42-7; **4**, 63074-46-4; **5**, 63035-43-8; **6**, 63035-40-5; **9**, 78782-20-4; **10a**, 78782-21-5; **10b**, 78782-22-6; **10c**, 78782-23-7; **12**, 6713-49-1; **13**, 51901-48-5; **14**, 62930-28-3; **16**, 78782-24-8; **17**, 78782-25-9; **19**, 78782-26-0; **20**, 78782-27-1; **21**, 66080-30-6; LiTMP, 38227-87-1; triphenylmethyllithium, 733-90-4; $CH_3(CH_2)_3I$, 542-69-8; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_3Cl$, 109-69-3; $CH_3(CH_2)_4Br$, 110-53-2; $CH_3(CH_2)_6I$, 4282-40-0; $CH_3(CH_2)_6OSO_2C_6H_4CH_3$, 24767-82-6; $C_6H_5CH_2Br$, 100-39-0; $Cl(CH_2)_4I$, 10297-05-9; $CH_3(CH_2)_4CHBrCH_3$, 1974-04-5; $(C_2H_5)_2CHI$, 1809-05-8; $NC(CH_2)_4Br$, 5414-21-1; $CH_3C(O_2C_2H_4)(CH_2)_3I$, 3695-28-1; CH_3I, 74-88-4; $C_6H_5CH_2CH_2I$, 17376-04-4; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_4CHO$, 66-25-1; $C_6H_5CH_2CHO$, 122-78-1; $Cl(CH_2)_4CHO$, 638-29-9; $CH_3(CH_2)_4CH(CH_3)CHO$, 16630-91-4; $(C_2H_5)_2CHCHO$, 97-96-1; $CH_3(CH_2)_4COCH_3$, 110-43-0; propanediol 1-phenyloctane-3,3-diboronate, 63035-44-9; heptanal, 111-71-7; cyclohexanone, 108-94-1; octanal, 124-13-0; cyclohexanecarboxaldehyde, 2043-61-0; C_6H_5CHO, 100-52-7; $C_6H_5CO_2CH_3$, 93-58-3; C_6H_5COCl, 98-88-4; $CH_3CO_2C_2H_5$, 141-78-6; $CH_3(CH_2)_2CO_2CH_3$, 623-42-7; $C_6H_5CH_2CO(CH_2)_4CH_3$, 6683-94-9; $C_6H_5CO(CH_2)_5CH_3$, 1671-75-6; $C_6H_5CO(CH_2)_5CH_3$ 2,4-DNP, 66591-15-9; $CH_3CO(CH_2)_5CH_3$, 111-13-7; $CH_3(CH_2)_2CO(CH_2)_5CH_3$, 624-16-8; $(HO)_2BCH_2^-$, 78782-28-2; $[(HO)_2B]_2CH^-$, 78782-29-3; $[(HO)_2B]_3C^-$, 78782-30-6; $(HO)_2BCH_2\cdot$, 78782-31-7; $[(HO)_2B]_2CH\cdot$, 78782-32-8; $[(HO)_2B]_3C\cdot$, 78782-33-9; 1,2-ethanediol, 107-21-1; 1,3-propanediol, 504-63-2; 2,3-dimethyl-2,3-butanediol, 76-09-5; 2,2-dimethyl-1,3-propanediol, 126-30-7; 1,2-benzenediol, 120-80-9; bis(dimethoxyboryl)methane, 17936-82-2; bis(dimethoxyboryl)phenylmethane, 17936-83-3; 1-phenyloctane-3,3-diboronic acid, 78782-34-0; propanediol 2-phenylethene-1,1-diboronate, 56998-81-3; propanediol 2-phenyl-1-propene-1,1-diboronate, 56998-82-4; propanediol cyclohexylidenemethane-1,1-diboronate, 56998-80-2; methaneboronic anhydride, pyridine complex, 78782-35-1; dimethyl benzylboronate, 25292-03-9; β-styreneboronic acid, 4363-35-3.

Organoboranes. 26. ^{11}B NMR Investigation of Reactions of 2,3-Dimethyl-2-butene with Monochloroborane Complexes. Preparation and Hydroboration Characteristics of Thexylchloroborane Reagents

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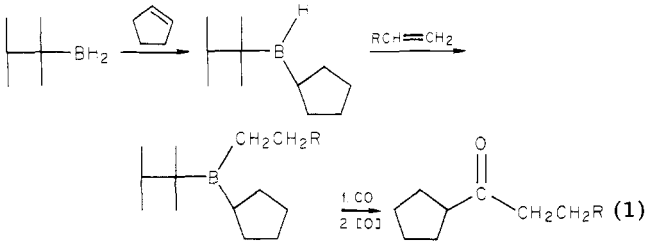
Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

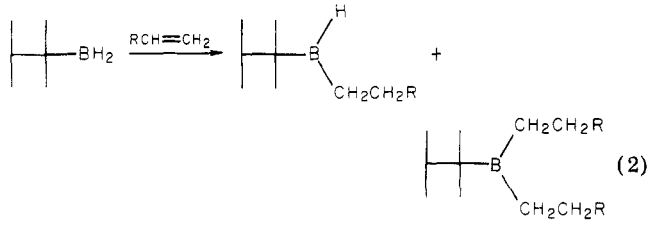
Received June 12, 1981

Under selected conditions, the hydroboration of 2,3-dimethyl-2-butene with 1 equiv of monochloroborane proceeds cleanly to give the monohydroboration product, thexylchloroborane (ThxBHCl). This reaction was examined with several monochloroborane complexes, including $BH_2Cl\cdot THF$, $BH_2Cl\cdot OEt_2$, and $BH_2Cl\cdot SMe_2$. The resulting thexylchloroboranes were fully characterized by IR and ^{11}B NMR spectroscopy. Monomeric ThxBHCl·THF was obtained cleanly from $BH_2Cl\cdot THF$. Similarly, monomeric $ThxBHCl\cdot SMe_2$ was obtained cleanly from $BH_2Cl\cdot SMe_2$. On the other hand, the product resulting from hydroboration of 2,3-dimethyl-2-butene with $BH_2Cl\cdot OEt_2$ was demonstrated to be a complex, equilibrating mixture of thexylborane (dimeric), thexylchloroborane, and thexyldichloroborane. The hydroboration properties of each of these reagents were also examined. Hydroboration of terminal alkenes with the ThxBHCl·THF and $ThxBHCl/Et_2O$ reagents led to complex mixtures containing trialkylborane, dialkylchloroborane, and alkyldichloroborane species. However, hydroboration of terminal alkenes with $ThxBHCl\cdot SMe_2$ in CH_2Cl_2 proceeded cleanly to the desired dialkylchloroborane product. Subsequent oxidation produced the desired primary alcohols in nearly quantitative yields with high regioselectivity.

Thexylborane is a particularly valuable reagent for the preparation of unsymmetrical trialkylboranes via sequential hydroboration. Subsequent carbonylation or cyanidation produces the corresponding unsymmetrical ketones in high yield[2] (eq 1).



In this procedure, it is important that the first alkene introduced be a relatively hindered one, such as cyclopentene or 2-methyl-1-butene. Treatment of thexylborane with an unhindered terminal alkene cannot be controlled to give exclusively monohydroboration[3] (eq 2). Consequently, this synthesis fails when one attempts to stitch together two different primary alkyl groups.



It occurred to us that this problem might be solved by employing a thexylchloroborane (ThxBHCl) derivative (eq

(1) Graduate research assistant on Grant GP 41169X from the National Science Foundation. Taken in part from the M.S. Thesis of J. A. Sikorski, Purdue University, West Lafayette, IN, 1976.

(2) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1967**, *89*, 5285–5287. Pelter, A.; Smith, K.; Hutchings, M. G.; Rowe, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 129–138. For a review of the synthetic applications of thexylborane, see: Negishi, E.; Brown, H. C. *Synthesis* **1974**, 77–89.

(3) Brown, H. C.; Negishi, E.; Katz, J.-J. *J. Am. Chem. Soc.* **1975**, *97*, 2791–2798.

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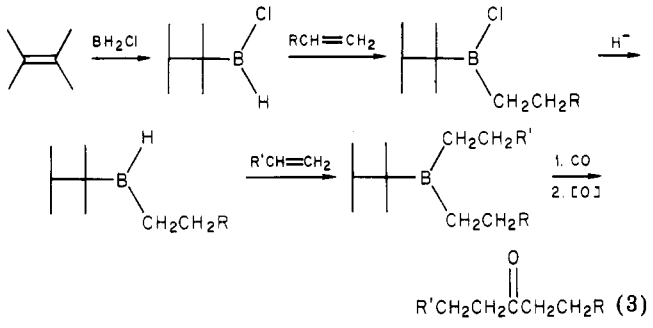
3). The success of this strategy is dependent upon the



(3)

clean monohydroboration of 2,3-dimethyl-2-butene with a monochloroborane species and the successful utilization of the resulting thexylchloroborane derivative in subsequent hydroborations. With this strategy there should be no limitation arising from the structural features of the alkenes employed in the sequence. Successful coupling of two different primary alkyl groups should be quite feasible. Accordingly, we undertook a detailed study of the reaction of 2,3-dimethyl-2-butene with various monochloroborane derivatives. The resulting thexylchloroboranes were fully characterized by ^{11}B NMR and infrared spectroscopy. The hydroboration properties of each of these reagents were also examined to determine their utility in the above sequence.

