using 1-hexyne is described as the typical example. The reaction flask was set up as in the previous experiment. BH_2Cl (10 mmol) in EE (7.4 ml) and 1.4 ml of EE were introduced into the flask. The mixture was stirred at 0 °C, and 10 mmol of 1-hexyne (1.15 ml) was added, and stirring was continued at 0 °C. (The mixture was 1.0 M in reactants.) Aliquots (1 ml) were withdrawn at 15 min and 1 h and analyzed for residual hydride by hydrolyzing and measuring the hydrogen evolved. Another aliquot taken at 15 min at 0 °C was analyzed for the presence of residual 1-hexyne by GC. After 1 h at 0 °C, the reaction mixture was brought to 25 °C. After 1 h at 25 °C, another 1-ml aliquot was analyzed for the residual hydride. The experiment was repeated using cyclohexylethyne, phenylethyne, and 3-hexyne.

References and Notes

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Hydroboration. XLI. Hydroboration of Alkenes and Alkynes with Dichloroborane Etherates. Convenient Procedures for the Preparation of Alkyl- and Alkenyldichloroboranes and Their Derivatives[1]

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Abstract: Reactions of alkenes with dichloroborane ethyl etherate ($BHCl_2$·EE) and alkynes with dichloroborane tetrahydrofuranate ($BHCl_2$·THF) and $BHCl_2$·EE were investigated in detail. The hydroboration of alkenes with $BHCl_2$·EE in ether or pentane is slow and incomplete. However, the reaction goes to completion when neat reagents are allowed to react, but the resulting product is predominantly the dialkylchloroborane (R_2BCl) and not the expected alkyldichloroborane ($RBCl_2$). In the presence of 1 mol equiv of boron trichloride in pentane, the alkenes and $BHCl_2$·EE react quantitatively to give the expected products $RBCl_2$ and boron trichloride ethyl etherate (BCl_3·EE) cleanly. A series of alkyldichloroboranes and their derivatives have been synthesized and isolated by this new convenient procedure. Similarly, the reactions of alkynes with $BHCl_2$·THF and $BHCl_2$·EE are also slow and incomplete and give mixed products. As in the case of alkenes, the alkynes also react with $BHCl_2$·EE quantitatively in the presence of 1 mol equiv of BCl_3 in pentane to yield the expected alkenyldichloroborane cleanly. These developments provide for the first time convenient low-temperature procedures for the general syntheses of alkyl- and alkenyldichloroboranes and their derivatives.

Introduction

Hydroboration of alkenes with borane–tetrahydrofuran (BH_3·THF) produces trialkylboranes.[3] The dialkyl- and dialkenylboron derivatives are easily prepared by the hydroboration of alkenes and alkynes, respectively, with monochloroborane ethyl etherate (BH_2Cl·EE).[4] However, no such convenient simple procedures are available for the preparation of monoalkyl- and monoalkenylboron derivatives. The hydroboration of alkenes and alkynes with a monofunctional borane, HBX_2, might produce such monoorganoboron compounds. In view of the synthetic utility of the triorganoboranes[3] and diorganoboron derivatives,[5-9] it is to be anticipated that the monoorganoboron derivatives should also find useful applications in organic syntheses. Therefore, the reactions of dichloroborane etherates with alkenes and alkynes were investigated in detail, and the results of that study are reported here.

Dichloroborane etherates were first reported by Brown and Tierney.[10] A few scant investigations of the reactions of a few alkenes with $BHCl_2$·THF have been reported by other workers[11,12] who have found that the reactions were extremely slow. Thus, in the reaction of $BHCl_2$·THF with 1-hexene at 25 °C after 4 h, only 40% olefin underwent hydroboration, according to Zweifel,[11] and only 15% 1-hexanol was obtained after oxidation, according to Pasto and Balasubramaniyan.[12] Similarly, only 50% reaction was observed for 2-methylpropene in 24 h and only 27% reaction with styrene in 72 h. Therefore, the reaction of $BHCl_2$ in

THF with alkenes is extremely slow, much more so than the corresponding reaction of BH_2Cl in THF. This is not surprising because $BHCl_2$ is expected to be a stronger Lewis acid, more strongly complexed than BH_2Cl with THF. The stronger the complexation of the reagent with the solvent, the lesser its reactivity toward olefins. Since our own investigations of the reaction of BH_2Cl in THF with alkenes did not yield the desired result, we did not examine the hydroboration of alkenes with $BHCl_2$ in THF. We successfully hydroborated alkenes with BH_2Cl in ethyl ether to obtain R_2BCl cleanly.[4] Therefore, we studied the hydroboration of alkenes only with $BHCl_2{\cdot}EE$.

