A Mechanistic Study of Hydroboration of 1-Octene with 1,3,2-Dithiaborolane and 1,3,2-Dithiaborinane. Part 1. Synthesis and Kinetic Studies

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ABSTRACT

Alkylthioboranes 1,3,2-dithiaborolane and 1,3,2-dithiaborinane have been synthesized from the reaction of $BH_3 \cdot SMe_2$ with 1,2-ethanedithiol and 1,3-propanedithiol, respectively. These heterocyclic boranes disproportionated significantly during their synthesis. The rate constants, and the enthalpies and entropies of the hydroboration reaction of 1-octene with 1,3,2-dithiaborolane and 1,3,2-dithiaborinane have been investigated, and we have shown that hydroboration with these boranes is slow and proceeds *via* an associative mechanism.

KEY WORDS

Hydroboration, disproportionation, boranes, transition states.

1. Introduction

For several years there has been intense research into the role of hydroborating species and several references by Brown *et al.*[1] testify to the usefulness of these reagents and their versatile application in organic synthesis.[1] Since the discovery of hydroboration by Brown *et al.*, an enormous volume of literature has been accumulated involving the use of this methodology.[2] Over the last three decades a range of different hydroborating agents has been developed, to furnish specific transformations desirable to organic chemists.[2]

However, in recent years, a class of sulphur-based borane compounds, also known as alkylthioboranes, has not received much scrutiny. In the early 1960s Mikhailov and co-workers showed that the reaction of mercaptans with diborane led to a mixture of mono- and bisalkylthioboranes in proportions that depended on the nature of the thiol.[3] The reaction of 1-propane-thiol with diborane afforded a mixture containing 73 % of mono(propylthio)borane and 27 % of bispropylthioborane and for 1-butanethiol, the product contained 60 % of the mono-substituted borane and 40 % of the bisalkylthioborane.[3] During their studies, trimers of monosubstituted boranes were observed.[4] In the mid 1960s Pasto *et al.* then demonstrated that reaction of mercaptans with diborane gave rise to a number of different products, depending on the experimental conditions under which the reactions were carried out.[5] Subsequent work by Egan *et al.* showed that heterocyclic derivatives of alkyl-thioboranes can be synthesized from diborane and 1,2-ethane-dithiol, and that the reaction is dependent upon the stoichio-metric ratios of the reactants (Scheme 1).[6]

Much attention on alkylthioborane chemistry has been based on hydrolysis, and complex formation with phosphines,[6] amines[7] and sulphides,[8] and only very little on hydroboration.[9,10] Thaisrivongs *et al.*[8] reported hydroboration of a range of alkenes with 1,3,2-dithiaborolane-triethyl amine complex, with the aid of $BF_3 \cdot OEt_2$. However, not much work has been done to date in

terms of kinetics and thermodynamics using ^{11}B NMR spectros-copy on alkylthioboranes with a single site available for hydro-boration. Our interest in the role of sulphur-containing boranes has stemmed from attempts to moderate the rate at which the hydroboration reaction takes place.

2. Results and Discussion

2.1. Synthesis of 1,3,2-Dithiaborolane

During studies in our laboratory on the synthesis and charac-terization of heterocyclic derivatives of alkylthioboranes, it was found, based on ^{11}B NMR spectroscopy, that 1,3,2-dithiaborolane (**4**) and the disproportionation product 2,2′-(ethylenedithio)bis-(1,3,2-dithiaborolane) (**5**) were produced from the reaction of $BH_3 \cdot SMe_2$ and 1,2-ethanedithiol (Scheme 2), as was proposed by Egan *et al.*[6] However, the yields of the target molecule (**4**) were significantly hampered by the formation of large amounts of the disproportionation product (**5**). Consequently, different approaches were attempted in the synthesis of this compound in order to optimize the yield of 1,3,2-dithiaborolane (**4**). These approaches included varying the stoichiometric ratio of $BH_3 \cdot SMe_2$ to 1,2-ethanediol, and varying the reaction time and temperature.

Firstly, $BH_3 \cdot SMe_2$ was allowed to react with 1.8 molar equiva-lents of 1,2-ethanedithiol at 0 °C. ^{11}B NMR analysis showed a small amount of unreacted $BH_3 \cdot SMe_2$ and a doublet at δ 61 ppm (Fig. 1), corresponding to 1,3,2-dithiaborolane (**4**) (Scheme 2). A low yield of *ca.* 48 % was obtained. A singlet at δ 64 ppm was attributed to 2,2′-(ethylenedithio)bis-(1,3,2-dithiaborolane) (**5**) (Scheme 2) with a 50 % yield (Table 1, Entry 1).