Recently, Zweifel and Pearson reported the successful synthesis of thexylchloroborane–methyl sulfide from thexylborane–methyl sulfide and hydrogen chloride[4] (eq 4). This reagent has been shown to hydroborate terminal

(4)

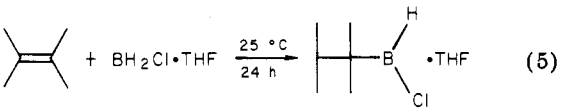
alkenes cleanly and quantitatively.[4,5a] The present investigation, leading to the development of practical synthetic routes to this new reagent via hydroboration, was carried out independently,[1] prior to the publication of the above synthesis (eq 4). Our study provides a highly convenient synthetic route to this valuable new reagent for application to the "stitching" of two terminal olefins.[5b]

Results and Discussion

Hydroboration of 2,3-Dimethyl-2-butene with BH_2Cl·THF in THF. Prior to this study, the reaction of 2,3-dimethyl-2-butene with BH_2Cl·THF in THF[6] had been examined by two different workers.[7] In neither case was there an attempt to characterize the borane products produced in this reaction or to utilize the reagent for subsequent hydroborations. For the present objective, it was important to establish the actual structure of the product and the cleanness of the subsequent reaction of the product with alkenes. The rate of reaction of 2,3-dimethyl-2-butene with BH_2Cl·THF was measured at 25 °C (Table I). The reaction was essentially complete after 24 h when the initial concentrations of the reagents were 0.40 M. Only terminal B–H species were observed at 2475 cm^{-1} by infrared spectroscopy. The ^{11}B NMR spectrum of this solution (doublet, δ 13.9 J_{BH} = 133 Hz) indicated >95% conversion to a monomeric product, presumably the THF complex, ThxBHCl·THF (eq 5).

Table I. Rate of Reaction of 2,3-Dimethyl-2-butene (0.40 M) with BH_2Cl·THF (0.40 M) in THF at 25 °C

BH_2Cl·THF, mmol	2,3-dimethyl-2-butene, mmol	time, h	alkene reacted, mmol
10	10	0.5	1.6
		1.0	2.5
		2.0	4.0
		4.0	5.7
		24.0	9.2



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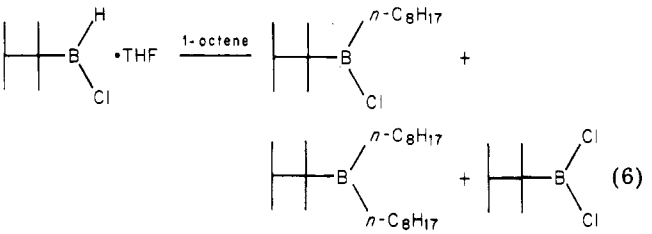
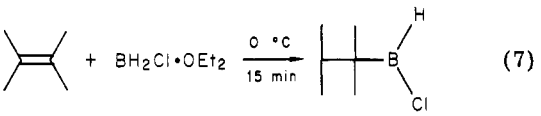
The utility of ThxBHCl·THF as a hydroboration reagent was then determined by examining its reaction with 1-octene. The reaction was found to be slow and incomplete at 0 °C. Only 44% of the 1-octene was utilized after 22 h when the initial concentration of reagents was 0.70 M. At 25 °C, complete uptake of 1-octene was observed after 3 h. However, ^{11}B NMR examination of this reaction mixture indicated that the desired dialkylchloroborane product was contaminated with significant amounts of trialkylborane and alkyldichloroborane species (eq 6).



(6)

This problem of product redistribution has been observed previously in the hydroboration of alkenes with BH_2Cl·THF.[8] These results prompted us to examine other systems for the preparation of a useful thexylchloroborane reagent.

Hydroboration of 2,3-Dimethyl-2-butene with BH_2Cl·OEt_2 in Et_2O. The hydroboration of 2,3-dimethyl-2-butene with BH_2Cl·OEt_2 in ethyl ether has been described previously.[9] The reaction was reported to be complete in 15 min at 0 °C. No further uptake of alkene was observed when a twofold excess was employed in the reaction. This observation led Ravindran to propose the 1:1 adduct, ThxBHCl, as the probable product[8] (eq 7). However, here also, no further characterization of this product was undertaken.



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Consequently, we examined the rate of reaction of 1 equiv of 2,3-dimethyl-2-butene with 1 equiv of BH_2Cl·OEt_2 in ethyl ether at 0 °C (Table II). Essentially complete

(4) Zweifel, G.; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919–5920.
(5) (a) Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.* **1980**, *45*, 4540–4542. (b) Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *Ibid.* **1980**, *45*, 4542–4543.
(6) Brown, H. C.; Tierney, P. A. *J. Inorg. Nucl. Chem.* **1959**, *9*, 51–55.
(7) (a) Zweifel, G. *J. Organomet. Chem.* **1967**, *9*, 215–221. (b) Pasto, D. J.; Kang, S.-Z. *J. Am. Chem. Soc.* **1968**, *90*, 3797–3800.
(8) Ravindran, N. Ph.D. Thesis, Purdue University, 1972.
(9) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1976**, *98*, 1785–1798.

Table II. Rate of Reaction of 2,3-Dimethyl-2-butene (1.0 M) with $BH_2Cl{\cdot}OEt_2$ in Et_2O at 0 °C

$BH_2Cl{\cdot}OEt_2$, mmol	2,3-dimethyl-2-butene, mmol	time, h	alkene reacted, mmol
10	10	0.10	5.8
		0.25	8.3
		0.50	9.7
		1.0	9.8
10	20	0.25	9.7
		1.0	9.8
		24.0	9.8

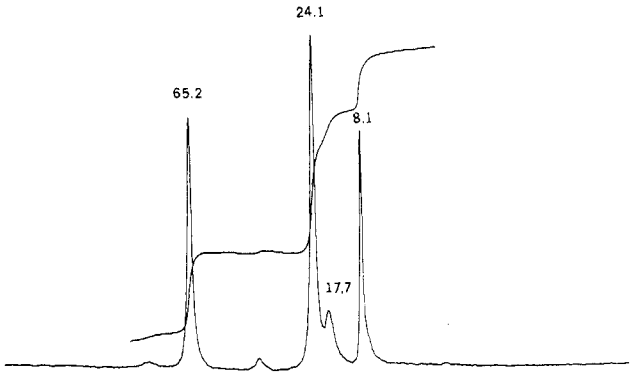
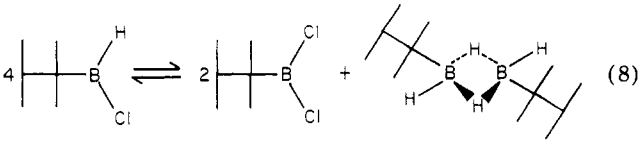


Figure 1. ^1H-decoupled ^{11}B NMR spectrum of the product resulting from the reaction of 2,3-dimethyl-2-butene with $BH_2Cl{\cdot}OEt_2$.

reaction was observed after 1 h at 0 °C. No additional uptake of alkene was observed when a twofold excess was employed. These results confirm the earlier observations that only 1 mmol of alkene per mmol of $BH_2Cl{\cdot}OEt_2$ is consumed. This product was fully characterized by chemical and spectral analyses.

Chemical analysis for active hydride and chloride was consistent with the formation of a 1:1 adduct. Methanolysis of 10 mmol of this reagent produced an essentially quantitative yield (8.9 mmol) of $ThxB(OMe)_2$ by ^1H NMR spectroscopy. Oxidation of 10 mmol of this reagent provided 9.7 mmol of 2,3-dimethyl-2-butanol by GLC. The infrared spectrum of this reagent exhibited both bridged B–H absorption at 1565 cm^{-1} and terminal B–H absorption at 2530 and 2550 cm^{-1}. These observations are consistent with the formation of a species containing thexyl, hydride, and chloride groups attached to boron, i.e., ThxBHCl in Et_2O (eq 7).

The ^{11}B NMR spectrum forced us to revise our conclusion as to the exact nature of this $ThxBHCl/Et_2O$ reagent. The observed ^1H-decoupled ^{11}B NMR spectrum (Figure 1) was surprisingly complex, consisting of four signals (Table III). The ^{11}B NMR spectrum of this reagent was fully consistent with a product mixture resulting from a disproportionation reaction (eq 8). As shown in Table III,

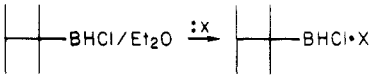


(8)

there is good agreement between the ^{11}B NMR signals observed in the $ThxBHCl/Et_2O$ system and those obtained for authentic samples of $ThxBCl_2$ and $(ThxBH_2)_2$ in diethyl ether. Integration of these ^{11}B NMR signals indicates that these disproportionation products must be the major products of the reaction. The doublet at δ 8.1 is assigned to the compound $BHCl_2{\cdot}OEt_2$, a known impurity in the $BH_2Cl{\cdot}OEt_2$ starting material.[8] The remaining doublet at δ 17.7 is consistent with the desired $ThxBHCl{\cdot}OEt_2$ product, although no good model compounds are available to predict the chemical shift for such a species. Removal of the diethyl ether in vacuo results in the complete disappearance of the ^{11}B NMR signal at δ 17.7 as well as the terminal B–H absorption at 2550 cm^{-1} in the infrared spectrum. This indicates that the complexed monomer, $ThxBHCl{\cdot}OEt_2$, is present in solution.

Similar disproportionations of monoalkylchloroborane intermediates have been proposed in several other systems to explain unusual product mixtures.[8,11] In each example, the disproportionation is presumed to occur in exceedingly low concentration. To the best of our knowledge, this $ThxBHCl/Et_2O$ system constitutes the first example where such disproportionation is directly observable. This offered us a unique opportunity to study the interactions of such species. Consequently, we examined the properties of this mixture in more detail. The equilibrium described in eq 8 was demonstrated by the following experiments.

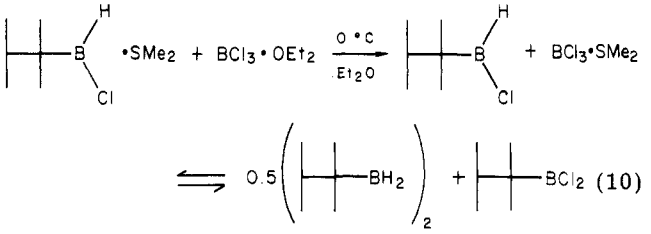
Treatment of the $ThxBHCl/Et_2O$ mixture with several complexing agents (SMe_2, THF, NMe_3) resulted in the rapid and complete conversion (>95%) to the ThxBHCl complexes by ^{11}B NMR (eq 9). On the other hand, sub-



(9)

X	^{11}B NMR, ppm
SMe_2	6.9
THF	13.9
NMe_3	8.9

sequent treatment of these complexes with a reagent designed to effectively remove this complexing reagent restored the original $ThxBHCl/Et_2O$ ^{11}B NMR spectrum completely. For example, treatment of $ThxBHCl{\cdot}SMe_2$ in ethyl ether with $BCl_3{\cdot}OEt_2$ at 0 °C (eq 10) gave a so-



(10)

lution whose ^{11}B NMR spectrum agreed closely with the original ^{11}B NMR spectrum of $ThxBHCl/Et_2O$ with an additional peak attributed to $BCl_3{\cdot}SMe_2$. Signals due to $ThxBCl_2{\cdot}SMe_2$, $(ThxBH_2)_2$, ThxBHCl, and $BCl_3{\cdot}SMe_2$ were readily assigned.