Since no study had been reported on the hydroboration of alkynes with dichloroboranes, we investigated this reaction employing both reagents, $BHCl_2{\cdot}THF$ and $BHCl_2{\cdot}EE$.

Results and Discussion

Hydroboration of Alkenes with $BHCl_2$ in Diethyl Ether (EE). The $BHCl_2$ solution in ethyl ether (EE) was prepared by the reaction of $LiBH_4$ in EE with BCl_3 in EE at 0 °C:

$$LiBH_4 + 3BCl_3 + 4EE \xrightarrow[0\ {}^\circ C]{EE} 4BHCl_2{\cdot}EE + LiCl\downarrow \quad (1)$$

On standing, the LiCl settled, leaving a clear solution of $BHCl_2$ in EE. The strength of the $BHCl_2$ solution was determined by hydrolyzing an aliquot and measuring the hydrogen evolved and, also, by titrating the HCl produced in the hydrolysis of $BHCl_2$. A stock solution prepared this way was 1.84 M in $BHCl_2$ (Cl/H = 1.99, expected Cl/H = 2.00). ^{11}B NMR spectrum of the solution displayed a symmetrical doublet at −8.05 ± 0.1 ppm relative to $BF_3{\cdot}OEt_2$ with J_{BH} = 164 Hz. Heteronuclear spin decoupling produced a singlet. (Trace amounts of BCl_3 and BH_2Cl could be seen in the decoupled spectrum.) The purity of the sample was estimated to be >95%. The solution was stored in a cold room where it was stable for several months.

The reaction was studied using 1-hexene as the alkene by adding $BHCl_2$ in EE to 1-hexene (1:1) in EE and stirring at the desired temperature. The reaction mixture contained a known amount of *n*-octane to serve as internal standard for GC analysis. The solution was 1.0 M in reactants. Aliquots were withdrawn at intervals and analyzed for the residual 1-hexene by GC. The results are given in Table I. The reaction was slow and incomplete. Therefore, no attempt was made to characterize the products formed. Apparently, the complexation of $BHCl_2$ with EE is strong enough to reduce severely its reactivity with the olefin, unlike the case of $BH_2Cl{\cdot}EE$.[4]

Hydroboration of Alkenes with Neat Dichloroborane Diethyl Etherate ($BHCl_2{\cdot}EE$). It was thought if the reaction could be done with neat $BHCl_2{\cdot}EE$ in the absence of excess EE, the hydroboration might go faster than in the solution. Neat $BHCl_2{\cdot}EE$ was prepared by removing the excess EE under vacuum from a solution of $BHCl_2{\cdot}EE$ in EE containing about 10% excess BCl_3. The reagent is a liquid. One milliliter of the neat $BHCl_2{\cdot}EE$ on hydrolysis gave 6.60 mmol of hydrogen and 14.35 mmol of hydrochloric acid. This corresponds to the presence of about 6% $BCl_3{\cdot}EE$ as impurity. The neat reagent is 6.60 M in $BHCl_2{\cdot}EE$. ^1H NMR of $BHCl_2{\cdot}EE$ in CCl_4 solution gave a quartet at δ 4.45 (4 H) and a triplet at δ 1.53 (6 H). The presence of $BCl_3{\cdot}EE$ could not be detected by ^1H NMR. ^{11}B NMR spectrum of neat $BHCl_2{\cdot}EE$ displayed a doublet (somewhat distorted due to the overlap of $BCl_3{\cdot}EE$ resonance) at −8.0 ± 0.2 ppm relative to $BF_3{\cdot}EE$ with J_{BH} = 163 Hz. Proton heteronuclear spin decoupling produced a singlet. The presence of $BCl_3{\cdot}EE$ could be clearly seen in the decoupled spectrum. This analysis assured us that the reagent was of satisfactory purity. $BHCl_2{\cdot}EE$ is miscible with benzene, CCl_4, and EE, but not with pentane or other saturated hydrocarbons. The neat reagent does not remain stable at room temperature for more than 2 days, but can be stored in a cold room for a few weeks without any noticeable change. However, one sample which had been kept in the cold room was found to have deteriorated when examined after about 10 weeks.

