DOI: 10.1002/ejoc.200600564

Rhodium-Catalyzed Hydroboration Reactions with Sulfur and Nitrogen Analogues of Catecholborane

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Keywords: Rhodium / Homogeneous catalysis / Hydroboration / Boranes / Olefins

Rhodium-catalyzed hydroboration of 1-octene and *trans*-4-octene with sulfur- and nitrogen analogues of catecholborane are demonstrated with the use of in situ ^{11}B NMR spectroscopy. Our study shows that the sulfur- and nitrogen analogues are significantly less prone to disproportionation than catechol, which results in enhanced yields of the desired compounds.

Introduction

Transition-metal catalyzed hydroboration reactions have been studied extensively by a number of research groups because of their potential applications within organic synthesis.[1–4] In the mid 1970's, Kono et al.[5] showed that the B–H bond of catecholborane (**1**) oxidatively adds directly to the metal centre of the $RhCl(PPh_3)_3$ catalyst. $RhCl(PPh_3)_3$ was previously reported to only catalyze the hydrogenation[6] and the hydrosilylation[7] of alkenes; therefore, Kono's work opened up the possibility of rhodium-catalyzed hydroboration reactions. Kono's work was exploited by Männig and Nöth[8] who were able to demonstrate that $RhCl(PPh_3)_3$ could catalyze the hydroboration of olefins. It has been subsequently shown in the literature that the reactions of multifunctional substrates can be chemoselectively influenced by the catalyst.[1,8] That is, without a catalyst, catecholborane adds to the carbonyl group preferentially, whilst in the presence of the rhodium catalyst, hydroboration of the alkene is the major product (Scheme 1).[8]

Männig and Nöth proposed a mechanism for the rhodium-catalyzed hydroboration of olefins that involves the oxidative addition of a B–H bond to the coordinatively unsaturated metal centre. This is followed by alkene insertion, then hydride migration to the coordinated alkene and subsequent reductive elimination to afford the B–C bond. This mechanism is analogous to the proposed homogeneous hydrogenation model.[9]

Further mechanistic investigations by Evans et al.[10–12] were performed with the use of deuteriocatecholborane and they revealed that there is a significant amount of deuterium at C1 (from the reaction between 1-decene and-deuteriocatecholborane in the presence of Wilkinson's catalyst). This study showed that exclusive generation of the terminal alkylborane is, in fact, due to the reversibility of deuteride migration, coupled with a high preference for the reductive elimination of the boron-primary alkyl moiety rather than the boron-secondary alkyl moiety from the metal centre.[10,11] The mechanism of rhodium(I)-catalyzed olefin hydroboration has been further elucidated by ab intio molecular modelling studies.[13]

Recently, Srebnik et al.[14] successfully used Rh^I to catalyze the hydroboration of alkenes with pinacolborane (**2**) which was previously reported to be unsuccessful.[15] Terminal octylpinacolboronate was obtained in high yields in the $RhCl(PPH_3)_3$-catalyzed hydroboration of *trans*-4-octene.[14] It has also been reported that the regioselectivity is also reversed in the rhodium-catalyzed hydroboration of allylbenzene.[16] A unique reversal in the regioselectivity has also been reported in the hydroboration of 1-octene catalyzed by rhodium trichloride.[17]

Since the discovery of the transition-metal-catalyzed hydroboration reaction, a number of research groups have used catecholborane (**1**) [1,3,2-benzodioxaborolane abbreviated as HBCat where Cat = $1,2\text{-}O_2C_6H_4$] and recently pinacolborane (**2**) [4,4,6,6-tetramethyl-1,3,2-dioxaborolane abbreviated as HBPin where Pin = $1,2\text{-}O_2C_6H_{12}$] in rhodium-catalyzed transformations with much attention focused on the mechanistic, regio- and stereoselectivity implications of the reaction.[1–4,10–13] More recently, attention has been focused on the enhancement of Rh-type catalysts with an emphasis on different phosphane ligands.[18–20] However, Burgess and coworkers[21] reported evidence of the disproportionation (also known as degradation) of CatBH in the catalyzed hydroboration of alkenes with $RhCl(PPh_3)_3$. In our previous studies of the Rh-promoted hydroboration of alkenes with HBPin, a varying degree of disproportionation was noted.[22a] We were intrigued by the possibility that new heterosubstituted hydroborating agents with increased sta-