In addition, the fresh preparation of the $ThxBHCl/Et_2O$ reagent at −30 °C resulted in a dramatic increase in the relative amount of $ThxBHCl{\cdot}OEt_2$ present in the sample when the ^{11}B NMR spectrum was obtained at −30 °C. Warming the sample to room temperature produced the normal ^{11}B NMR spectrum of $ThxBHCl/Et_2O$. Recooling the sample to −30 °C restored the original −30 °C spectrum. Addition of 2 equiv of $ThxBCl_2$ to 1 equiv of $(ThxBH_2)_2$ in diethyl ether at 0 °C produces a clear, colorless solution. The ^{11}B NMR spectrum of this solution exhibited resonance signals at δ 65.0, 24.0, and 19.3, in close agreement with the values obtained for the ThxBHCl/

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(11) Zaidlewicz, M. Final Report II, Purdue University, 1980.

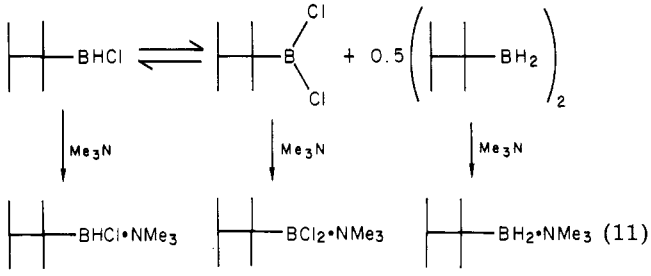
Table III. ^{11}B NMR Chemical Shift Assignments for the ThxBHCl/Et_2O System

compound	solvent	^{11}B NMR chemical shift, ppm	multiplicity	J_{BH}, Hz	assignment
$(ThxBH_2)_2$	THF	24.0	multiplet		
	Et_2O	24.0	multiplet		
$ThxBCl_2$	neat	65.2			
	Et_2O	64.9			
	CH_2Cl_2	65.4			
$BHCl_2 \cdot OEt_2$	Et_2O	7.9[10]	doublet	162	
ThxBHCl/Et_2O	Et_2O	65.2, 34%	singlet		$ThxBCl_2$
		24.1, 33%	multiplet		$(ThxBH_2)_2$
		17.7, 16%	doublet	145	$ThxBHCl \cdot OEt_2$
		8.1, 14%	doublet	160	$BHCl_2 \cdot OEt_2$

Et_2O system. These results indicate that the components of the ThxBHCl/Et_2O mixture are indeed equilibrating.

The $ThxBHCl \cdot OEt_2$ species was demonstrated to be the initial product of the reaction by the following experiment. Neat 2,3-dimethyl-2-butene was added to an equimolar amount of $BH_2Cl \cdot OEt_2$ under nitrogen in an NMR tube at −78 °C. The sample was then placed in the NMR probe. As the sample warmed to room temperature, the ^{11}B NMR spectrum was recorded with time. In this manner, a spectrum containing only $BH_2Cl \cdot OEt_2$, $BHCl_2 \cdot OEt_2$, and $ThxBHCl \cdot OEt_2$ was obtained. Only trace amounts of $(ThxBH_2)_2$ and $ThxBCl_2$ were observed after 3.5 min. Further reaction produced the usual room temperature ^{11}B NMR spectrum of equilibrated ThxBHCl/Et_2O.

Integration of the ^{11}B NMR spectrum of the ThxBHCl/Et_2O system indicated that the disproportionation products, $(ThxBH_2)_2$ and $ThxBCl_2$, represented the major products of the reaction (Table III). To corroborate this observation, we sought an independent chemical analysis that could quantify the relative amounts of each species in this mixture. Consequently, we examined the reaction of the ThxBHCl/Et_2O reagent with trimethylamine at −78 °C. Each species in the mixture should form its own trimethylamine adduct (eq 11). These complexes



(11)

are sufficiently different that each adduct should exhibit a distinct and separate ^1H NMR signal for the methyl protons of the trimethylamine group. Integration of the separate trimethylamine signals in the presence of a suitable internal standard would provide a convenient method for the quantitative determination of each species in the mixture.

Accordingly, standard solutions of $ThxBH_2 \cdot NMe_3$, $ThxBHCl \cdot NMe_3$, and $ThxBCl_2 \cdot NMe_3$ were prepared by reaction of $(ThxBH_2)_2$, $ThxBHCl \cdot SMe_2$, and $ThxBCl_2$, respectively, with exactly 1 equiv of trimethylamine in diethyl ether at −78 °C. The ^1H and ^{11}B NMR spectra were obtained for each adduct (Table IV). Essentially quantitative yields (>90%) were obtained for each of the reactions by ^1H NMR analysis with toluene as the internal standard. No significant difference in yield or chemical shifts was observed when the adducts were prepared with a large excess of trimethylamine.

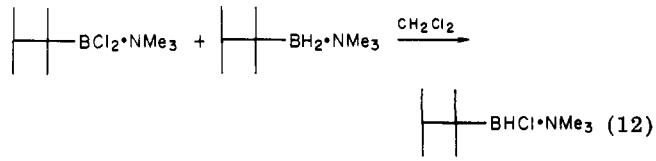
In a similar manner, 20 mmol of ThxBHCl/Et_2O was added to an excess of trimethylamine in diethyl ether at −78 °C. A clear solution above a white precipitate was

Table IV. Chemical Shift Data for the Trimethylamine Adducts of Thexylborane, Thexylchloroborane, and Thexyldichloroborane

compound	^{11}B NMR chemical shift, ppm	multiplicity	J_{BH}, Hz	^1H NMR chemical shift of Me_3N group (yield, %)
$ThxBH_2 \cdot NMe_3$	1.7	triplet	95	2.51 (92)
$ThxBHCl \cdot NMe_3$	8.8	doublet	120	2.65 (94)
$ThxBCl_2 \cdot NMe_3$	14.3	singlet		2.83 (97)
$HBCl_2 \cdot NMe_3$	4.7	doublet	147.5	2.94

obtained. The precipitate was removed from the cold reaction mixture and dissolved in CH_2Cl_2. The ^{11}B NMR spectrum of this CH_2Cl_2 solution consisted of a singlet at δ 14.1, in good agreement with that obtained for $ThxBCl_2 \cdot NMe_3$ in Table IV. Quantitative ^1H NMR analysis of this CH_2Cl_2 solution showed the presence of 1.09 mmol (5.5%) of $ThxBCl_2 \cdot NMe_3$ with a trimethylamine signal at δ 2.80 by ^1H NMR. Removal of the volatile components from the remaining ethereal layer gave a clear, colorless liquid. This liquid was dissolved in CH_2Cl_2, and a known amount of toluene was added as internal standard. The ^{11}B NMR spectrum of this solution consisted of a doublet at δ 8.82 (J_{BH} = 125 Hz) and a triplet at δ 1.97 (J_{BH} = 102 Hz), in good agreement with the values shown in Table IV for $ThxBHCl \cdot NMe_3$ and $ThxBH_2 \cdot NMe_3$. A small amount of $BHCl_2 \cdot NMe_3$ as a doublet (J_{BH} = 140 Hz) at δ 4.85 was also observed, confirming the earlier assignment of $BHCl_2 \cdot OEt_2$. Quantitative ^1H NMR analysis of this solution showed the presence of 15.4 mmol (77%) of $ThxBHCl \cdot NMe_3$ (trimethylamine signal at δ 2.63) and 1.38 mmol (6.9%) of $ThxBH_2 \cdot NMe_3$ (trimethylamine signal at δ 2.52). The reaction of ThxBHCl/Et_2O with trimethylamine in diethyl ether, therefore, supports the conclusion that all of the species in eq 11 are present.

The precipitate of $ThxBCl_2 \cdot NMe_3$ must be removed from the reaction mixture to prevent its reaction under homogeneous conditions with $ThxBH_2 \cdot NMe_3$. Under the heterogeneous conditions of the trimethylamine reaction at −78 °C, no reaction between the adducts is observed. However, if the $ThxBCl_2 \cdot NMe_3$ precipitate is left in the flask while the volatiles are removed at room temperature, a clear liquid results. The ^1H and ^{11}B NMR spectra of a CH_2Cl_2 solution of this liquid show no signals due to $ThxBCl_2 \cdot NMe_3$. The reaction of $ThxBCl_2 \cdot NMe_3$ with $ThxBH_2 \cdot NMe_3$ to produce $ThxBHCl \cdot NMe_3$ (eq 12) was



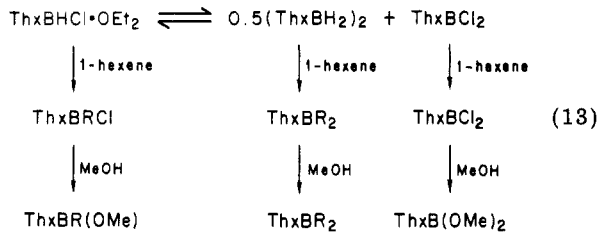
(12)

confirmed by adding a CH_2Cl_2 solution of $ThxBCl_2 \cdot NMe_3$ to a slight excess of $ThxBH_2 \cdot NMe_3$ in CH_2Cl_2 in an NMR

tube at room temperature. The reaction could be followed conveniently by obtaining the ^1H NMR spectrum of the mixture with time. After 10 min, all of the trimethylamine signal attributable to $ThxBCl_2 \cdot NMe_3$ had disappeared. In addition, the trimethylamine signal of $ThxBH_2 \cdot NMe_3$ had dramatically decreased in intensity, and a new signal at δ 2.62 attributable to $ThxBHCl \cdot NMe_3$ had appeared. The ^{11}B NMR spectrum of the reaction mixture exhibited a doublet (J_{BH} = 125 Hz) at δ 8.9, confirming the formation of $ThxBHCl \cdot NMe_3$ from $ThxBCl_2 \cdot NMe_3$ and $ThxBH_2 \cdot NMe_3$. No reaction was observed between the other trimethylamine complexes.