Table I. Reaction of $BHCl_2$ with 1-Hexene in Diethyl Ether

$BHCl_2{\cdot}EE$ concn, M	1-Hexene concn, M	Temp, °C	Time, h	1-Hexene reacted, %
1.0	1.0	0	24	31
1.0	1.0	25	24	70
1.0	1.0	~40[a]	26	90

[a] Refluxing ethyl ether solution.

Table II. Reaction of 1-Hexene with Neat[a] Dichloroborane Diethyl Etherate at 25 °C

Time, h	1	2	5	17	24
1-Hexene utilized, %	60	73	85	98	98

[a] A small quantity of *n*-octane was present in the reaction mixture.

The rate of reaction of 1-hexene with neat $BHCl_2{\cdot}EE$ was studied by stirring the two reactants neat in a 1:1 ratio at 25 °C (in the presence of a known amount of *n*-octane to serve as internal standard for GC analysis) and withdrawing the aliquots at intervals and analyzing for the unreacted 1-hexene by GC. (1-Hexene and $BHCl_2{\cdot}EE$ were immiscible. Therefore, it was a two-phase inhomogeneous reaction.) Toward the end of the reaction, a small amount of a white solid was found in the reaction flask. The results are given in Table II. Although 60% 1-hexene reacted in 1 h, almost 17 h was needed for the olefin to undergo the reaction completely. Since the reaction proceeded ultimately to completion, a product study was made in the reaction of 1-butene with neat $BHCl_2{\cdot}EE$. In an experiment using 20 mmol of $BHCl_2{\cdot}EE$ and 20 mmol of 1-butene at 25 °C, methanolysis of the mixture after 10 h gave 8.9 mmol of *n*-Bu_2BOCH_3 and 1.41 mmol of *n*-$BuB(OCH_3)_2$, corresponding to a yield of 96% in butyl groups. The *B*-methoxy compounds were derived from the corresponding *B*-chloro compounds by methanolysis. Thus, oddly enough, the major product of the reaction of neat $BHCl_2{\cdot}EE$ with olefin under these conditions is the dialkylchloroborane and not the expected monoalkyldichloroborane.

Hydroboration of Alkenes with $BHCl_2{\cdot}EE$ in Benzene Solution. The formation of the unexpected product, R_2BCl, in the above experiment might be due to the long reaction time needed, which in turn might be a consequence of the immiscibility of the two reactants. Therefore, it was thought that the reaction might go faster under homogeneous reaction conditions to give the expected product, $RBCl_2$. $BHCl_2{\cdot}EE$ was found to be miscible with benzene. Therefore, the hydroboration of 1-octene with $BHCl_2{\cdot}EE$ in benzene solution was studied. The reaction was carried out by adding neat $BHCl_2{\cdot}EE$ to a solution of 1-octene and a known amount of *n*-decane (internal standard for GC analysis) in benzene and stirring at 25 °C. The solution was 1.0 M in reactants. Aliquots were withdrawn at intervals and analyzed by GC for the residual 1-octene. The results are given in Table III. Even though more than 50% 1-octene reacted in 15 min, 6 h was required for 97% of the 1-octene to undergo the reaction. Still, this was very encouraging. Therefore, the product was analyzed in the reaction of 1-butene with $BHCl_2{\cdot}EE$ in benzene at 25 °C. After 6 h of re-

Table III. Reaction of 1-Octene with $BHCl_2 \cdot EE$ in Benzene Solution at 25 °C

Time, h	0.25	1.0	2.0	6.0	20.0
1-Octene utilized, %	57	74	91	97	98

Table IV. Reaction of Representative Alkenes with $BHCl_2 \cdot EE$ in the Presence of BCl_3 in Pentane

Alkene	Time, min	Alkene reacted, %
1-Octene	15[a]	93
	15[b]	100
cis-2-Octene	15[a]	85
	15[b]	99
2-Methyl-1-pentene	15[a]	90
	15[b]	100
2-Methyl-2-butene	15[a]	96
	15[b]	99
2,3-Dimethyl-2-butene	15[a]	84
	15[b]	97
Cyclohexene	15[a]	88
	15[b]	99
Styrene	15[a]	87
	15[b]	100

[a] At 0 °C. [b] 15 min at 0 °C followed by 15 min at 25 °C.

action (1.0 M in the reactants), the product was exclusively *n*-Bu_2BCl (analyzed as *n*-Bu_2BOCH_3 by GC after methanolysis) formed in quantitative yield.