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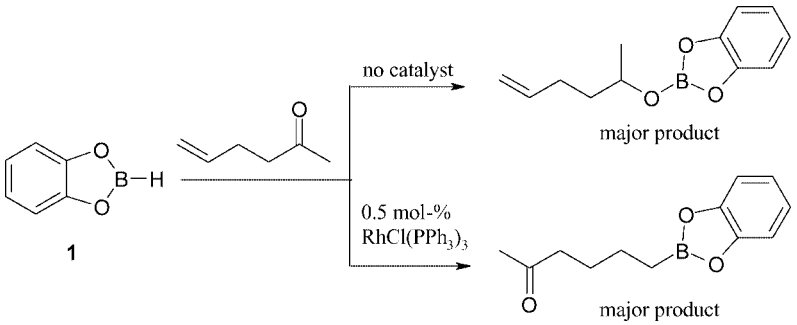


Scheme 1. Uncatalyzed and catalyzed hydroboration of 5-hexen-2-one with catecholborane – altered chemoselectivity.

bility (that is, less disproportionation) over that of HBCat or HBPin could be developed. Although Rh-catalyzed transformations are well-precedented, very few examples of the hydroboration of sulfur- or nitrogen analogues have been reported, which also includes the catalyzed hydroboration with (4*S*,5*R*)-ephedrineborane and (4*S*,5*R*)-pseudophedrineborane.[22b] In this paper we present the first $RhCl(PPh_3)_3$-catalyzed hydroboration of olefins with 1,3,2-benzodithiaborolane (**3**) (HBThia where Thia = 1,2-$S_2C_6H_4$) (Figure 1) and 1,3,2-benzodiazaborolane (**4**) (HBAza where Aza = 1,2-$N_2C_6H_6$), which are new potential alternatives to HBCat and HBPin that possess enhanced stability towards disproportionation.

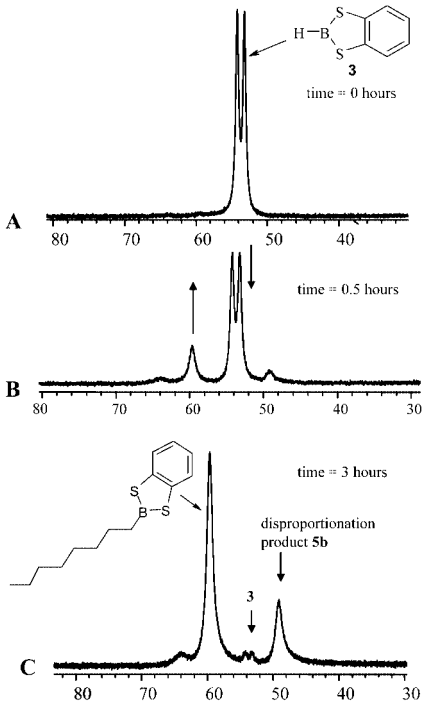


Figure 1. (A).^{11}B NMR spectrum of freshly synthesized 1,3,2-benzodithiaborolane in CH_2Cl_2. (B) ^{11}B NMR spectrum that shows the formation of 2-octyl-1,3,2-benzodithiaboronate ester after 0.5 h and (C) shows the product formation (65%, 21% of **5b** and 4% of **3**) after 3 h.

Results and Discussion

During studies in our laboratory on hydroboration reactions and the synthesis of potentially more stable monofunctional hydroborating agents, the following observations were noted.