This unusually rapid equilibration of $ThxBH_2 \cdot NMe_3$ with $ThxBCl_2 \cdot NMe_3$ under homogeneous conditions led us to question the validity of this analysis as an accurate quantitative description of the $ThxBHCl/Et_2O$ system. There is a large discrepancy between the composition of the original product mixture suggested by ^{11}B NMR and the composition inferred from the relative amounts of trimethylamine adducts described above. There is no doubt, however, from these results that the disproportionation described by eq 11 accurately describes the product mixture.

Hydroboration of 1-Hexene with $ThxBHCl/Et_2O$. The disproportionation of the $ThxBHCl/Et_2O$ system (eq 8) could make it an inefficient reagent for the preparation of ThxBRCl derivatives. Providing that both $(ThxBH_2)_2$ and $ThxBHCl \cdot OEt_2$ have competitive hydroboration rates, any ThxBRCl product would always be contaminated by $ThxBR_2$ compounds (eq 13). If, however, the



(13)

$ThxBHCl \cdot OEt_2$ hydroborates olefins very much faster than $(ThxBH_2)_2$, pure ThxBRCl products could be obtained by the rapid removal by hydroboration of the ThxBHCl species from the equilibrating system.

The hydroboration of 1-hexene with $ThxBHCl/Et_2O$ was studied in order to determine whether the pure ThxBRCl species could be prepared from this reagent. Since the hydroboration of terminal alkenes is rapid with thexylborane at 0 °C,[2] any reaction between $(ThxBH_2)_2$ and 1-hexene should proceed completely to give a relatively nonvolatile $ThxBR_2$ product. By utilizing such a reactive substrate, any ThxBR(OMe) produced upon methanolysis of the hydroboration product would arise solely from the amount of ThxBRCl present in the reaction mixture and not from a ThxBRH intermediate present because of incomplete reaction between thexylborane and the olefin. The amount of $ThxBCl_2$ present after hydroboration would equal the amount of $ThxBR_2$ produced. Methanolysis of the hydroboration product would yield a mixture containing $ThxBR_2$, ThxBR(OMe), and $ThxB(OMe)_2$ (eq 13). Since the ThxBR(OMe) and $ThxB(OMe)_2$ have distinct and separate ^1H NMR chemical shifts for the methoxy group,[3] quantitative ^1H NMR analysis could be used to determine the relative amounts of each species.

Accordingly, 11 mmol of 1-hexene was added to 10 mmol of $ThxBHCl/Et_2O$ maintained under nitrogen at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. It was readily apparent from the infrared spectrum of this solution that all of the 1-hexene had reacted. After methanolysis in the presence of pyridine, ^{11}B NMR spectroscopy of the resulting mixture showed signals attributable to trialkylborane (δ 84.5) and alkylboronate (δ 29.1) species, as well as the desired dialkylborinate product (δ 54.1). After the volatile components were removed and a known amount of toluene was added as an internal standard, quantitative ^1H NMR analysis revealed the presence of 4.3 mmol of ThxB(*n*-hexyl)OMe and 2.4 mmol of $ThxB(OMe)_2$. Assuming that the amount of $ThxB(n\text{-hexyl})_2$ produced in the reaction equals the amount of $ThxB(OMe)_2$ produced, a mass balance of 91% was realized. Pure thexylalkylchloroboranes, therefore, are not available via the $ThxBHCl/Et_2O$ reagent. The hydroboration sequence confirms the earlier characterization of this system as a disproportionated mixture.

We sought to take advantage of the complexation reactions of this system (eq 9) to improve the utility of this reagent for hydroboration. The ThxBHCl·THF complex was prepared by adding 3 equiv of THF to the $ThxBHCl/Et_2O$ reagent at 0 °C. Then 1 equiv of 1-octene was added at 0 °C, and the resulting solution was stirred at room temperature for 1 h. GLC analysis showed essentially complete disappearance of 1-octene while ^{11}B NMR indicated that all of the ThxBHCl·THF had been consumed. After methanolysis, however, ^{11}B NMR showed that the desired ThxBR(OMe) product was contaminated with significant amounts of trialkylborane, methyl borate, and alkylboronate species. These results are similar to those obtained earlier with the ThxBHCl·THF complex prepared from 2,3-dimethyl-2-butene and $BH_2Cl \cdot THF$ (eq 6). Analogous results were obtained with the $ThxBHCl \cdot SMe_2$ complex prepared from $ThxBHCl/Et_2O$ and methyl sulfide. These results prompted us to conclude our investigation of this system and look elsewhere for a solution to the problem.

Hydroboration of 2,3-Dimethyl-2-butene with $BH_2Cl \cdot SMe_2$ in CH_2Cl_2. The development of monochloroborane–methyl sulfide, $BH_2Cl \cdot SMe_2$, as a highly selective reagent for the preparation of dialkylchloroboranes led us to investigate this reagent for the preparation of a synthetically useful ThxBHCl species. For most alkenes, the reaction of 2 mmol of olefin per mmol of $BH_2Cl \cdot SMe_2$ proceeds cleanly and quantitatively to the dialkylchloroborane stage in 2 h at room temperature when the reagents are initially mixed at 0 °C.[12]

The $BH_2Cl \cdot SMe_2$ reagent offers several advantages over $BH_2Cl \cdot OEt_2$. First, $BH_2Cl \cdot SMe_2$ can be prepared in neat form from $BH_3 \cdot SMe_2$ and $BCl_3 \cdot SMe_2$ (eq 14). $BH_2Cl \cdot OEt_2$

$$2BH_3 \cdot SMe_2 + BCl_3 \cdot SMe_2 \xrightarrow{25\ °C} 3BH_2Cl \cdot SMe_2 \qquad (14)$$

cannot be conveniently prepared neat or in solutions whose concentration is higher than 1 M. In addition, the neat form of $BH_2Cl \cdot SMe_2$ permits its use in either ethereal or nonethereal solvents. Finally, since solutions of $BH_2Cl \cdot OEt_2$ lose active hydride at 25 °C by loss of diborane, the reagent must be stored at 0 °C. However, neat $BH_2Cl \cdot SMe_2$ is stable at ambient temperatures. Thus, $BH_2Cl \cdot SMe_2$ is a much more convenient shelf reagent for the synthesis of dialkylchloroboranes.

The rate of reaction of 2,3-dimethyl-2-butene (2.0 M) with $BH_2Cl \cdot SMe_2$ (2.0 M) was measured in CH_2Cl_2. The results are summarized in Table V. At 25 °C, the reaction was essentially complete after 10 min. However, at this temperature, addition off the alkene to the chloroborane caused an exotherm sufficient to reflux the CH_2Cl_2. To circumvent this problem, we initially mixed the reagents at 0 °C. The resulting solution was then stirred at room

(12) Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1977**, *42*, 2533–2534.

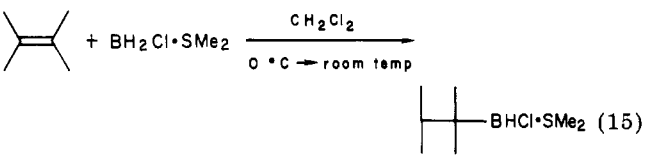
Table V. Rate of Reaction of 2,3-Dimethyl-2-butene with $BH_2Cl{\cdot}SMe_2$ in CH_2Cl_2 (2.0 M)

$BH_2Cl{\cdot}SMe_2$, mmol	2,3-dimethyl-2-butene, mmol	time, min	alkene reacted, mmol
10[a]	10	2	8.8
		6	9.0
		10	9.4
		30	9.6
10[b]	10	5	7.2
		10	8.2
		15	8.9
		30	9.6
		60	9.9
		90	9.9
10[b]	20	30	9.9
		60	9.9
		240	9.9
		1440	9.9

[a] At 25 °C. [b] The reagents were mixed at 0 °C and then stirred at 25 °C.

temperature. Under these conditions (Table V), the reaction was 99% complete after 1 h. No additional uptake of alkene was observed when a twofold excess was employed in the reaction. The resulting product was fully characterized by chemical and spectral analysis.

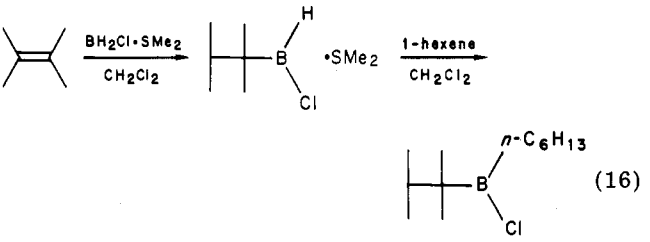
Chemical analysis for active hydride and chloride was consistent with the formation of a 1:1 adduct. Methanolysis of 10 mmol of this reagent produced an essentially quantitative yield (9.7 mmol) of $ThxB(OMe)_2$ by ^1H NMR. ^{11}B NMR of this methanolysis product confirmed that $ThxB(OMe)_2$ was the only boron species produced (δ 30.9). Oxidation of 10 mmol of this reagent gave a quantitative yield (9.5 mmol) of 2,3-dimethyl-2-butanol by GLC. The infrared spectrum of this reagent exhibited a strong terminal B–H absorption at 2450 cm^{-1}. No bridged B–H species were observed in the 1565-cm^{-1} region. The ^{11}B NMR spectrum of this reagent exhibited a clean doublet (J_{BH} = 128 Hz) at δ 6.9. Treatment of this reagent with trimethylamine at −78 °C results in a clean, quantitative yield of the $ThxBHCl{\cdot}NMe_3$ adduct, as shown by ^1H and ^{11}B NMR (Table IV). These observations are consistent with the clean and quantitative production of a monomeric species, $ThxBHCl{\cdot}SMe_2$, from the reaction of 2,3-dimethyl-2-butene and $BH_2Cl{\cdot}SMe_2$ (eq 15). The reaction



(15)

proceeds cleanly to the 1:1 adduct, despite the fact that the $BH_2Cl{\cdot}SMe_2$ starting material contains approximately 15% each of $BHCl_2{\cdot}SMe_2$ and $BH_3{\cdot}SMe_2$ by ^{11}B NMR.[13] Despite this fact, there is absolutely no indication that either of these species is present in the $ThxBHCl{\cdot}SMe_2$ product or that this product contains any redistributed $ThxBCl_2$ or $(ThxBH_2)_2$ species.