The same reaction was conducted at –80 °C and allowed to warm up to room temperature for 15 to 30 min, when it was found that the percentage yield of 1,3,2-dithiaborolane had increased to approximately 50 % of the total mixture (Table 1, Entry 2). Interestingly, an appreciable 71 % yield was achieved upon the use of excess $BH_3 \cdot SMe_2$ at low reaction temperature. The disproportionation product yield was also lower (Entry 3). However, the amount of unreacted $BH_3 \cdot SMe_2$ was slightly

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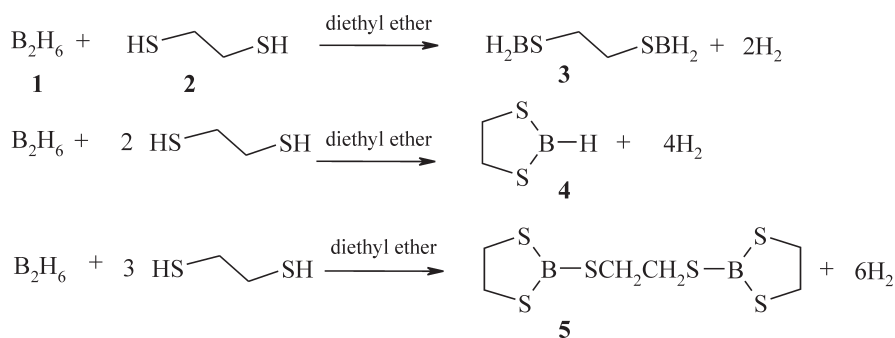
Scheme 1
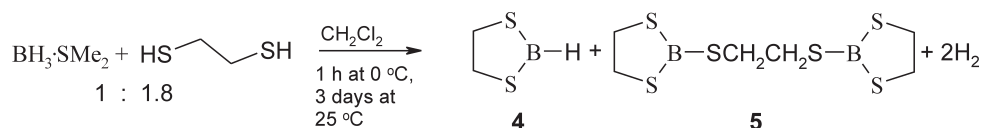
Scheme 2

higher. It was noteworthy that when equimolar amounts of reactants were used in conjunction with longer reaction times at low temperature, a good 65 % yield was obtained (Entry 7). Maintaining the reaction at low temperature for 14 days did not enhance the yield of 1,3,2-dithiaborolane (**4**) (entry 8), yielding results comparable with entry 1.

Conditions used for entries 1 and 8 were chosen to be the most suitable for the synthesis of 1,3,2-dithiaborolane, to be used in the hydroboration kinetics study, due to the low percentage of BH_3·SMe_2 obtained. This reduces the possible competition between BH_3 and 1,3,2-dithiaborolane towards the alkene on subsequent hydroboration.

2.2. Synthesis of 1,3,2-Dithiaborinane

A synthetic procedure proposed by Kim *et al.*[11] was used. In this method, borane-dimethyl sulphide complex reacted with an equimolar amount of 1,3-propanedithiol in CH_2Cl_2 at 0 °C and was allowed to stir for a week at 25 °C. Careful ^{11}B NMR spectroscopic analysis of the product mixture showed a doublet at δ 55.7 ppm (Fig. 2), attributed to the desired product, 1,3,2-dithiaborinane (**6**) (*ca.* 35 % yield). A singlet was also observed in the same mixture at δ 57.5 ppm. This was the major product of the reaction (*ca.* 55 % yield) and it was attributed to the disproportionation product 2,2′-(propylenedithio)-(1,3,2-dithia-

borinane) (**7**) (Scheme 3). A triplet at δ 16 ppm may be attributed to a mono-substituted borane fragment or the intermediate species in the disproportionation reaction (7 % yield). Some unreacted BH_3·SMe_2 (3 % yield) was also observed as a quartet. Alternative approaches were employed, as indicated in Table 1. Despite many attempts we were unable to obtain higher yields.

It was found that the alkylthioboranes (compounds **4** and **6**) are highly air- and moisture-sensitive and thermally unstable. Upon exposure to moisture these compounds are rapidly oxidized. This means that the B-H bond breaks and the B-OH bond forms. After oxidation, these reagents are not useful in subsequent hydroboration reactions. At elevated temperatures, these reagents were also shown to disproportionate to (**5**) and (**7**), respectively. Therefore it was of prime importance that these reagents be kept under inert atmosphere and low temperatures (*ca.* 5 °C).

2.3. Hydroboration of 1-Octene with 1,3,2-Dithiaborolane and 1,3,2-Dithiaborinane

During the hydroboration reaction conducted in our study, it was found that the olefin did not react at all with the disproportionation product. It was also interesting to note that no further disproportionation occurred during hydroboration. For both boranes, the desired octyl-boronate esters were characterized by a singlet resonating at δ 70.2 ppm (Fig. 3). No other
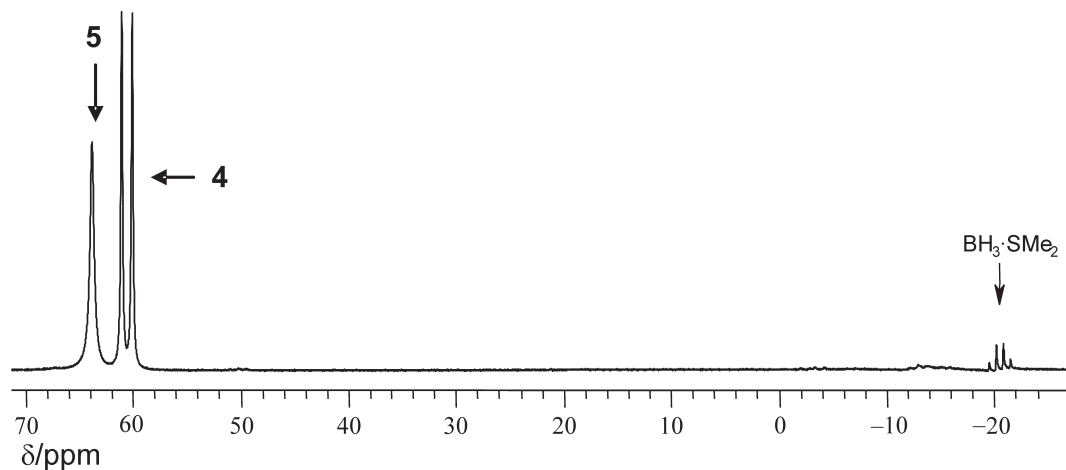