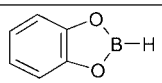
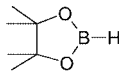
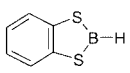
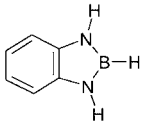
1. Uncatalyzed Hydroboration of Olefins

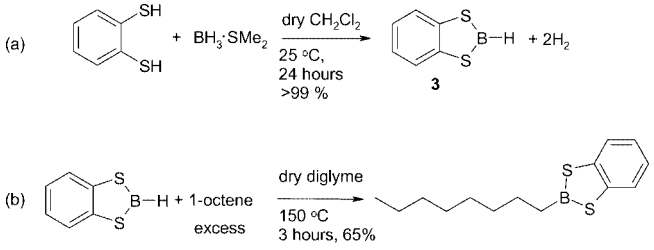
Uncatalyzed hydroboration reactions were conducted with a range of heterosubstituted borolanes (as indicated in Table 1) in order to evaluate their reactivities towards olefins prior to the use of Wilkinson's catalyst. HBCat effected the hydroboration of a terminal olefin when heated at 100 °C for 2 h (Table 1) to afford a yield of 37% of the desired product, which is in contrast to the yield reported by Brown et al.[23] The low yield is attributed to significant formation of tris(catecholato)diboron (**5a**), $(Cat)_3B_2$ (ca. 40%), which is produced when the reaction is heated.[24] Interestingly, the sulfur analogue, HBThia (freshly prepared in situ from the reaction of $BH_3{\cdot}SMe_2$ with 1,2-benzenedithiol, Scheme 2a), effected the hydroboration of 1-octene and *trans*-4-octene when heated at 150 °C for 3 h to afford terminal octyl-1,3,2-benzodithiaboronate ester in 65% yield (Scheme 2b) [ca. 21% of $(Thia)_3B_2$ (**5b**)] and 15% of internal octyl-1,3,2-benzodithiaboronate ester, which were both characterized by a singlet at 59.6 ppm (identical chemical shift for both products) in the ^{11}B NMR spectra.

The reactions with nitrogen analogue 1,3,2-benzodiazaborolane (**4**) did not proceed at all for both 1-octene and 4-octene even after 10 days while heated at reflux. Motry et al.[24] noted a similar lack of reactivity in borylation-type chemistry.

Our observations revealed a reactivity trend of these reagents towards alkenes: O > S > N (Figure 2). The above trend, though not unexpected, may be attributed to the fact that heteroatoms such as nitrogen and sulfur are able to back-donate electron density from the heteroatom lone pair of electrons to the vacant p_Z-orbital of the boron atom. Thus, the Lewis acidity of the boron reagent is lowered.[25] Because of this fact, attention was then focused on the utilization of a rhodium catalyst.

Table 1. Rhodium-catalyzed hydroboration of 1-octene and *trans*-4-octene with yields for the formation of octylboronate ester (Prod.) and the disproportionation products (Disp.) (Excluding unreacted starting material, boric acid and $BH_3{\cdot}PPh_3$).

Borane	Octene	Uncatalyzed		$RhCl(PPh_3)_3$	
		Prod. [%]	Disp. [%]	Prod. [%]	Disp. [%]
	1	37	40	67	31
	4	4	80	33	44
1					
	1	0	0	79	19
	4	0	0	0	50–75
2					
	1	65	21	85	<2
	4	15	22	80	<2
3					
	1	0	0	70	0
	4	0	0	0	0
4					



Scheme 2. (a) Synthesis of 1,3,2-benzodithiaborolane (**3**). (b) Uncatalyzed hydroboration of 1-octene with **3**. Yields are based on ^{11}B NMR spectroscopy.

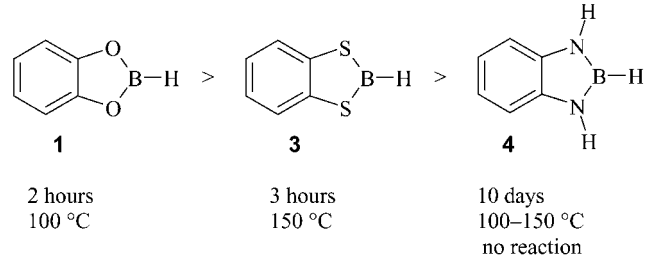


Figure 2. Observed reactivity trend from hydroboration of **1** and 4-octene.