Hydroboration of 1-Hexene with $ThxBHCl{\cdot}SMe_2$. These highly encouraging results led us to examine the hydroboration properties of this reagent. Accordingly, 10 mmol of 1-hexene was added to 10 mmol of freshly prepared $ThxBHCl{\cdot}SMe_2$ in sufficient CH_2Cl_2 at 0 °C to make the overall reactant concentration 1.0 M. When the addition was complete, the reaction mixture was stirred at room temperature for 1 h. GLC analysis indicated that all of the 1-hexene had been consumed. ^{11}B NMR of the resulting solution showed that all of the $ThxBHCl{\cdot}SMe_2$ starting material had disappeared and that the product exhibited a single resonance at δ 78.0, consistent with the formation of a thexylalkylchloroborane, ThxBRCl, species. After methanolysis, ^{11}B NMR showed a single resonance at δ 52.0, consistent with the formation of pure methyl dialkylborinate. Quantitative ^1H NMR analysis indicated that this product was obtained in essentially quantitative yield (9.2 mmol). After oxidation, a nearly quantitative yield (94%) of 1-hexanol was observed by GLC. These results led us to conclude that pure thexylalkylchloroboranes could be prepared in high yield via $ThxBHCl{\cdot}SMe_2$ (eq 16).



(16)

With these results in hand, we examined the directive effects in the hydroboration of a few simple terminal alkenes with $ThxBHCl{\cdot}SMe_2$. The reactions were carried out by adding 10 mmol of neat alkene to 10 mmol of freshly prepared $ThxBHCl{\cdot}SMe_2$ at 0 °C in sufficient CH_2Cl_2 to make the overall concentration 1.0 M. When the addition of the alkene was complete, the reaction was stirred at room temperature for 1 h. At the end of this time, the reaction was cooled to 0 °C and oxidized with alkaline hydrogen peroxide with ethanol as the cosolvent. The isomeric terminal and internal alcohols were analyzed by GLC. The results are summarized in Table VI. In each case, the total yield of alcohol was 95 ± 5% by GLC. In addition, a quantitative yield of 2,3-dimethyl-2-butanol was observed in each reaction. The results indicate that the $ThxBHCl{\cdot}SMe_2$ reagent is a highly selective hydroboration agent.

Conclusion

This study has shown that $ThxBHCl{\cdot}SMe_2$ provides a simple and convenient solution to the problem of preparing isomerically pure thexylalkylchloroboranes essentially free of contamination from trialkylborane or alkyldichloroborane species. A detailed study to determine the applicability of this approach to the "stitching" of unsubstituted terminal olefins, $RCH{=}CH_2$ and $R'CH{=}CH_2$, as well as their functionalized derivatives, to produce the corresponding ketones is in progress.

Experimental Section

The reaction flasks and other glassware required for the experiments were predried at 140 °C for several hours, assembled hot, and cooled under a stream of prepurified nitrogen (Airco). Syringes were assembled, fitted with needles while hot, and then cooled. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered side arms by using standard techniques for handling air-sensitive materials.[14]

Materials. Commercial grade THF was distilled from excess lithium aluminum hydride and stored under nitrogen prior to use. Reagent grade ethyl ether, dimethyl sulfide, and pentane were degassed and stored under nitrogen over type 5-Å molecular sieves. Spectroquality methylene chloride was degassed and stored under nitrogen over anhydrous potassium carbonate. Spectroquality,

(13) Unpublished observation by H. C. Brown and J. A. Sikorski.

(14) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.
(15) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708–4712.

Table VI. Directive Effects in the Hydroboration of Representative Alkenes with Thexylchloroborane-Methyl Sulfide

alkene	isomeric alcohols	relative yields of products		
		ThxBHCl·SMe_2	$BH_2Cl·OEt_2$[9]	$BH_3·THF$[15]
1-hexene	1-hexanol	99	99.2	94
	2-hexanol	1	0.8	6
1-octene	1-octanol	99		
	2-octanol	1		
1-decene	1-decanol	99		
	2-decanol	1		
2-methyl-1-butene	2-methyl-1-butanol	99	99.9	99
	2-methyl-2-butanol	1	0.1	1
2-methyl-2-butene	3-methyl-2-butanol	99	99.7	98
	2-methyl-2-butanol	1	0.3	2
cis-2-pentene	2-pentanol	76	58	55
	3-pentanol	24	41	45

anhydrous methanol was degassed and stored under nitrogen over type 3-Å molecular sieves. Reagent grade trimethylamine, boron trichloride, pyridine, ethanol, and toluene were used without further purification. The hydrocarbons employed as internal standards for GLC analyses were obtained from Phillips Petroleum Co. and were labeled >99% pure. All alkenes were obtained from the Chemical Samples Division of Albany International. 2,3-Dimethyl-2-butene, 1-octene, and 1-hexene were distilled from lithium aluminum hydride and stored under nitrogen. All other alkenes employed in these studies were used as received after checking their refractive indices and ^1H NMR spectral characteristics. THF solutions of thexylborane and ethereal solutions of boron trichloride and monochloroborane were prepared as described previously.[14] $BH_2Cl·THF$,[8] $BH_2Cl·SMe_2$,[12] and $BHCl_2·SMe_2$[12] were prepared by literature procedures. Each of these reagents was carefully standardized for active hydride and chloride prior to use.[14]

GLC Analyses. GLC analyses were carried out by using a Varian Model 1200 FID chromatograph. When residual alkenes were analyzed, the injection port was lined with a 6 in. × 0.25 in. column of 20% THEED on 100/120 mesh Varaport 30. Residual 2,3-dimethyl-2-butene was analyzed on a 6 ft × 0.125 in. column of 30% adiponitrile on 60/80 mesh Firebrick. Residual 1-octene was analyzed on a 6 ft × 0.125 in. column of 10% SE-30 on 100/120 mesh Varaport 30. Alcohols were analyzed on a 6 ft × 0.125 in. column of 10% OV-225 on 100/120 mesh Varaport 30 or a 6 ft × 0.125 in. column of 10% Carbowax 400 on 100/120 mesh Varaport 30. All GLC yields were determined with a suitable internal standard and authentic synthetic mixtures.

Spectra. Spectra were obtained under inert atmosphere by using apparatus and techniques described elsewhere.[14] Infrared spectra were obtained with a Perkin-Elmer Model 700 spectrometer by using sealed liquid cells and the two-syringe technique.[14] ^{11}B NMR spectra were recorded on a Varian XL 100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data acquisition system. Each spectrum was recorded in the CW mode with an external ^{19}F lock. All ^{11}B NMR chemical shifts are reported relative to $BF_3·OEt_2$ (δ 0) with the chemical shifts downfield from $BF_3·OEt_2$ assigned as positive. ^1H NMR spectra were obtained with a Varian T-60 (60 MHz) spectrometer. All ^1H NMR chemical shifts are reported relative to tetramethylsilane (δ 0).

Rate of Reaction of 2,3-Dimethyl-2-butene with $BH_2Cl·THF$ in THF. A 100-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and reflux condenser topped by a connector tube leading to a mercury bubbler was flushed with nitrogen. The flask was immersed in a constant temperature bath maintained at 25 ± 0.01 °C. Then 31.7 mL of THF and 11.6 mL of 1.72 M $BH_2Cl·THF$ (20 mmol) were added via syringe. The resulting solution was stirred for 2 h. Then 6.6 mL of a THF solution consisting of 3.0 M 2,3-dimethyl-2-butene (20 mmol) and 2.26 M *n*-nonane (15.0 mmol, internal standard) was added via syringe. Thus, the overall concentration of alkene and $BH_2Cl·THF$ was 0.40 M. Aliquots of 0.25 mL were withdrawn at specified intervals, quenched by injection into 0.25 mL of acetone in a septum-covered vial at −78 °C, and then analyzed for residual olefin by GLC. The amount of olefin reacted was calculated for each interval from the amount of residual alkene obtained. The results are summarized in Table I. After 24 h, essentially all of the olefin had been utilized. The ^{11}B NMR spectrum of this solution exhibited a doublet (J_{BH} = 133 Hz) at δ 13.9. The infrared spectrum of this solution showed a strong terminal B–H absorption at 2475 cm^{-1}. No bridged B–H absorption in the region of 1565 cm^{-1} was observed.

Rate of Reaction of 1-Octene with ThxBHCl·THF in THF. ThxBHCl·THF (12.5 mL, 0.8 M, 10 mmol) was prepared in a 50-mL round-bottom flask as described above. The flask was then immersed in an ice-water bath, and 0.63 mL of *n*-undecane (3.0 mmol, internal standard) and 1.57 mL of neat 1-octene (10 mmol) were added via syringe. The initial concentration of reactants was approximately 0.7 M. Aliquots of 0.25 mL were withdrawn at specified intervals, quenched by injection into 0.50 mL of acetone in a septum-covered vial at −78 °C, and then analyzed for residual 1-octene by GLC. The amount of 1-octene consumed was calculated for each interval from the amount of residual olefin obtained. After 22 h, only 4.4 mmol (44%) of the 1-octene had been consumed.

The reaction was repeated at 25 °C. In this case, essentially all of the 1-octene (95%) was consumed after 3 h. ^{11}B NMR of this reaction mixture showed that all of the ThxBHCl·THF (δ 13.9) had been consumed. The reaction mixture was then treated with 1.22 mL of absolute methanol (30 mmol) at 0 °C. ^{11}B NMR of the methanolyzed mixture showed the major product to be the desired dialkylborinate species (δ 53.9). However, the product also contained significant quantities of trialkylborane (δ 85.4), alkylboronate (δ 30.9), and methylborate (δ 18.2) species as contaminants.