These investigations established that in the reaction of dichloroborane diethyl etherate ($BHCl_2 \cdot EE$) with olefins, neat or in solution, little of the expected product $RBCl_2$ was produced. The unexpected product, R_2BCl, was formed as the major product in these reactions. The formation of R_2BCl can be rationalized on the assumption that $BHCl_2 \cdot EE$ remains in equilibrium with small quantities of $BH_2Cl \cdot EE$ and $BCl_3 \cdot EE$ (eq 2). We have reported previously[4] that $BH_2Cl \cdot EE$ hydroborates olefins very rapidly to give R_2BCl. Therefore, all of the $BHCl_2 \cdot EE$ disproportionates to BH_2Cl and BCl_3 prior to the reaction with olefin. The white solid formed in the prolonged reaction of neat $BHCl_2 \cdot EE$ with 1-hexene must be $BCl_3 \cdot EE$, the other product of the disproportionation of $BH_2Cl \cdot EE$.

$$2BHCl_2 \cdot EE \rightleftharpoons BH_2Cl \cdot EE + BCl_3 \cdot EE \qquad (2)$$

Hydroboration of Alkenes with $BHCl_2 \cdot EE$ in the Presence of BCl_3 in Pentane. From the low-field position of the OCH_2 proton resonance in the ^1H NMR spectrum of $BHCl_2 \cdot EE$ (δ 4.45), it is clear that there is strong complexation between the basic oxygen of the ether molecule and the acidic boron of the $BHCl_2$ molecule. This strong complexation should naturally render the $BHCl_2$ very unreactive toward olefins. Therefore, we reasoned that if we could remove the ether molecule by complexing it with a stronger Lewis acid, say BCl_3, and generate the free $BHCl_2$ in the presence of the olefin, the hydroboration of the olefin with $BHCl_2$ would take place in normal fashion to produce the expected product, $RBCl_2$ (eq 3).

$$\begin{array}{c} BHCl_2 \cdot EE + BCl_3 \rightarrow BCl_3 \cdot EE + BHCl_2 \\ \underline{BHCl_2 + 1\text{-butene} \rightarrow n\text{-}BuBCl_2} \\ BHCl_2 \cdot EE + BCl_3 + 1\text{-butene} \rightarrow BCl_3 \cdot EE + n\text{-}BuBCl_2 \end{array} \qquad (3)$$

$BCl_3 \cdot EE$ is virtually insoluble in pentane. Therefore, if the reaction goes cleanly in pentane, the pentane solution of $RBCl_2$ could be easily separated from the crystalline $BCl_3 \cdot EE$ providing a simple synthesis of alkyldichloroboranes.

Table V. Directive Effects in the Hydroboration of 1-Hexene and Styrene with Various Reagents

	Relative yield of alcohols, %			
	1-Hexene		Styrene	
Reagent	Terminal	Internal	Terminal	Internal
$BHCl_2$ (in pentane)[a]	99.7	0.3	96.3	3.7
$BHCl_2 \cdot THF$	99.0[b]	1.0[b]	94.0[c]	6.0[c]
$BH_2Cl \cdot EE$[d]	99.5	0.5	96.0	4.0
$BH_3 \cdot THF$[e]	94.0	6.0	80.0	20.0
Sia_2BH[e]	99.0	1.0	98.0	2.0

[a] Present work. [b] Reference 12. [c] Reference 11. [d] Reference 4. [e] Reference 3; Sia_2BH, disiamylborane.

Accordingly, the reaction of olefins with $BHCl_2 \cdot EE$ in the presence of BCl_3 in pentane solution was studied. First, the rate of reaction of 1-octene was examined. $BHCl_2 \cdot EE$ (5 mmol) was slowly added to a mixture of 5 mmol of 1-octene, 2.5 mmol *n*-decane (internal standard for GC analysis), and 5 mmol of BCl_3 in pentane (total volume, 10 ml) at 0 °C with vigorous stirring. As soon as the $BHCl_2 \cdot EE$ was added, a white thick solid, presumably $BCl_3 \cdot EE$, started depositing on the sides of the flask. Aliquots of the solution were withdrawn and analyzed for the residual 1-octene by GC. Within 5 min after the addition of $BHCl_2 \cdot EE$, 90% 1-octene had undergone reaction. However, thereafter the reaction slowed down considerably. In 15 min, only 93% 1-octene had undergone reaction. Afterward, on stirring the reaction mixture at 25 °C for 15 min, all of the 1-octene underwent reaction. Thus, the reaction is quite fast under these conditions.