2. Rhodium-Catalyzed Hydroboration of Olefins

The rhodium catalysis study (Table 1) showed that the reaction of 1-octene with HBCat in the presence of $RhCl(PPh_3)_3$ afforded the desired octylboronate ester in 67% yield after a reaction time of 2 h at ambient temperature, and also that 33% of HBCat was converted into the disproportionation products [tris(catecholato)diboron, H_3B/PPh_3 and other minor fragments including boric acid (Figure 3)].

The identities of the disproportionation products were in good agreement with those reported previously by Burgess et al.[21] The formation of the disproportionation products was accounted for mechanistically by Westcott et al.[26a] (Scheme 3), who also reported the crystal structure of tris-(catecholato)diboron.[26a] In our reactions, the yields of the hydroboration reactions were dependent on the degree of disproportionation of HBC, and it was found to be more pronounced in the catalyzed hydroboration of internal olefins, which led to significantly reduced yields. To our surprise, HBPin, despite the fact that it is more stable than HBCat, afforded the octylpinacolboronate ester in 79% yield and a combination of disproportionation products in a 19% yield, which was contrary to that found by Srebnik et al.[14,27] who reported no disproportionation of HBPin. Of the disproportionation products formed, a singlet resonating at δ = 22.1 ppm in the ^{11}B NMR spectrum can be attributed to tris(pinacolato)diboron (15%) [also known as 2,2′-(2,3-dimethyl-2,3-butanediyldioxy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[26b]]. We observed no reaction with *trans*-4-octene, again, unlike the observations by Srebnik et al.[14,27] These observations are in agreement with previous reports by Yamamoto et al.[28] and Tucker et al.[15]

We attributed the discrepancy in the experimental results to the fact that the B–H bond of the bulky pinacolborane has to be inserted into the metal centre oxidatively, followed by alkene insertion. Therefore, if the alkene is internal and hindered, insertion to the metal centre would be difficult; as a result, no reaction would occur. We have recently reported that internal olefins are able to effectively undergo hydroboration and isomerization with pinacolborane to afford terminal boronate esters with the use of $RhCl(PPh_3)_3$

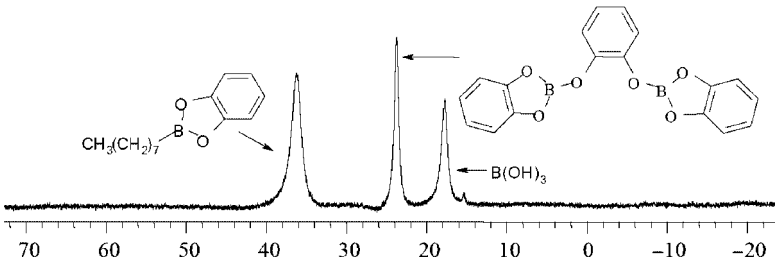
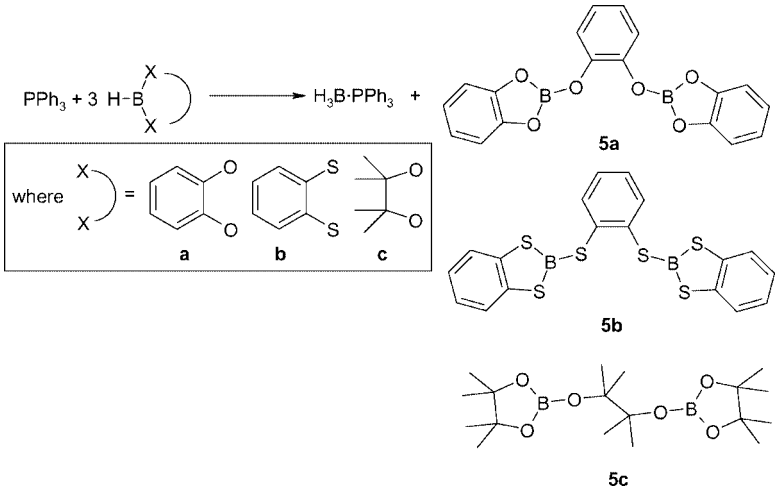


Figure 3. Typical ^{11}B NMR spectrum of the product mixture of the catalyzed hydroboration of 1-octene with CatBH, which shows a varying distribution of products formed during catalysis.