Rate of Reaction of 2,3-Dimethyl-2-butene with $BH_2Cl·OEt_2$ in Ethyl Ether. A 50-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercury bubbler was immersed in an ice–water bath and charged with 9.35 mL of 1.07 M $BH_2Cl·OEt_2$ (10.0 mmol) and 0.383 mL of methylcyclohexane (3.0 mmol, internal standard). The resulting solution was stirred for 30 min at 0 °C, and then 1.20 mL of neat 2,3-dimethyl-2-butene (10 mmol) was added via syringe. Aliquots of 0.25 mL were withdrawn at specified intervals, quenched by injection into 1 mL of acetone in a septum-covered vial at −78 °C, and then analyzed for residual olefin by GLC. The amount of 2,3-dimethyl-2-butene consumed was calculated for each interval from the amount of residual olefin obtained. The results are summarized in Table II.

The experiment was repeated by adding 2.40 mL of neat 2,3-dimethyl-2-butene (20 mmol) to the cold solution of BH_2Cl (10 mmol) in ethyl ether. The resulting solution contained 2 mmol of olefin per mmol of $BH_2Cl·OEt_2$. The amount of residual alkene was then determined by GLC after an acetone quench as described above. The results are summarized in Table II.

Preparation of ThxBHCl/Et_2O in Ethyl Ether. The standard procedure for the preparation of ThxBHCl/Et_2O is as follows. A 25-mL round-bottom flask equipped with magnetic stirring bar, septum-covered sidearm, and connector tube leading to a mercury bubbler was immersed in an ice–water bath and charged with 9.35 mL of 1.07 M $BH_2Cl·OEt_2$ (10.0 mmol) in ethyl ether. After 15 min at 0 °C, 1.30 mL of neat 2,3-dimethyl-2-butene (11 mmol) was added via syringe. The resulting clear solution was then stirred at 0 °C for 30–60 min. In all cases, this reagent was freshly prepared before further use. This solution exhibited both bridged B–H absorption (1565 cm^{-1}) and terminal B–H

absorption (2530, 2550 cm^{-1}) by infrared spectroscopy. The ^{11}B NMR spectrum (Figure 1, Table III) consisted of four signals: a singlet at δ 65.2 (34%), a multiplet at δ 24.1 (33%), a doublet (J_{BH} = 145 Hz) at δ 17.7 (16%), and a doublet (J_{BH} = 160 Hz) at δ 8.1 (14%).

Methanolysis of ThxBHCl/Et_2O. ThxBHCl/Et_2O (10 mmol) was prepared according to the standard procedure and then was treated at 0 °C with 0.84 mL of pyridine (10.5 mmol) and 1.26 mL of absolute methanol (30 mmol). A white precipitate formed immediately as a vigorous evolution of gas occurred. After warming to room temperature, the white precipitate was collected by filtration, air-dried, and weighed; 1.0 g (8.6 mmol) was obtained. The ^1H NMR spectrum of this material was identical with that of an authentic sample of pyridinium hydrochloride. The volatiles were removed from the remaining ethereal filtrate. The resulting oil was dissolved in 3 mL of CH_2Cl_2, and 1.06 mL of toluene (10 mmol, internal standard) was added. Quantitative ^1H NMR analysis of this solution showed a nearly quantitative yield of $ThxB(OMe)_2$ (8.9 mmol) with the CH_3–O–B resonance at δ 3.60. When 10 mmol of freshly prepared ThxBHCl/Et_2O was treated at 0 °C with 0.84 mL of absolute methanol (20 mmol) in a flask connected to a gas buret, 10.2 mmol of hydrogen evolved.

Oxidation of ThxBHCl/Et_2O. To 10 mmol of freshly prepared ThxBHCl/Et_2O at 0 °C was added 0.97 mL of *n*-decane (5.0 mmol, internal standard), 10.0 mL of 3.0 N aqueous NaOH (30 mmol), 20 mL of absolute ethanol, and 4.0 mL of 30% aqueous hydrogen peroxide (40 mmol). After 1 h at 0 °C, the reaction mixture was warmed to 50 °C for 30 min and then cooled to room temperature. Absolute ethyl ether (20 mL) was added, and the aqueous layer was saturated with potassium carbonate. GLC analysis of the ethereal layer showed the formation of 9.7 mmol (97%) of 2,3-dimethyl-2-butanol.

Reaction of 2,3-Dimethyl-2-butene with BH_2Cl·OEt_2: ^{11}B NMR Profile. To an oven-dried 12-mm NMR tube, cooled under nitrogen, was added 2.80 mL of 1.07 M BH_2Cl·OEt_2 (3.0 mmol). The tube was cooled to −78 °C in a dry ice–acetone bath. Then 0.356 mL of neat 2,3-dimethyl-2-butene (3.0 mmol) was added via syringe. The mixture was shaken well and then placed immediately in the ^{11}B NMR probe. Spectra were rapidly recorded (25-s scan) as the sample warmed to room temperature. Spectra were obtained at 2, 2.5, 3.5, 4.5, 6, and 7.25 min after the addition of the olefin. The spectrum recorded after 3.5 min contained signals due to unreacted BH_2Cl·OEt_2 and $BHCl_2$·OEt_2. In addition, a doublet, centered at δ 18, was also observed. This signal was assigned to the transient species, ThxBHCl·OEt_2. Only trace amounts of $ThxBCl_2$ or $(ThxBH_2)_2$ could be seen in this spectrum. All spectra obtained after this time resembled the normal room temperature ^{11}B NMR spectrum of ThxBHCl/Et_2O (Figure 1).

Preparation and ^{11}B NMR of ThxBHCl/Et_2O at −30 °C. To an oven-dried 12-mm NMR tube, cooled under nitrogen, was added 2.80 mL of 1.07 M BH_2Cl·OEt_2 (3.0 mmol). The tube was cooled to −78 °C in a dry ice–acetone bath, and then 0.356 mL of neat 2,3-dimethyl-2-butene (3.0 mmol) was added. The tube was then placed in a constant temperature bath, maintained at −30 °C for 2 days. The tube was then removed and immediately placed in the ^{11}B NMR probe, maintained at −30 °C. The ^{11}B NMR spectrum at −30 °C showed a considerable increase in the relative intensity of the doublet at δ 18 compared to the normal room temperature spectrum. Warming the sample to 0 °C caused a decrease in the intensity of the doublet at δ 18. Further warming to room temperature gave the normal room temperature spectrum. However, upon recooling of the sample to −30 °C, the original −30 °C spectrum was restored, with an increased amount of the doublet at δ 18 readily apparent.

Removal of Et_2O from ThxBHCl/Et_2O. The volatile components of 10 mmol of freshly prepared ThxBHCl/Et_2O were removed by using a water aspirator and then a vacuum pump. A clear liquid resulted which was dissolved in 2.5 mL of CH_2Cl_2. The ^1H NMR of this solution showed that only a trace of Et_2O was present. The strong terminal B–H absorption at 2550 cm^{-1} was no longer present in the infrared spectrum. The ^{11}B NMR spectrum showed signals at δ 65, 24, 10.8, and 5.7. No signal at δ 17.7 was observed, indicating that this species is dependent on the Et_2O concentration.

Treatment of ThxBHCl/Et_2O with Excess THF. To 10 mmol of freshly prepared ThxBHCl/Et_2O at 0 °C was added 2.4 mL of THF (30 mmol). A vigorous exothermic reaction was observed at 0 °C. The resulting clear solution was stirred at 0 °C for 30 min. The ^{11}B NMR (doublet, J_{BH} = 133 Hz, δ 13.9) and infrared (2475 cm^{-1}) data were identical with those obtained previously for ThxBHCl·THF from the reaction of 2,3-dimethyl-2-butene with BH_2Cl·THF.

Treatment of ThxBHCl/Et_2O with Excess Methyl Sulfide. To 10 mmol of freshly prepared ThxBHCl/Et_2O at 0 °C was added 2.20 mL of methyl sulfide (30 mmol). An exothermic reaction occurred at 0 °C. The resulting clear solution was stirred at 0 °C for 30 min. The ^{11}B NMR (doublet, J_{BH} = 128 Hz, δ 6.9) and infrared (2450 cm^{-1}) data were identical with those obtained for ThxBHCl·SMe_2 from the reaction of 2,3-dimethyl-2-butene with BH_2Cl·SMe_2.

Treatment of ThxBHCl·SMe_2 with BCl_3·OEt_2. A solution of 10 mmol of 2.0 M ThxBHCl·SMe_2 in CH_2Cl_2 was prepared according to the standard procedure and then was treated at 0 °C with 15.0 mL of 0.91 M BCl_3·OEt_2 (13.5 mmol) in ethyl ether. The reaction mixture was then stirred at 0 °C for 1 h. ^{11}B NMR of this reaction mixture gave signals attributable to $ThxBCl_2$·SMe_2 (δ 42.5), $(ThxBH_2)_2$ (δ 22.8), ThxBHCl·OEt_2 (δ 18.9), and BCl_3·SMe_2 (δ 4.92).

Preparation of Thexyldichloroborane. A 300-mL round-bottom flask equipped with a magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercuby bubbler was cooled under nitrogen, immersed in an ice–water bath, and charged with 150 mL of pentane. Meanwhile, 13.1 mL of BCl_3 (150 mmol) was condensed under nitrogen in a gas trap with a dry ice–acetone bath. The cold bath was removed and the BCl_3 was allowed to distill slowly under nitrogen into the flask containing pentane. The resulting clear solution was stirred for 1 h at 0 °C. Then 20 mL of neat 2,3-dimethyl-2-butene (180 mmol) and 17.5 mL of 8.55 M $BHCl_2$·SMe_2 (150 mmol) were added. A white precipitate of BCl_3·SMe_2 formed immediately. The reaction mixture was stirred overnight at room temperature. The precipitate was removed by filtration and washed several times with pentane. The pentane solutions were combined and reduced on a water aspirator. The resulting clear liquid was distilled at reduced pressure to yield 15.2 g (61%) of thexyldichloroborane as a clear liquid, bp 75–76 °C (90 mm); ^{11}B NMR δ 65.2 (neat), 64.9 (Et_2O), 65.4 (CH_2Cl_2). Anal. Calcd for $C_6H_{13}BCl_2$: C, 43.18; H, 7.85; B, 6.48; Cl, 42.49. Found: C, 43.00; H, 8.08; B, 6.60; Cl, 42.25.