Figure 1 The 160 MHz ^{11}B NMR spectrum, showing a mixture of products obtained in the reaction of 1,2–ethanedithiol with borane-dimethyl sulphide complex.

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Table 1 Survey of optimum conditions for the synthesis of 1,3,2 dithiaborolane.

| No. | Time | Temperature/°C | Stoichiometric molar ratio | | Product yield/% | | |
			BH_3	1,2-ethanedithiol	**4**	**5**	BH_3
1	1 h	0	1	1.8	48	50	2
2	0.5 h	–80 to 25	1	1.8	50	46	4
3	1 h	–84	1.5	1	71	18	11
4	1 h	–84	1.25	1	64	29	16
5	1 h	–84	1.04	1	45	52	3
6	1.5 h	–84	1	1	55	41	4
2	0.5 h	–80 to 25	1	1.8	50	46	4
3	1 h	–84	1.5	1	71	18	11
4	1 h	–84	1.25	1	64	29	16
5	1 h	–84	1.04	1	45	52	3
6	1.5 h	–84	1	1	55	41	4
7	2 days	–84 to –55	1	1	65	17	18
8	14 days	–84 to –55	1	1	58	40	2

products were formed in this reaction, and no intermediates were observed, based on spectroscopic evidence.

2.3.1. *Concentration Dependence Study*

For both 1,3,2-dithiaborolane (**4**) and 1,3,2-dithiaborinane (**6**), a concentration dependence study was conducted in order to determine the second order rate constant (k_2) for hydroboration of 1-octene. These reactions were conducted under pseudo-first order conditions. In this study, the concentration of the hydroborating agent was kept constant while that of 1-octene was varied from 10× to 25× (the actual concentrations and the methods used are discussed in the experimental section). It was not possible to monitor beyond 25× because the reactions were too fast and went to completion within a few hundred seconds after mixing the reagents.

^{11}B NMR spectroscopy was used to monitor the progress of the hydroboration reaction (Fig. 3). During the course of the reaction, the concentration of the reactant (1,3,2-dithiaborolane) could be seen decreasing with simultaneous formation of the desired alkylborolane. This was more evident when viewed as arrayed spectra, as shown in Fig. 4.

Using the Microcal™ Origin™ 5.0[12] software and fitting the exponential decay for the first order, the plots shown in Fig. 5

were observed, where the experimental data are shown as squares and the smooth curve is the first order exponential decay. Taking the inverse of the first order exponential decay time (t_1) obtained from the software's exponential decay curve fitted in these plots gives the observed rate constant (k_{obs}) at each concentration.
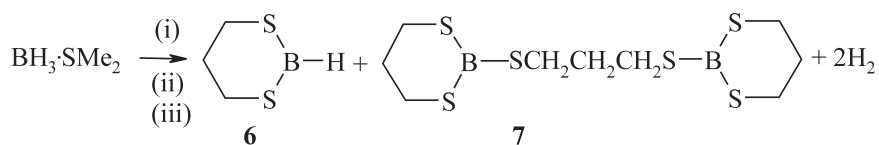
For each concentration, the observed rate constant was obtained. The results obtained from the concentration dependence studies for both (**4**) and (**6**) are summarized in Table 2. Upon comparison of the observed rate constants for both reagents at each concentration and fixed temperature (Table 2), it was shown that both reagents reacted with 1-octene at almost the same rate, as would be expected. Calculation of the second order rate constants for both reactions, from the plots of observed rate constants against concentration, produced linear plots (Fig. 6) with slopes corresponding to the second order rate constants (k_2). For 1,3,2-dithiaborolane this constant was found to be $1.548 \pm 0.009 \times 10^{-4}$ L mol^{-1} s^{-1} and for 1,3,2-dithiaborinane it was found to be $1.652 \pm 0.013 \times 10^{-4}$ L mol^{-1} s^{-1}.