Scheme 3. Formation of disproportionation products **5a**,[26a] **5b** and **5c**[26b] catalyzed by PPh_3.

as a catalyst in conjunction with microwave irradiation or with the use of $[O_2RhCl(PPh_3)_2]_2$.[22a]

To our delight, the reaction of 1,3,2-benzodithiaborolane (HBThia) with 1-octene and *trans*-4-octene catalyzed by $RhCl(PPh_3)_3$, under the same reaction conditions, resulted in an immediate change in colour from brick-red to dark-green when all off the reagents were mixed. This indicates that HBThia has spontaneously added the B–H bond into the metal centre. After a 24 hour period, ^{11}B NMR spectroscopic analysis of the product mixture revealed an intense singlet at δ = 59.6 ppm, which can be attributed to the terminal (ca. 86% yield, Figure 4) and internal (ca. 60–80%, Figure 5) 2-octyl-1,3,2-benzodithiaboronate esters, respectively. This was further corroborated by oxidative workup of the product mixtures, which were characterized by ^1H- and ^{13}C NMR and GC–MS spectroscopic analysis and confirm the formation of 1-octanol and 4-octanol. 1,3,2-Benzodithiaborolane (**3**) proved to be a potentially superior hydroborating agent in Rh-catalyzed hydroboration when compared to its oxygen analogue because of the high yield of the obtained octylboronate esters and the significantly low quantity of the disproportionation products (ca. 1.8%).

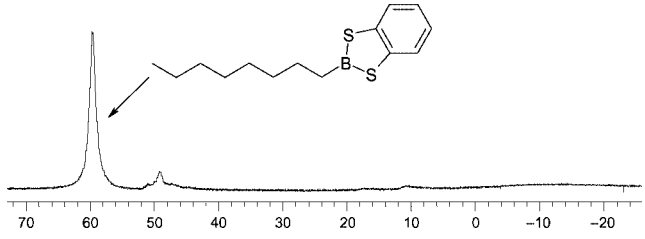


Figure 4. ^{11}B NMR spectrum (measured in ppm) obtained from the catalyzed hydroboration of 1-octene with 1,3,2-benzodithiaborolane.

Wilkinson's catalyst has demonstrated its usefulness in the promotion of the hydroboration of 1-octene with 1,3,2-benzodiazaborolane at 25 °C, which has been shown from the early studies to be unreactive.[24] ^{11}B NMR spectroscopy displayed a new singlet at δ = 31.6 ppm (Figure 6) attributed to the exclusive formation of the terminal octyl-1,3,2-benzodiazaboronate ester (ca. 70% yield) formed after a reaction time of 24 hours as characterized by GC–MS spectroscopy. No disproportionation of 1,3,2-benzodiazaborolane was observed.

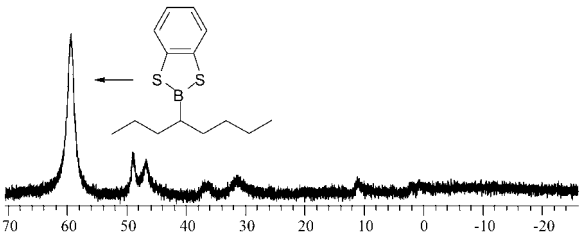


Figure 5. ^{11}B NMR spectrum (measured in ppm) obtained from the catalyzed hydroboration of *trans*-4-octene with 1,3,2-benzodithiaborolane.