Preparation of Thexylborane in Ethyl Ether. A 25-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercury bubbler was cooled under nitrogen and charged at 0 °C with 4.15 mL of 2.41 M BH_3·THF (10 mmol) and 1.30 mL of neat 2,3-dimethyl-2-butene (11 mmol). The resulting clear solution was stirred at 0 °C for 2 h. The THF was removed with a water aspirator and vacuum pump. The resulting clear liquid was then dissolved in 5 mL of ethyl ether. ^{11}B NMR of this solution showed a multiplet at δ 24.0.

Reaction of Thexylborane with Thexyldichloroborane in Ethyl Ether. Thexylborane (2.5 mL, 2.0 M, 5 mmol) in ethyl ether was prepared according to the above procedure. Then 0.81 g of neat thexyldichloroborane (5 mmol) was added with stirring at room temperature. The resulting clear solution was stirred at room temperature for 12 h. ^{11}B NMR spectroscopy of this solution exhibited signals at δ 65.0, 24.0 and 19.3.

Reaction of Thexylborane with Trimethylamine in Ethyl Ether. Thexylborane (10 mmol) in ethyl ether was prepared according to the standard procedure. This solution was cooled to −78 °C and was then treated with 4.76 mL of 2.10 M trimethylamine (10 mmol) in ethyl ether. A turbid mixture resulted. This was stirred at −78 °C for 15 min and then at room temperature for 1 h. The volatile components were removed with a water aspirator. The resulting clear liquid was dissolved in 5 mL of CH_2Cl_2. ^{11}B NMR of this solution showed only a triplet (J_{BH} = 95 Hz) at δ 1.7. Quantitative ^1H NMR analysis after addition of 0.898 g of toluene (9.74 mmol) as internal standard showed the formation of 9.22 mmol (92%) of $ThxBH_2$·NMe_3 with Me_3N–B resonance at δ 2.51.

When the experiment was repeated with a twofold excess of trimethylamine (9.52 mL of 2.1 M, 20 mmol) in ethyl ether, similar workup gave a solution containing 9.32 mmol (93%) of

$ThxBH_2{\cdot}NMe_3$ with exactly the same spectral characteristics.

Reaction of $ThxBHCl{\cdot}SMe_2$ with Trimethylamine in Ethyl Ether. A 25-mL round-bottom flask equipped with magnetic stirring bar, septum-covered sidearm, and connector tube leading to a mercury bubbler was charged at 0 °C with 1.16 mL of 8.6 M $BH_2Cl{\cdot}SMe_2$ (10 mmol), 3.0 mL of ethyl ether, and 1.30 mL of neat 2,3-dimethyl-2-butene (11 mmol). The resulting clear solution was stirred at room temperature for 3 h, recooled to −78 °C, and treated with 4.76 mL of 2.1 M trimethylamine (10 mmol) in ethyl ether. The resulting cloudy reaction mixture was stirred at −78 °C for 20 min and then allowed to come to room temperature overnight. The volatile components were removed with a water aspirator. The resulting turbid liquid was dissolved in 5 mL of CH_2Cl_2. ^{11}B NMR of this clear solution showed only a doublet (J_{BH} = 120 H) at δ 8.8. Quantitative ^1H NMR analysis after the addition of 0.915 g of toluene (9.93 mmol, internal standard) showed the formation of 9.42 mmol (94%) of $ThxBHCl{\cdot}NMe_3$, with Me_3N–B resonance at δ 2.65.

When the reaction was repeated with 9.56 mL of 2.1 M trimethylamine (20 mmol) in ethyl ether, similar workup gave a solution containing 9.77 mmol (98%) of $ThxBHCl{\cdot}NMe_3$ with exactly the same spectral characteristics.

Reaction of Thexyldichloroborane with Trimethylamine in Ethyl Ether. A 25-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercury bubbler was charged with 0.65 g of neat thexyldichloroborane (3.9 mmol) and 5 mL of ethyl ether. The resulting clear solution was cooled to −78 °C and treated with 1.85 mL of 2.1 M trimethylamine (3.9 mmol) in ethyl ether. A white precipitate formed immediately. The reaction mixture was stirred at −78 °C for 10 min and at room temperature for 30 min. The volatile components were removed with a water aspirator. The resulting white solid was dissolved in 5 mL of CH_2Cl_2. ^{11}B NMR spectroscopy of this clear solution showed only a singlet at δ 14.3. Quantitative ^1H NMR analysis after the addition of 0.530 mL of toluene (5.0 mmol, internal standard) showed the formation of 3.8 mmol (97%) of $ThxBCl_2{\cdot}NMe_3$ with Me_3N–B resonance at δ 2.83.

When the experiment was repeated using 2 equiv of trimethylamine, similar workup gave a solution containing a 88% yield of $ThxBCl_2{\cdot}NMe_3$ with exactly the same spectral characteristics.

Preparation of $ThxBHCl{\cdot}NMe_3$. A 100-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercury bubbler was charged at 0 °C with 15 mL of ethyl ether and 5.80 mL of 8.6 M $BH_2Cl{\cdot}SMe_2$ (50 mmol). The resulting clear solution was stirred at 0 °C for 30 min and then was treated with 7.0 mL of neat 2,3-dimethyl-2-butene (60 mmol). The reaction mixture was stirred at room temperature for 3 h and cooled to −78 °C, and 35.7 mL of 2.1 M trimethylamine (75 mmol) in ethyl ether was added. The reaction mixxture was allowed to come to room temperature overnight. A clear, ethereal solution above a small amount of white solid resulted. The ether layer was removed by filtration and reduced by using a water aspirator. The resulting turbid liquid was distilled at reduced pressure to yield 8.2 g (86%) of $ThxBHCl{\cdot}NMe_3$ as a clear liquid, bp 86–86.5 °C (0.02 mm): ^{11}B NMR (CH_2Cl_2) δ 8.8 (doublet, J_{BH} = 120 Hz); ^1H NMR Me_3N–B resonance at δ 2.65. Anal. Calcd for $C_9H_{23}BClN$: C, 56.4; H, 12.1; N, 7.31. Found: C, 56.19; H, 12.25; N, 7.05.

Reaction of $ThxBHCl/Et_2O$ with Trimethylamine in Ethyl Ether. A 50-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercury bubbler was cooled to −78 °C with a dry ice–acetone bath and charged with 9.52 mL of 2.1 M trimethylamine (20 mmol) in ethyl ether. Then 20 mmol of freshly prepared $ThxBHCl/Et_2O$ was transferred to this cold solution via a double-ended needle. A small amount of white precipitate formed immediately. The ^{11}B NMR spectrum of this heterogeneous mixture showed signals at δ 14.1 ($ThxBCl_2{\cdot}NMe_3$), 8.82 ($ThxBHCl{\cdot}NMe_3$), 4.85 ($BHCl_2{\cdot}NMe_3$), and 1.97 ($ThxBH_2{\cdot}NMe_3$). The precipitate was removed from the cold reaction mixture by filtration and dissolved in 2 mL of CH_2Cl_2. The ^{11}B NMR spectrum of this CH_2Cl_2 solution consisted of only a singlet at δ 14.1. Quantitative ^1H NMR analysis after the addition of 0.265 mL of toluene (2.5 mmol, internal standard) showed the formation of 1.09 mmol (5.5%) of $ThxBCl_2{\cdot}NMe_3$ with Me_3N–B resonance at δ 2.80. The volatile components were removed from the remaining ethereal filtrate with a water aspirator to give a clear liquid which was dissolved in 10 mL of CH_2Cl_2. ^{11}B NMR of this solution showed signals at δ 8.8, 4.8, and 1.97. Quantitative ^1H NMR analysis after the addition of 1.70 mL of toluene (16 mmol, internal standard) showed the formation of 15.4 mmol (77%) of $ThxBHCl{\cdot}NMe_3$ with Me_3N–B resonance at δ 2.63 and 1.38 mmol (6.9%) of $ThxBH_2{\cdot}NMe_3$ with Me_3N–B resonance at δ 2.52 along with a small amount of $BHCl_2{\cdot}NMe_3$.

Reaction of $ThxBCl_2{\cdot}NMe_3$ with $ThxBH_2{\cdot}NMe_3$. CH_2Cl_2 solutions of $ThxBCl_2{\cdot}NMe_3$ and $ThxBH_2{\cdot}NMe_3$ were prepared as described above by substituting CH_2Cl_2 for the ethyl ether solvent. Addition of a slight excess of $ThxBH_2{\cdot}NMe_3$ to $ThxBCl_2{\cdot}NMe_3$ at room temperature in CH_2Cl_2 gave a clear solution. After 30 min, the ^{11}B NMR spectrum of this solution showed only a doublet (J_{BH} = 118 Hz) at δ 8.9 along with a small amount of $ThxBH_2{\cdot}NMe_3$ at δ 1.97. ^1H NMR spectroscopy of this solution showed a strong signal at δ 2.65 consistent with the formation of $ThxBHCl{\cdot}NMe_3$. No reaction was observed between CH_2Cl_2 solutions of $ThxBH_2{\cdot}NMe_3$ annd $ThxBHCl{\cdot}NMe_3$ or between CH_2Cl_2 solutions of $ThxBCl_2{\cdot}NMe_3$ and $ThxBHCl{\cdot}NMe_3$ at room temperature.