2.3.2. *Temperature Dependence Study*

It was of great importance to conduct a temperature dependence study in order to obtain the activation parameters for
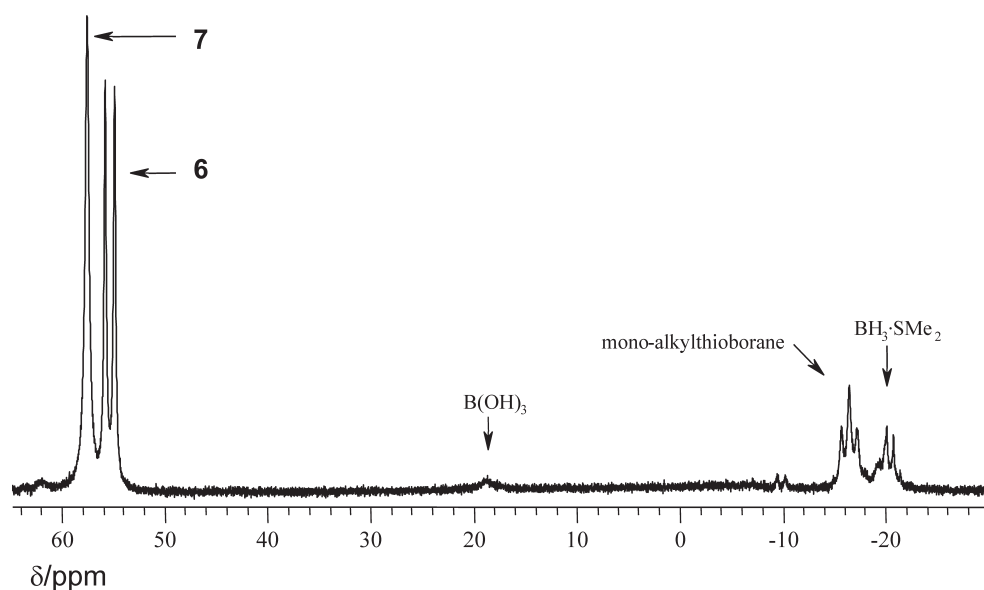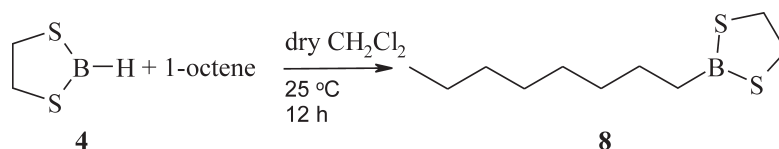

Figure 2 The 160 MHz ^{11}B NMR spectrum showing the fragments obtained in the reaction of propanedithiol with borane-dimethyl sulphide complex.

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Scheme 3

(i) CH_2Cl_2
(ii) 1,3-propanedithiol, 0 °C, 1 h
(iii) 3 days at 25 °C

Scheme 4

both hydroborating agents with the intention to justify the mechanism of hydroboration from the values of the entropy of activation $\Delta S^{\neq}$ and the enthalpy of activation $\Delta H^{\neq}$.[14] From the observed rate constants, Eyring plots were computed (Figs. 7A and B).

The temperature dependence study showed that the ring size of the reagent had no effect on the hydroborating activity of the reagent. $\Delta H^{\neq}$ values for both reagents are small and positive, which is indicative of slow, endothermic reactions. $\Delta S^{\neq}$ values obtained for both reagents are large and negative which indicate that hydroboration of 1-octene with 1,3,2-dithiaborolane (**4**) or 1,3,2-dithiaborinane (**6**) proceeds *via* an associative mechanism, in which the hydroborating agent and the olefin unite to form the transition state.

These boranes are indeed slow hydroborating agents. This was evident when compared with $BH_3 \cdot SMe_2$. They were found to be about 90-fold slower and about six-fold slower than with $BH_3 \cdot SMe_2$ and with the dialkyl substituted borane dicyclohexylborane, respectively (Table 3). This was due to the electron density donated by the sulphur atoms to the boron atom, which makes the boron atom less electropositive, thus slowing the interaction of the olefinic double bond with the B-H bond.[17]

3. Experimental

3.1. General

All glassware was thoroughly dried overnight in an oven at *ca.* 150 °C. The glassware was further flame-dried by heating with a hot air gun under reduced pressure and allowed to cool under a stream of dry nitrogen, which was passed through a mixture of silica gel and 0.4 nm molecular sieves prior to use. Glass syringes, cannulae and needles were oven-dried and stored in a desiccator (charged with a mixture of silica gel and 0.4 nm molecular sieves) prior to use. Disposable syringes and needles were stored in the desiccator before use, and they were discarded after single use. On assembling the glassware, all joints were wrapped with Teflon® tape, and were subsequently sealed with Parafilm 'M'® to ensure a closed system.