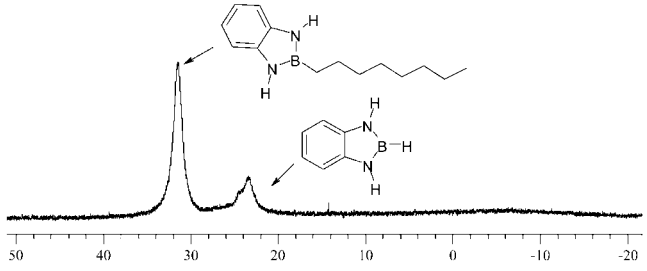


Figure 6. ^{11}B NMR spectrum (measured in ppm) obtained from the catalyzed hydroboration of 1-octene with 1,3,2-benzodiazaborolane after 24 h at 25 °C.

No product was obtained from the catalyzed hydroboration of *trans*-4-octene with HBAza under the same reaction conditions. No hydroboration was observed even after the reaction mixture was heated at 40 °C for 30 h in the presence of $RhCl(PPh_3)_3$. This was attributed to the sterically demanding structures of both *trans*-4-octene and HBAza. As a result, it would be difficult for olefin insertion to the metal centre to be achieved. Subsequent addition of 1-octene to the reaction mixture showed the formation of the terminal octylboronate ester, which indicates that the rhodium–boryl complex was already preformed. However, interestingly, no disproportionation of HBAza was observed from the analysis of the ^{11}B NMR spectrum even when heated at reflux in CH_2Cl_2 for 40 h. This is indicative of the increased stability of 1,3,2-benzodiazaborolane (**4**) over that of catecholborane (**1**) against catalyzed disproportionation induced by PPh_3.

Conclusions

In conclusion, we have shown that 1,3,2-benzodithiaborolane and 1,3,2-benzodiazaborolane are potentially superior hydroborating agents in $RhCl(PPh_3)_3$-catalyzed hydroboration reactions because these derivatives are less susceptible to disproportionation, catalyzed by PPh_3, than catecholborane. Consequently, the desired compounds are formed in excellent yields. We have also shown that the hydroboration reactions can be monitored in situ with the use of ^{11}B NMR spectroscopy. With this technique, the formation of the desired compounds is observed, but it also reveals other species (that are readily destroyed upon workup) that result from competing side reactions that can vastly affect the overall yield of catalyzed hydroboration reactions. We are currently working to expand the applicability of these hydroborating reagents in similar hydroboration reactions, including aryl- and cyclic olefins. We are also investigating the role of ligands in the reaction to possibly design a Rh-type catalyst with enhanced applicability. In addition, we are exploring the suitability of these compounds within the realm of Suzuki-coupling-type chemistry.

Experimental Section

General: All glassware was thoroughly dried overnight in an oven heated at ca. 150 °C. The glassware was further flame-dried with a hot air gun under reduced pressure and cooled 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 a single use. The glassware was assembled, and all joints were wrapped with Teflon® tape and subsequently sealed with Parafilm "M"® to ensure a closed system.

All ^1H-, ^{13}C- and ^{11}B NMR spectra were recorded with a Varian Unity-Inova 500 MHz spectrometer. ^1H NMR spectra are referenced to the residual chloroform signal at δ = 7.25 ppm. All ^{11}B NMR spectra were referenced to $BF_3{\cdot}OEt_2$ as an external standard (δ = 0 ppm) contained within a sealed capillary insert. ^{11}B NMR spectroscopy was utilized in order to identify the compounds as well as to monitor the progress of the reactions. ^{13}C- and ^1H NMR spectroscopy and GC–MS were used to identify the hydroboration products. Quartz NMR tubes (5 cm) were used for the ^{11}B NMR spectroscopic experiments and were all oven-dried, flushed with dry nitrogen and sealed with a rubber septum prior to injection of the sample or reagents.

GC–MS analyses were performed with a Thermofinnigan® (GC) coupled with a PolarisQ® (MS) system. Thin layer chromatography was performed with silica gel (60 F_{254}) plates from Merck. Flash column chromatography was performed with SP Silica Gel 60 (230–400-mesh ASTM) from Merck.