The experiment was repeated using 1-butene, and the reaction mixture was methanolyzed and analyzed for the products by GC. The yield of *n*-$BuB(OCH_3)_2$ was 90%, and only a trace of *n*-Bu_2BOCH_3 was detected. (The methanolysis transformed *n*-$BuBCl_2$ into *n*-$BuB(OCH_3)_2$.) This result shows that the product of the reaction of 1-butene with $BHCl_2$ under these conditions is the desired product, *n*-$BuBCl_2$. These findings strongly suggested that this approach would provide a simple and convenient synthesis of alkyldichloroboranes. Accordingly, the generality of the reaction was studied using a representative list of olefins. The results are given in Table IV. The olefins examined all underwent reaction similar to 1-octene. Representative alkyldichloroboranes were synthesized and isolated using this method. (See the section on the synthesis of alkyldichloroboranes and dimethyl alkylboronates.)

Directive Effects in the Hydroboration of Alkenes with $BHCl_2 \cdot EE$ in the Presence of BCl_3 in Pentane. Owing to its strong electrophilic character, $BHCl_2$ is expected to exhibit a pronounced directive effect in the hydroboration. Therefore, this aspect was briefly examined in the reaction of $BHCl_2$ with 1-hexene and styrene. The procedure was to carry out the hydroboration as in the case of 1-octene and to oxidize the alkyldichloroboranes to the alcohols with $NaOH-H_2O_2$ using ethanol as the cosolvent. The isomeric terminal and internal alcohols produced were analyzed by GC using a suitable internal standard. The results are given in Table V along with the data in THF and other similar data for comparison. Although the reagent exhibits strong selectivity, the effect is not greatly pronounced over that of $BH_2Cl \cdot EE$ or even $BHCl_2$ in THF. $BHCl_2$ (in pentane), BH_2Cl in EE, and disiamylborane in THF, all show comparable directive effects in the hydroboration of alkenes.

Synthesis of Alkyldichloroboranes and Dimethyl Alkylboronates. The data presented in Table IV show that the reaction of olefins with $BHCl_2 \cdot EE$ in the presence of BCl_3 in pentane is facile and would provide a very convenient general synthesis of alkyldichloroboranes ($RBCl_2$). Since $RBCl_2$ readily undergoes solvolysis with water or alcohols, this method could also be adopted for the preparation of alkylboronic acids and their derivatives (eq 4 and 5).

$$RBCl_2 + 2H_2O \rightarrow RB(OH)_2 + 2HCl \qquad (4)$$

$$RBCl_2 + 2R'OH \rightarrow RB(OR')_2 + 2HCl \qquad (5)$$

Accordingly, a series of monoalkyldichloroboranes and dimethyl alkylboronates were synthesized using this reaction. The results are given in Table VI.

The reaction goes to essential completion in all cases examined. The clear solution of $RBCl_2$ in pentane is decanted or filtered from the crystalline $BCl_3{\cdot}EE$ formed during the reaction. The $RBCl_2$ is easily purified by distillation. The reaction mixture is directly methanolyzed (without removing the $BCl_3{\cdot}EE$) for the preparation of the boronates.

The conventional methods for the synthesis of $RBCl_2$ are the exchange reaction of BCl_3 and BR_3 in the presence of boron hydrides at elevated temperatures,[13,14] the reaction of trialkylboroxines with BCl_3,[15] and the reaction of tetraalkyltin compounds with BCl_3.[16] These are time-consuming, multistep syntheses, and generally the overall yields are low. During the redistribution reaction of BR_3 and BCl_3 in the presence of boron hydrides at elevated temperatures, the boron atoms tend to migrate from internal carbon atoms toward terminal carbon atoms of the alkyl group.[14] It is evident that the isolation of pure $RBCl_2$ is essential if these are to be used as intermediates in organic synthesis. The procedure described here is very simple, and the $RBCl_2$ is obtained in essentially pure form in pentane solution, applicable directly for further synthetic operations. Since the development of this procedure, many applications of $RBCl_2$ as intermediates in organic syntheses have been uncovered.[17-20]

Monohydroboration of Alkynes with $BHCl_2$ Etherates. Monohydroboration of alkynes with $BHCl_2$ would produce the alkenyldichloroboranes. The reaction was studied using $BHCl_2$ in THF, $BHCl_2$ in EE, neat $BHCl_2{\cdot}EE$, and $BHCl_2{\cdot}EE$ in the presence of BCl_3 in pentane.