All ^{11}B NMR spectra were recorded on a Varian Unity-Inova 500 MHz NMR spectrometer (Varian, Palo Alto, CA, USA), and were referenced to $BF_3 \cdot OEt_2$ as an external standard (δ 0.0 ppm) contained within a sealed capillary insert. [11]B spectroscopy was utilized in order to identify the compounds as well as to monitor the progress of the reactions. Quartz NMR tubes (5 cm) were used for the ^{11}B NMR spectroscopic experiments and were all oven-dried and flushed with dry nitrogen and sealed with a
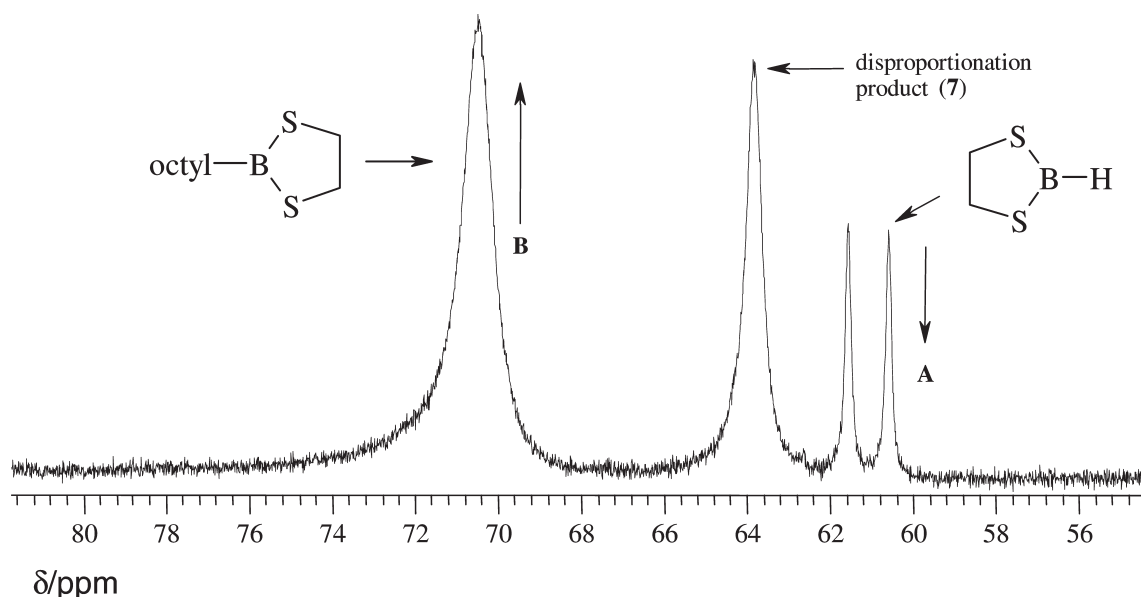

Figure 3 ^{11}B NMR spectrum showing the progress of a typical hydroboration of 1-octene with 1,3,2-dithiaborolane.

SW36_2 in CH2C12
Pulse Sequence: s2pul

SW36_2 in CH2C12
Pulse Sequence: s2pul
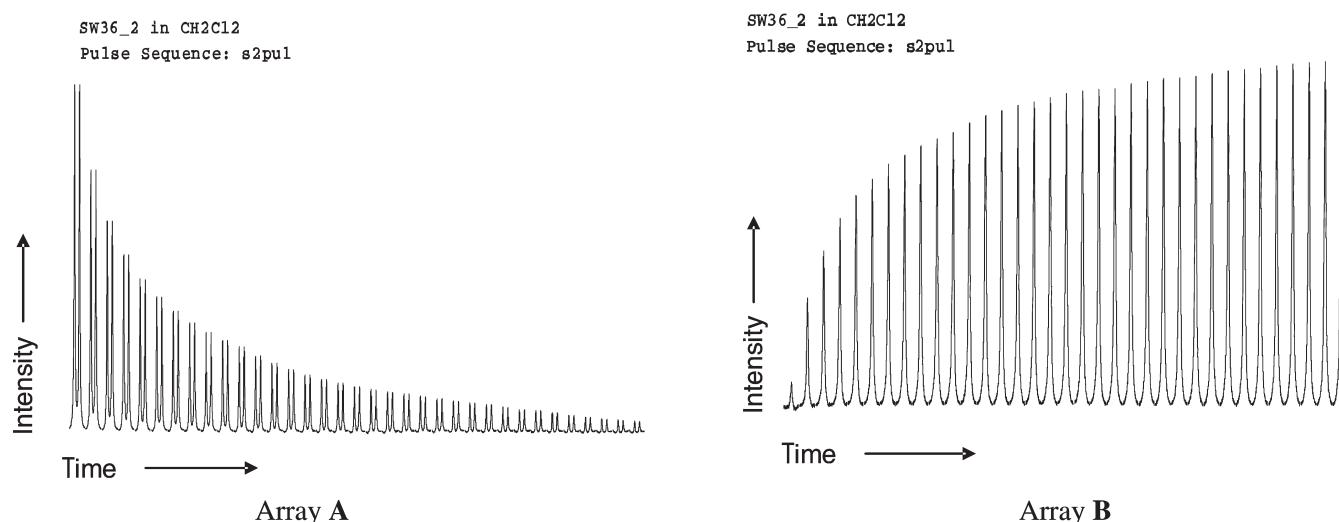
Array **A**

Array **B**

Figure 4 The arrayed reagent depletion (array A) and product formation (array B).[13]

rubber septum prior to injection of the sample or reagents.

