	14.7	14.7	1.6	**36**	13.0	12.4		
17	5.9	10.6	10.6	1.2	**37** (−55°C)	12.9	12.5		2.0
18	14.0	14.0	14.0	2.1	**38** (25°C)		12.7		
19	14.0	14.0	14.0	2.1					

H 6.09, Cl 34.83, N 6.62. − Adduct **20** was obtained in 85% yield (0.28 g). − $C_5H_{13}BClNS_2{\cdot}CH_2Cl_2$ (282.49): calcd. C 25.51, H 5.35, N 4.96; found C 25.05, H 5.47, N 5.11.

Preparation of 3,5-Diisopropyl-1,3,5,6-thiadiazaboracyclohexane (31): To a solution of **1** (0.25 g, 1.33 mmol) in 20 mL of dry THF, was added a solution of $BH_3{\cdot}$THF (1.2 mmol) at −78°C; the resultant mixture was stirred for 5 min. It was then warmed to 25°C, stirred for 5 min, and the solvent was removed under vacuum. The adduct was obtained as a white solid (70%, 0.19 g). − ^{15}N NMR ($CDCl_3$, 25°C, 270 MHz): δ = −238.

Preparation of 6-Chloro-5-methyl-1,3,5,6-dithiazaboracyclohexanes 32−36. − General Procedure: To a solution of the corresponding heterocyclohexane (0.25 g) in 20 mL of dry CH_2Cl_2, was added 3 equiv. of a mixture of $BHCl_2$, BH_2Cl, and BH_3 in $S(CH_3)_2$ (90:8:2). The reaction mixture was stirred at 40°C for 8 h, and the solvents were subsequently removed by evaporation to afford the dithiazaboracyclohexane **32−36** which were characterized by NMR spectroscopy.

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