Monohydroboration of 1-Hexyne with $BHCl_2$ in Tetrahydrofuran. $BHCl_2$ in THF for these studies was prepared by the reaction of diborane in THF with BCl_3 in tetrahydropyran (THP)[12] (eq 6).

$$B_2H_6 + 4BCl_3 + 6THF \xrightarrow{\text{THF-THP}} 6BHCl_2{\cdot}THF \qquad (6)$$

The ^{11}B NMR spectrum of the solution gave a doublet at -7.0 ± 0.05 ppm (relative to $BF_3{\cdot}EE$) with $J_{BH} = 162$ Hz. Proton heteronuclear spin decoupling gave a singlet. Trace amounts of $BCl_3{\cdot}THF$ and $BH_2Cl{\cdot}THF$ could be detected in the decoupled spectrum. The reagent was estimated to be >95% pure.

The rate of reaction of 1-hexyne with $BHCl_2$ in THF was studied. The reaction involved adding 1-hexyne to $BHCl_2$ (1:1) in THF and stirring at the desired temperature (0 or 25 °C). The reaction mixture contained 22% THP by volume and a known amount of *n*-octane to serve as internal standard for GC analysis. The solution was 1.0 M in reactants. Aliquots were withdrawn after specified periods of time, and the residual hydride and alkyne were analyzed by hydrolysis and GLC, respectively. The reaction was extremely slow. At 0 °C in 24 h, only 18% hydride and 18% alkyne underwent reaction. At 25 °C in 48 h, 75% hydride and 76% alkyne reacted. The 1:1 ratio of the hydride and alkyne reaction indicates that the product is the alkenyldichloroborane. Since the reaction did not go to completion, no further attempt was made to characterize the product.

Table VI. Synthesis of Alkyldichloroboranes and Dimethyl Alkylboronates by the Hydroboration of Alkenes with Dichloroborane

$RBCl_2$[a]/$RB(OCH_3)_2$	Yield, %	Bp, °C (mm)
1-Bu-$B(OCH_3)_2$	90[b]	
2-Bu-$B(OCH_3)_2$	88[b]	
2-Me-1-Pr-$B(OCH_3)_2$	97[b]	
1-Hex-BCl_2	81[c]	102–104 (100)
3-Hex-BCl_2	77[c]	88–90 (102)
exo-Norbornyl-BCl_2[d]	83[c]	95–98 (50)
c-Pent-BCl_2	79[c]	136–138 (751)
c-Pent-$B(OCH_3)_2$	76[c]	76–78 (40)
2-Me-1-Bu-BCl_2	87[c]	110–112 (746)

[a] $RBCl_2$ was identified by methanolyzing and characterizing the $RB(OCH_3)_2$ formed by ^1H NMR; $B(OCH_3)_2$ proton resonance at δ 3.55. In all cases the methoxy protons and the alkyl protons integrated correctly. [b] GC yield. [c] Isolated yield. [d] Stereochemistry established by oxidation to *exo*-norbornanol using H_2O_2–NaOH.

Monohydroboration of 1-Hexyne with $BHCl_2$ in Diethyl Ether. The reaction was studied by measuring the rate of disappearance of 1-hexyne in the reaction with $BHCl_2$ in EE at 0 and 25 °C using a 0.74 M solution of the two reactants. The reaction in this case also was very slow. In 24 h at 0 °C, 15% 1-hexyne and in 72 h at 25 °C, 90% 1-hexyne disappeared from the reaction mixture. Since the reaction was extremely slow, no attempts were made to identify the products in this reaction.

Reaction of 1-Hexyne with Neat $BHCl_2{\cdot}EE$ (1:1) in Pentane at 25 °C. The reaction of 1-hexyne with neat $BHCl_2{\cdot}EE$ in 1:1 ratio in pentane at 25 °C was studied by following the 1-hexyne uptake by GC. The reaction mixture was inhomogeneous due to the immiscibility of $BHCl_2{\cdot}EE$ in pentane. The pentane solution was 1.0 M in 1-hexyne. The reaction was slow, but 95% 1-hexyne reacted in 12 h. ^1H NMR spectrum of the crude product, obtained after the methanolysis of the reaction mixture, shows that the product was a mixture of dialkenylchloroborane, alkenyldichloroborane, and the dihydroboration product. The major component was the expected alkenyldichloroborane. Since the reaction was not clean, no further studies were made in this case.