THF and *trans*-4-octene were distilled from sodium wire in the presence of benzophenone as an indicator.[29] The solvents were distilled and transferred by cannula 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 use.

Catecholborane (**1**), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane) (**2**), $BH_3{\cdot}SMe_2$ in CH_2Cl_2, 1,2-benzenedithiol and tris-(triphenylphosphane)rhodium(I) chloride were obtained from Sigma–Aldrich Co; 1,2-phenylenediamine was obtained from Merck–Schuchardt. All of these reagents were used without further purification.

Synthesis of 1,3,2-Benzodithiaborolane (3): 1,2-Benzenedithiol (497 mg, 3.50 mmol) in dichloromethane (5 mL) was added to a stirred solution of borane-dimethyl sulfide complex (1.0 M solution in dichloromethane, 3.50 mL, 3.50 mmol) at 25 °C. The reaction was mild with no observable liberation of hydrogen gas. The reaction mixture was stirred for 24 h at room temperature to afford the desired product as a light yellow liquid (≥ 99% based on ^{11}B NMR). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 53.4 (d, J = 162.6 Hz, 1 H, B*H*) ppm. Proton noise decoupling (PND) was carried out with subsequent collapse of the doublet to the expected singlet. ^{11}B

NMR (160 MHz, $BF_3{\cdot}OEt_2$): PND δ = 53.4 (s) ppm. Because of the high purity and instability of this product, it was used directly in the hydroboration step.

Synthesis of 1,3,2-Benzodiazaborolane (4): 1,2-Diaminobenzene (541 mg, 5.0 mmol) was dissolved in dichloromethane (5 mL) in a flame-dried round-bottomed flask. After complete dissolution of the solid, borane-dimethyl sulfide complex (1 M solution in dichloromethane, 5.0 mL, 5.0 mmol) was introduced dropwise through the septum. The resulting mixture was stirred and heated at reflux for 4 h under an atmosphere of dry nitrogen to afford **4** as a clear liquid (95%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 23.9 (d, J = 153.2 Hz, 1 H, B*H*) ppm.

Representative Procedure for Uncatalyzed Hydroboration (Method A): 1,3,2-Benzodithiaborolane (**3**; 25.3 mg, 0.165 mmol) in diglyme (0.4 mL) was mixed with 1-octene (0.26 mL, 1.65 mmol) in a dry nitrogen-flushed NMR tube, capped with a rubber septum and sealed with Parafilm.® The tube was then inserted in an aluminium heating block, which was immersed in a silicon oil bath heated at 150 °C. The contents of the tube were heated at reflux; the pressure build-up in the tube was vented with a nitrogen purged syringe every 20 min for 3 h. This afforded a clear liquid of 2-octyl-1,3,2-benzodithiaborolane (65%) ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 59.6 (s) ppm.

Synthesis of 2-(1-Propylpentyl)-1,3,2-benzodithiaborolane: Method (A) was also employed for *trans*-4-octene, to afford 2-(1-propylpentyl)-1,3,2-benzodithiaborolane (15%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 59.6 (s) ppm.

Representative Procedure for Rhodium-Catalyzed Hydroboration (Method B): The hydroborating agent under investigation was injected into an oven-dried, nitrogen-purged and septum-capped quartz NMR tube and then analyzed by high field ^{11}B NMR spectroscopy prior to the addition of the other reagents in order to confirm its purity. To this solution was added simultaneously the olefin and tris(triphenylphosphane)rhodium(I) chloride (2 mol-%), which had been dissolved in dichloromethane or THF (0.5 mL) in a separate flame-dried, nitrogen-flushed flask. The contents of the tube were shaken vigorously, and the tube was inserted into the NMR spectrometer. The contents of the tube were subsequently analyzed every 2 h for 24 h at 25 °C to monitor the progress of the formation of the target alkylboronate ester. The amounts for each reactant used and yields of alkylboronate esters produced for each experiment are given in the following sections, where method B was used.