All solvents were purified by distillation and dried prior to use.[18] CH_2Cl_2 was distilled over P_2O_5 under dry nitrogen. 1-Octene was distilled over sodium wire in the presence of benzophenone indicator. The solvents were distilled and transferred *via* cannulae to a flame-dried, nitrogen-flushed flask containing 0.4 nm molecular sieves (activated in the furnace at 600 °C and cooled under dry nitrogen) prior to use. 1,2-Ethanedithiol and 1,3-propanedithiol were obtained from Merck-Schuchardt (Hohenbrunn, Germany). The $BH_3·SMe_2$ complex in CH_2Cl_2 was obtained from Sigma-Aldrich Co. (Johannesburg, South Africa).

3.2. Preparation of 1,3,2-Dithiaborolane

Following a modification to the procedure described by Egan *et al.*,[6] borane-dimethyl sulphide complex in CH_2Cl_2 (5.0 mL, 5.0 mmol) was transferred into a flame-dried, nitrogen-purged 25 mL two-necked round-bottomed flask. The contents of the flask were subsequently cooled to –84 °C in a liquid nitrogen/ethyl acetate slurry, following which a solution of 1,2-ethanedithiol (471 mg, 5.0 mmol) in CH_2Cl_2 (3 mL) was added dropwise to the stirred flask. The reaction mixture was subsequently stirred for 30 min at –84 °C and allowed to warm up to -60 °C. The flask was then transferred to the cryostat (chiller), and allowed to stir for 14 days at –55 °C under a dry atmosphere of nitrogen to afford a clear liquid comprising a mixture of 1,3,2-dithiaborolane (58 %) ^{11}B NMR (160 MHz, $BF_3·OEt_2$): δ = 60.5 ppm (d, *J* = 156.4 Hz, 1H, B*H*); 2,2′-(ethylenedithio)bis-(1,3,2-dithiaborolane) (40 %) ^{11}B NMR (160 MHz, $BF_3·OEt_2$): δ = 64.0 ppm (s); and

10 x 1-octene + 1,3,2 dithiaborolane

Data: Data2_B
Model: ExpDecay1
Chi^2 = 0.00002
y0   0.02589 ± 0.00137
x0   0 ± 0
A1   0.12496 ± 0.00236
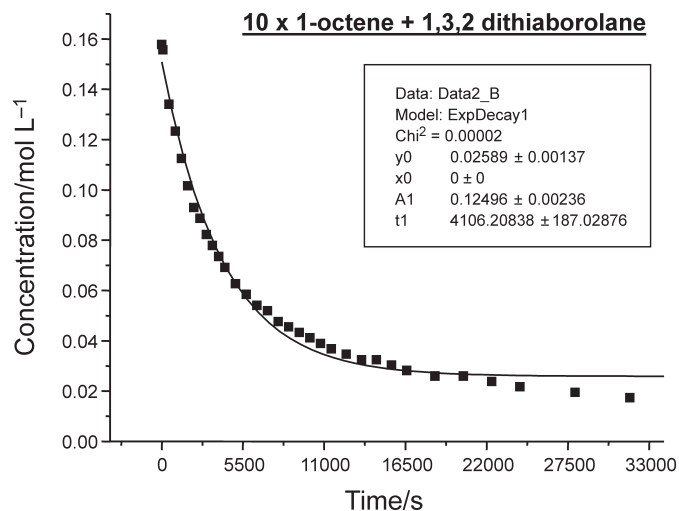t1   4106.20838 ± 187.02876