Monohydroboration of Alkynes with $BHCl_2{\cdot}EE$ in the Presence of BCl_3 in Pentane. Since we had been successful with the reaction of alkenes with $BHCl_2{\cdot}EE$ in the presence of BCl_3 to obtain the alkyldichloroboranes, the corresponding reaction with alkynes was studied to see whether or not the alkenyldichloroboranes could be synthesized this way. As the procedure involved the addition of $BHCl_2{\cdot}EE$ to a solution of BCl_3 and alkyne in pentane, first the stability of 1-hexyne in the presence of BCl_3 in pentane was studied. It was found that little or no 1-hexyne was destroyed by BCl_3 during short periods of contact at 0 °C (15 min), but considerable loss of 1-hexyne occurred over longer periods of time at 25 °C.

The reaction of 1-hexyne and 3-hexyne with $BHCl_2{\cdot}EE$ in the presence of BCl_3 in pentane was studied. The procedure involved the addition of 5 mmol of $BHCl_2{\cdot}EE$ to a solution of 5 mmol of alkyne, 2.5 mmol of *n*-octane (internal standard for GC analysis), and 5 mmol of BCl_3 in pentane at 0 °C while being stirred vigorously. The reaction mixture was 0.5 M in reactants. As soon as the $BHCl_2{\cdot}EE$ was added, solid $BCl_3{\cdot}EE$ started depositing on the sides of the flask. Aliquots were withdrawn after 15 min and analyzed for residual alkyne by GC. After 15 min at 0 °C, the reaction mixture was brought to 25 °C and the analysis for residual alkyne repeated with an aliquot withdrawn after 1 h at 25 °C. At the end of this time, the residual hydride was measured in a 2 ml aliquot of the reaction mixture by hydrolyzing and measuring the hydrogen evolved. The results

Table VII. Reaction of Alkynes with Nascent $BHCl_2$ Generated in Solution by the Reaction of $BHCl_2 \cdot EE$ with BCl_3 in Pentane (0.5 M Alkyne, 0.5 M BCl_3, and 0.5 M $BHCl_2$)

Alkyne	Time, h	Alkyne reacted, %	Hydride remaining, %	Alkenyldichloroborane, and %[c]
1-Hexyne	0.25[a]	92.5		
	1.00[b]	95.5	0.00	91
3-Hexyne	0.25[a]	94.0		
	1.00[b]	97.0	0.00	94

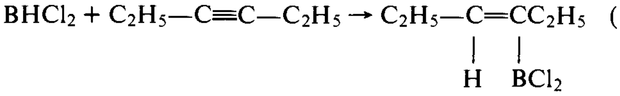
[a] At 0 °C. [b] The reaction mixture was stirred at 0 °C for 15 min, followed by 1 h at 25 °C. [c] Expected yield.

are given in Table VII. More than 90% alkyne reacted in 15 min at 0 °C in both cases. On warming the reaction mixture to 25 °C and stirring for 1 h, the reaction went virtually to completion, as indicated by the fact that no residual hydride remained in the reaction mixture at the end of this time. From the stoichiometry of the reaction, the formation of the alkenyldichloroboranes evidently proceeds in yields of more than 90% in both cases.

As expected, the free $BHCl_2$, formed in situ by the reaction of $BHCl_2 \cdot EE$ with BCl_3, reacts with the alkyne to form the alkenyldichloroborane (eq 7–9).

$$BHCl_2 \cdot EE + BCl_3 \rightarrow BCl_3 \cdot EE + BHCl_2 \tag{7}$$

$$BHCl_2 + n\text{-}C_4H_9-C\equiv CH \rightarrow n\text{-}C_4H_9-CH=CH-BCl_2 \tag{8}$$



$$BHCl_2 + C_2H_5-C\equiv C-C_2H_5 \rightarrow C_2H_5-\underset{\substack{|\\ H}}{C}=\underset{\substack{|\\ BCl_2}}{C}C_2H_5 \tag{9}$$

To avoid the formation of minor amounts of the dihydroboration products, it is recommended that some 10% excess alkyne be used.

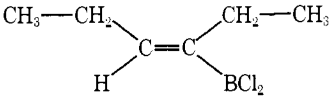
Synthesis of Alkenyldichloroboranes. *trans*-1-Hexenyldichloroborane and *cis*-3-hexenyldichloroborane were synthesized by this procedure and isolated. The procedure was very simple. The $BHCl_2 \cdot EE$ was added to a mixture of an equivalent amount of BCl_3 and 10% excess alkyne in pentane at 0 °C (~0.5 M in each reactant). The reaction mixture was stirred vigorously for 15 min at 0 °C, followed by 1 h at 25 °C. The mixture was then cooled to 0 °C, and the pentane solution of the alkenyldichloroborane was separated from the solid $BCl_3 \cdot EE$ under nitrogen. The pentane was removed under vacuum, and the alkenyldichloroborane was purified by distillation at low pressure. The product was characterized by ^1H NMR. The results are given in Table VIII. The reaction was so clean that the crude product obtained by removing the solvent gave a clean ^1H NMR spectrum. The crude product could be used directly for further synthetic operations, if desired.