Synthesis of 4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane: Pinacolborane (1 M solution in THF, 0.4 mL, 0.4 mmol), *trans*-4-octene (63 μL, 0.4 mmol) and $RhCl(PPh_3)_3$ (7.4 mg, 0.008 mmol). Orange-yellow solution (79%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 34.4 (s), 21.7 [s, $B_2(O_2C_6H_{12})_3$] ppm. The contents of the tube were subsequently quenched by the addition of water (1 mL). The product was extracted with ether (3×2 mL) and dried with $MgSO_4$. Flash chromatography on silica gel with ethyl acetate/hexane, 2:98 and removal of solvent in vacuo afforded 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane. ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 34.3 (s) ppm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (t, J = 7.9 Hz, 2 H), 0.82 (t, J = 5.6 Hz, 3 H), 1.19 (s, 12 H), 1.20–1.24 (m, 10 H), 1.32–1.39 (m, 2 H) ppm. ^{13}C NMR (125·MHz, $CDCl_3$): δ = 14.7, 22.7, 23.1, 24.0, 24.8, 29.7, 30.1, 32.1, 82.7 ppm. IR (neat): $\tilde{\nu}$ = 2960 (s), 1744 (s), 1376 (s), 1234 (s), 1146 (s), 1073 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 241 (40) $[M]^+$, 225 (100), 224 (24), 183 (10), 127 (22), 97 (30), 69 (54).

Synthesis of 2-Octyl-1,3,2-benzodithiaborolane: 1,3,2-Benzodithiaborolane (**3**; 0.40 mL, 0.248 mmol), 1-octene (0.39 mL, 2.48 mmol), $RhCl(PPh_3)_3$ (46.3 mg, 0.050 mmol) in CH_2Cl_2 (0.50 mL). Yield 85%. ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 59.6 (s) ppm.

Synthesis of 2-(1-Propylpentyl)-1,3,2-benzodithiaborolane: 1,3,2-Benzodithiaborolane (**3**; 0.40 mL, 0.248 mmol), *trans*-4-octene (0.39 mL, 2.48 mmol), $RhCl(PPh_3)_3$ (46.3 mg, 0.050 mmol) in CH_2Cl_2 (0.50 mL). Clear liquid (80%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 59.6 (s) ppm. This product was subsequently oxidized by the addition of NaOH (3 M, 0.83 mL) and H_2O_2 (0.02 mL of 50% v/v solution) to afford the desired compound. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.1 Hz, 3 H, 2×C*H*$_3$), 1.41 (m, 2 H, 2×$CH_3CH_2CH_2CH_2$), 1.32 (m, 2 H, $CH_3CH_2CH_2CHOHCH_2$), 4.71 (s, 1 H, $CH_2CHOHCH_2$), 3.61 (m, 1 H, $CH_2CHOHCH_2$), 1.49 (m, 2 H, $CH_3CH_2CH_2CHOHCH_2$) 1.39 (m, 2 H, $CH_3CH_2CH_2CHOHCH_2CH_2$) ppm. MS (EI): *m*/*z* (%) = 130 (20) $[M]^+$, 87 (100) 73 (52), 69 (36), 55 (66).

Synthesis of 2-Octyl-1,3,2-benzodiazaborolane: 1,3,2-Benzodiazaborolane (**4**; 0.40 mL, 0.20 mmol), 1-octene (0.31 mL, 2.0 mmol), $RhCl(PPh_3)_3$ (37.0 mg, 0.040 mmol) in CH_2Cl_2 (0.50 mL). Orange-yellow solution (70%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ = 31.6 (s) ppm. MS (EI): *m*/*z* (%) = 231 (18) $[M]^+$, 230 (100), 229 (15), 145 (15), 132 (16), 119 (17), 118 (31).

Acknowledgments

We gratefully acknowledge Sasol for financial assistance, as well as Mr. Arno de Klerk and Dr. Hein Strauss for collaborative involvement in this ongoing project.

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Received: July 1, 2006
Published Online: September 5, 2006