Figure 5 A typical concentration *vs.* time plot, showing fitted experimental data for the hydroboration of 1-octene with 1,3,2-dithiaborolane.
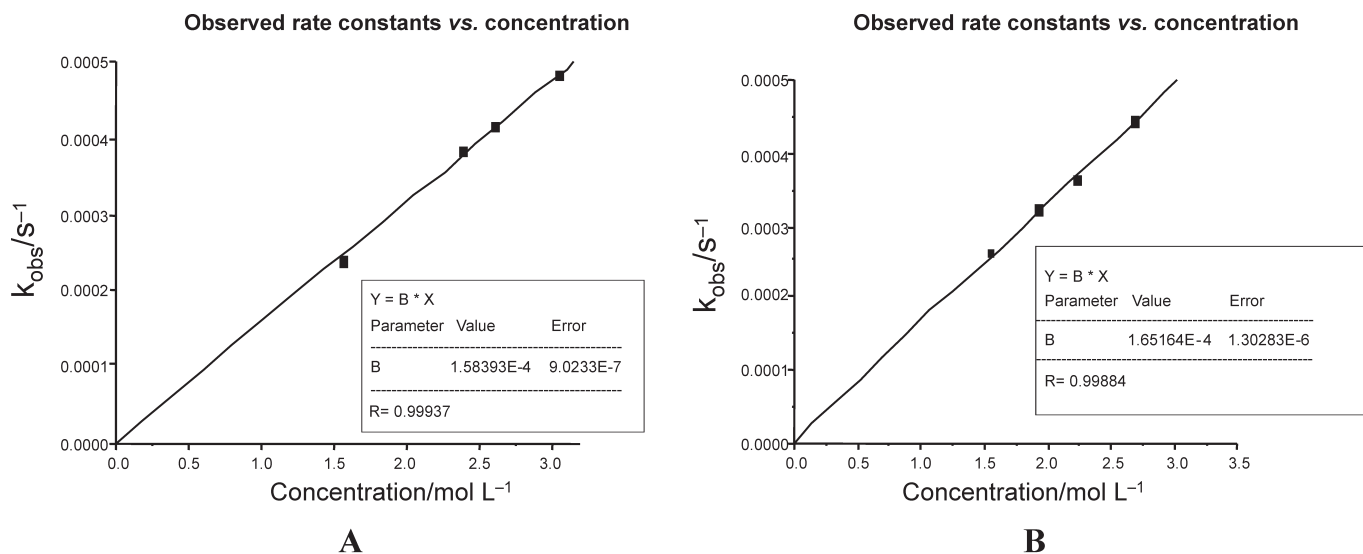
unreacted $BH_3·SMe_2$ (2 %) ^{11}B NMR (160 MHz, $BF_3·OEt_2$): δ = –20.5 ppm (q, *J* = 105.5 Hz, 3H, B*H_3*).
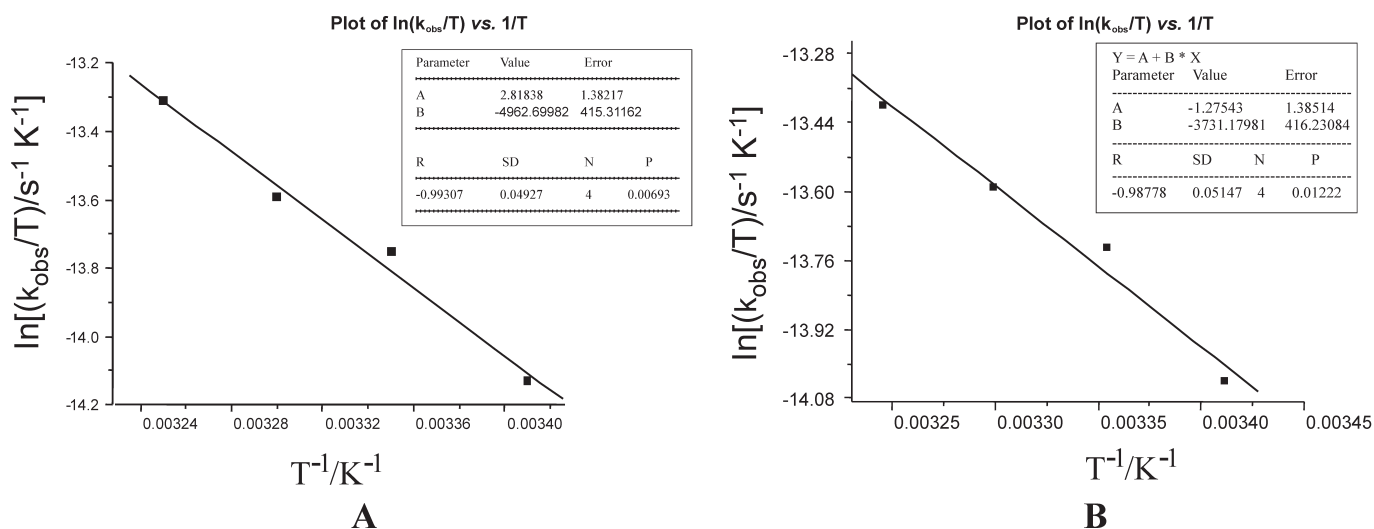
3.3 Preparation of 1,3,2-Dithiaborinane

Borane-dimethyl sulphide complex in CH_2Cl_2 (1.0 mol L^{-1}, 5.0 mL, 5.0 mmol) was stirred at 0 °C under a nitrogen atmosphere. 1,3-Propanedithiol (0.50 mL, 5.0 mmol) was added dropwise over a period of 10 min. The resulting mixture was allowed to stir at room temperature for 7 days to afford a cloudy

Table 2 The observed rate constants for 4 and 6 at each concentration.

Temperature/°C	Concentration factor	4 k_{obs}/10^{-4} s^{-1}	6 k_{obs}/10^{-4} s^{-1}
25	10×	2.436	2.645
25	15×	3.855	3.235
25	20×	4.162	3.650
25	25×	4.842	4.435

Observed rate constants *vs.* concentration

Observed rate constants *vs.* concentration

A

B

Figure 6 Plots of the observed rate constants *vs.* concentrations. **A** was obtained from the reaction of 1,3,2-dithiaborolane, and **B** from 1,3,2-dithiaborinane with 1-octene. Original acquisition data are available as Supplementary Material.