Hydroboration/Methanolysis of 1-Hexene with $ThxBHCl/Et_2O$. To 10 mmol of freshly prepared $ThxBHCl/Et_2O$ at 0 °C was added 1.40 mL of neat 1-hexene (11 mmol). The reaction mixture was stirred for 90 min at 0 °C, and then 0.84 mL of pyridine (10.5 mmol) and 1.26 mL of absolute methanol (30 mmol) were added. A white precipitate formed immediately, but only a little gas evolution was observed. The reaction mixture was warmed to room temperature. The ^{11}B NMR spectrum of the ethereal supernatant solution showed that trialkylborane (δ 84.2, $ThxB(n\text{-}C_6H_{13})_2$), dialkylborinate (δ 54.1, $ThxB(n\text{-}C_6H_{13})OMe$), and alkylboronate (δ 29.1, $ThxB(OMe)_2$) species were present. The precipitate of pyridinium hydrochloride was removed by filtration. The remaining ethereal filtrate was reduced to a clear liquid on a water aspirator and dissolved in 5 mL of CH_2Cl_2. Quantitative ^1H NMR analysis after the addition of 1.06 mL of toluene (10 mmol, internal standard) showed the formation of 4.3 mmol (43%) of $ThxB(n\text{-}C_6H_{13})OMe$ with CH_3O–B resonance at δ 3.67 and 2.4 mmol (24%) of $ThxB(OMe)_2$ with CH_3O–B resonance at δ 3.58. Assuming that the amount of $ThxB(n\text{-}C_6H_{13})_2$ formed was equal to that of $ThxB(OMe)_2$, a mass balance of 91% was realized.

Rate of Reaction of 2,3-Dimethyl-2-butene with $BH_2Cl{\cdot}SMe_2$ in CH_2Cl_2. A 25-mL round-bottom flask equipped with magnetic stirring bar, septum-covered side arm, and connector tube leading to a mercury bubbler was charged at 25 °C with 1.16 mL of 8.6 M $BH_2Cl{\cdot}SMe_2$ (10 mmol), 0.89 mL of *n*-nonane (4.66 mmol, internal standard), and 1.75 mL of CH_2Cl_2. The resulting clear solution was stirred at 25 °C for 30 min, and then 1.20 mL of neat 2,3-dimethyl-2-butene (10 mmol) was added via syringe. The overall initial concentration of reactants was 2.0 M. Addition of the alkene caused an exothermic reaction sufficient to reflux the solution. Aliquots of 0.25 mL were withdrawn at specified intervals, quenched by injection into 3 mL of acetone at −78 °C, and then analyzed for residual olefin by GLC. The amount of alkene consumed was calculated for each interval from the amount of residual olefin obtained. The results are summarized in Table V.

To avoid the exotherm problem, we repeated the experiment by adding neat 2,3-dimethyl-2-butene to a CH_2Cl_2 solution of $BH_2Cl{\cdot}SMe_2$ and *n*-nonane maintained at 0 °C. When the addition of alkene was complete, the ice–water bath was removed, and the reaction mixture was stirred at room temperature. Aliquots were removed and analyzed as above. The reaction was found to be 99% complete after 1 h at room temperature (Table V). No additional uptake of 2,3-dimethyl-2-butene was observed under these conditions when a twofold excess was employed in the reaction.

Preparation of 2.0 M $ThxBHCl{\cdot}SMe_2$ in CH_2Cl_2. A standard 2.0 M solution of $ThxBHCl{\cdot}SMe_2$ in CH_2Cl_2 was prepared as follows. A 25-mL round-bottom flask equipped with magnetic stirring bar, septum-covered sidearm, and connector tube leading to a mercury bubbler was charged at 0 °C with 3.0 mL of CH_2Cl_2 and 1.16 mL of 8.6 M $BH_2Cl{\cdot}SMe_2$ (10 mmol). The resulting clear

solution was stirred at 0 °C for 30 min. Then, 1.30 mL of neat 2,3-dimethyl-2-butene (11 mmol) was added via syringe. The reaction mixture was then stirred at room temperature for 1 h. ^{11}B NMR of this solution showed only a doublet (J_{BH} = 128 Hz) at δ 6.89. The infrared spectrum of this solution showed a strong terminal B–H absorption at 2450 cm^{-1}. No bridged B–H absorption at 1565 cm^{-1} was observed.

Oxidation of ThxBHCl·SMe_2 in CH_2Cl_2. To 10.0 mmol of freshly prepared ThxBHCl·SMe_2 was added successively at 0 °C 0.97 mL of *n*-decane (5.0 mmol, internal standard), 8.0 mL of 3 N aqueous NaOH (24 mmol), 20 mL of absolute ethanol, and 4.0 mL of 30% aqueous hydrogen peroxide (40 mmol). After 1 h at 0 °C, the reaction mixture was heated at 50 °C for 30 min and then cooled to room temperature. Absolute ether (20 mL) was added and the aqueous layer was saturated with potassium carbonate. GLC analysis of the ether layer showed the formation of 9.5 mmol (95%) of 2,3-dimethyl-2-butanol.

Methanolysis of ThxBHCl·SMe_2 in CH_2Cl_2. Freshly prepared ThxBHCl·SMe_2 (10 mmol) was cooled to 0 °C and treated with 0.84 mL of pyridine (10.5 mmol) and 1.06 mL of toluene (10 mmol, internal standard). The resulting clear solution was stirred at 0 °C for 15 min. Then 1.26 mL of absolute methanol (30 mmol) was added. A white precipitate formed immediately as a vigorous evolution of gas occurred. After warming to room temperature, the white precipitate was collected by filtration, air-dried, and weighed; 1.06 g (9.2 mmol) was obtained. The ^1H NMR spectrum of this material was identical with that of an authentic sample of pyridinium hydrochloride. Quantitative ^1H NMR analysis of the remaining ethereal filtrate showed a nearly quantitative (9.2 mmol) yield of ThxB$(OMe)_2$ was obtained with CH_3O–B resonance at δ 3.58. ^{11}B NMR spectroscopy of this solution showed only a singlet at δ 29.1. No $(MeO)_3B$ species was observed.

When 10 mmol of freshly prepared ThxBHCl·SMe_2 in CH_2Cl_2 was treated with 0.84 mL of absolute methanol (20 mmol) at 0 °C in a flask connected to a gas buret, 11 mmol of hydrogen evolved.

Hydroboration/Methanolysis of 1-Hexene with ThxBHCl·SMe_2. To 10 mmol of freshly prepared ThxBHCl·SMe_2 in CH_2Cl_2 at 0 °C was added 1.40 mL of neat 1-hexene (11 mmol). The reaction mixture was stirred at room temperature for 2.5 h. The ^{11}B NMR spectrum of this solution showed the complete consumption of ThxBHCl·SMe_2 and the appearance of a broad singlet at δ 78.0. The reaction was cooled to 0 °C and treated with 0.84 mL of pyridine (10.5 mmol) and 0.43 mL of absolute methanol (10.5 mmol). After warming to room temperature, the precipitate of pyridinium hydrochloride was collected by filtration and air-dried to give a white solid (1.06 g, 9.21 mmol). The ^{11}B NMR spectrum of the remaining ethereal filtrate showed only a singlet at δ 58.2 corresponding to the desired dialkylborinate product. No trialkylborane, alkylboronate, or borate species were observed. Quantitative ^1H NMR analysis after the addition of 1.06 mL of toluene (10 mmol, internal standard) showed the clean formation of 9.23 mmol (92%) of ThxB(*n*-C_6H_{13})OMe with CH_3O–B resonance at δ 3.65.

Directive Effects in the Hydroboration of Alkenes with ThxBHCl·SMe_2 in CH_2Cl_2 (Table VI). The procedure employed for 1-hexene is representative. To 10 mmol of freshly prepared 2.0 M ThxBHCl·SMe_2 in CH_2Cl_2 at 0 °C was added 2.75 mL of CH_2Cl_2 and 1.00 mL of *n*-tridecane (4.10 mmol, internal standard). The resulting clear solution was stirred at 0 °C for 30 min, and then 1.25 mL of neat 1-hexene (10 mmol) was added. The overall concentration of reactants then was 1.0 M. The resulting solution was stirred at room temperature for 60–90 min and then recooled to 0 °C. Oxidation was carried out by successive addition of 8.0 mL of 3 N aqueous NaOH (24 mmol), 7.5 mL of absolute ethanol, and 4.0 mL of 30% aqueous hydrogen peroxide (40 mmol). After 1 h at 0 °C, the reaction mixture was heated at 50 °C for 30 min and then recooled to room temperature. Absolute ethyl ether (7.5 mL) was added, and the aqueous layer was saturated with potassium carbonate. The relative amounts of isomeric hexanols were determined by GLC analysis of the ether layer. The results are summarized in Table VI.

Registry No. BH_2Cl·THF, 55606-72-9; BH_2Cl·OEt_2, 36594-41-9; $HBCl_2$·NMe_3, 25741-83-7; BH_2Cl·SMe_2, 63348-81-2; BCl_3·OEt_2, 2102-03-6; $(ThxBH_2)_2$, 37099-64-2; $ThxBCl_2$, 79200-82-1; ThxBHCl·OEt_2, 79200-86-5; $ThxBH_2$·NMe_3, 79200-87-6; ThxBHCl·NMe_3, 79200-88-7; $ThxBCl_2$·NMe_3, 79200-89-8; ThxBHCl·SMe_2, 75067-06-0; ThxBHCl·THF, 79200-90-1; ThxB$(OMe)_2$, 56118-62-8; $ThxBCl_2$·SMe_2, 79200-91-2; $ThxBH_2$, 3688-24-2; ThxB(*n*-C_6H_{13})OMe, 79200-83-2; 2,3-dimethyl-2-butene, 563-79-1; 1-hexene, 592-41-6; 1-octene, 111-66-0; 1-decene, 872-05-9; 2-methyl-1-butene, 563-46-2; 2-methyl-2-butene, 513-35-9; *cis*-2-pentene, 627-20-3; 1-hexanol, 111-27-3; 1-octanol, 111-87-5; 1-decanol, 112-30-1; 2-methyl-1-butanol, 137-32-6; 3-methyl-2-butanol, 598-75-4; 2-pentanol, 6032-29-7; 3-pentanol, 584-02-1; 2,3-dimethyl-2-butanol, 594-60-5.