Plot of ln(k_{obs}/T) *vs.* 1/T

Plot of ln(k_{obs}/T) *vs.* 1/T

A

B

Figure 7 Eyring plots for hydroboration of 1-octene with 1,3,2-dithiaborolane (**A**) and with 1,3,2-dithiaborinane (**B**). Original acquisition data are available as Supplementary Material.
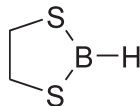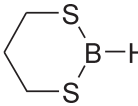
liquid of 1,3,2-dithiaborinane[19] (35 %) ^{11}B NMR (160 MHz, BF$_3$·OEt$_2$): δ = 52.2 ppm (d, J = 145.8 Hz, 1H, BH); and 2,2′-(pro-pylenedithio)bis-(1,3,2-dithiaborinane) (55 %) ^{11}B NMR (160 MHz, BF$_3$·OEt$_2$): δ = 56.6 ppm (s); BH$_3$·SMe$_2$ (3 %) ^{11}B NMR (160 MHz, BF$_3$·OEt$_2$): δ = –20.5 ppm (q, J = 105.5 Hz, 3H, BH_3); and HSCH$_2$CH$_2$SBH$_2$ (7 %) ^{11}B NMR (160 MHz, BF$_3$·OEt$_2$): δ = –16.9 ppm (t, J = 122.3 Hz, 2H, BH_2).

3.4. Kinetic Studies

In order to determine the rate constants for hydroboration of 1-octene with 1,3,2-dithiaborolane or with 1,3,2-dithiaborinane, the following standard procedure for conducting a concentration dependence study was employed.

To an oven-dried, nitrogen-purged quartz NMR tube 1,3,2-dithiaborolane (0.40 mL, 0.16 mol L^{-1}) was added *via* a

Table 3 Calculated values of the second order rate constant, and enthalpy and entropy of activation for both heterocyclic hydroborating agents.[15]

			CyBH[16] (0 °C)	BH$_3$·SMe$_2$[16] (0 °C)
k_2/10^{-4} L mol^{-1} s^{-1}	1.548 ± 0.009	1.652 ± 0.013	9.7 ± 1.2	140 ± 10
ΔH$^{\neq}$/kJ mol^{-1}	41.30 ± 3.45	31.02 ± 3.46		
ΔS$^{\neq}$/J K^{-1} mol^{-1}	–174.45 ± 11.49	174.49 ± 11.52		

syringe. The sample was analyzed to verify that no degradation of the compound had taken place prior to addition of the other reagents. 1-Octene in CH_2Cl_2 (0.40 mL, $10\times$ [1,3,2-dithiaborolane] = 1.6 mol L^{-1}) (a 1.6 mol L^{-1} solution of 1-octene was prepared in a 25 mL volumetric flask, and dichloromethane was used as a solvent for dilutions) was then added to the NMR tube. The tube was then agitated prior to analysis. The time delay taken from injection of the 1-octene to the first scan in the spectrometer was measured by a stopwatch (time delay ranged between 35 and 40 s), and the time delay was used accurately to measure the time intervals between data sets in the NMR spectrometer. The spectrometer program was set to scan the contents of the tube initially very regularly and with time at slower intervals. Initially scans were recorded after every 5 min for the first 50 min, then after every 10 min for a subsequent 100 min, then after every 15 min for 75 min, then every 30 min for 150 min and finally every 1 h for a further 5 h. One hundred and twenty transients were used for each acquisition set, which in turn represented a single data point.

The concentrations of 1-octene were increased from 10-fold to 25-fold that of the hydroborating agent and the above method was repeated for each concentration. The data obtained were fitted using Microcal™ Origin™ 5.0[12] software. The raw data for each concentration dependence experiment are included as Supplementary Material.

In order to determine the thermodynamic parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$ for the hydroboration of 1-octene with 1,3,2-dithiaborolane or with 1,3,2-dithiaborinane, the following typical procedure for the temperature dependence study was employed.

1,3,2-Dithiaborolane (0.40 mL, 0.16 mol L^{-1}) in CH_2Cl_2 was injected into an oven-dried, nitrogen-purged quartz NMR tube, 1-octene (0.40 mL, $15\times$ [1,3,2-dithiaborolane] = 2.4 mol L^{-1}) (a 2.4 mol L^{-1} solution of 1-octene was prepared in a 25 mL volumetric flask, and dichloromethane was used as a solvent for dilutions) was then added to this solution. The resulting mixture was shaken vigorously, vented and placed in the NMR probe for analysis. Time delay measurements and acquisition time intervals were done in the same manner as discussed above. Hydroboration experiments were conducted at 20 to 35 °C increasing in steps of 5 °C. For each experiment, the concentrations of the hydroborating agent and the olefin were kept constant. The data acquired were fitted with Microcal™ Origin™ 5.0[12] software to yield the activation parameters for each compound towards 1-octene. The raw data for each temperature dependence experiment are included as Supplementary Material.

4. Conclusions

From the above observations, it can be concluded that the reaction of 1,2-ethanedithiol or 1,3-propanedithiol with $BH_3 \cdot SMe_2$ leads to the formation of both the target borolanes, as well as significant quantities of the disproportionation products.

The disubstituted heterocyclic compounds studied in this project were found to exhibit very slow hydroboration properties when compared with $BH_3 \cdot SMe_2$ or dialkylboranes. In order fully to understand the complexity of the chemistry of these compounds we conducted a follow-up computational study to rationalize our observations.[17]

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