The alkenyldichloroboranes do not seem to be very stable compounds suitable for storing. They distill colorless, but quickly turn yellow and finally red.

The hydrolysis and alcoholysis of the alkenyldichloroboranes would give the corresponding alkenylboronic acids and their esters, respectively (eq 10–13). The dimethylboronates derived from the two alkenyldichloroboranes were prepared by methanolysis and characterized by ^1H NMR. (In addition to the vinyl and alkyl proton resonances, these show strong $B(OCH_3)_2$ proton resonance at δ 3.58.)

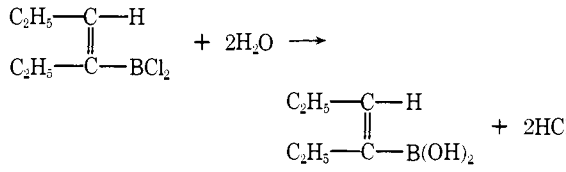
The synthesis of ethenyldichloroborane by the reaction of BCl_3 with diethenylzinc[21] and also by the reaction of BCl_3 with tetraethenyltin[22] has been reported. A general method for the synthesis of alkenyldichloroboranes has not been available. The procedure developed here is very convenient and could be very general starting with the alkynes.

Table VIII. Synthesis of Alkenyldichloroboranes by the Monohydroboration of Alkynes with Dichloroborane

Alkenyldichloroborane[a]	Isolated yield, %	Bp, °C (mm)
trans-1-Hexenyldichloroborane	69	66–68 (18)
	83	56–58 (17)

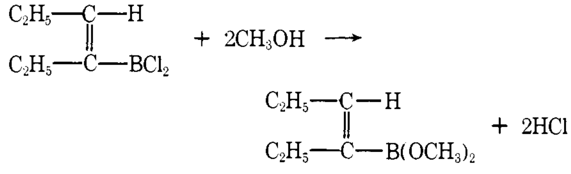
[a] The products were characterized by ^1H NMR and protonolysis, followed by the identification of the resulting olefin by GC.

$$CH_3(CH_2)_3CH{=}CHBCl_2 + 2H_2O \longrightarrow CH_3(CH_2)_3CH{=}CHB(OH)_2 + 2HCl \tag{10}$$



$$\begin{array}{l} C_2H_5-C-H \\ \qquad \| \\ C_2H_5-C-BCl_2 \end{array} + 2H_2O \longrightarrow \begin{array}{l} C_2H_5-C-H \\ \qquad \| \\ C_2H_5-C-B(OH)_2 \end{array} + 2HCl \tag{11}$$

$$CH_3(CH_2)_3CH{=}CHBCl_2 + 2CH_3OH \longrightarrow CH_3(CH_2)_3CH{=}CHB(OCH_3)_2 + 2HCl \tag{12}$$



$$\begin{array}{l} C_2H_5-C-H \\ \qquad \| \\ C_2H_5-C-BCl_2 \end{array} + 2CH_3OH \longrightarrow \begin{array}{l} C_2H_5-C-H \\ \qquad \| \\ C_2H_5-C-B(OCH_3)_2 \end{array} + 2HCl \tag{13}$$

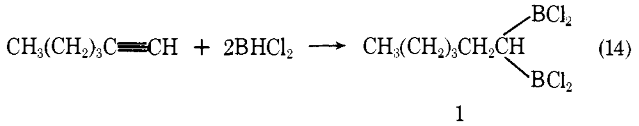
The ready availability of alkenyldichloroboranes by this simple procedure will facilitate the further exploration of the chemistry of these interesting new organoboron compounds and their derivatives.

Dihydroboration of Alkynes with $BHCl_2 \cdot EE$ in the Presence of BCl_3 in Pentane. The reaction of alkyne with $BHCl_2$ in 1:2 ratio would give the dihydroboration product. The reactions of 1-hexyne and 3-hexyne with $BHCl_2$ in 1:2 ratio of the reagents were studied in pentane. The reaction was carried out by adding 10 mmol of $BHCl_2 \cdot EE$ to a mixture of 5 mmol of alkyne and 10 mmol of BCl_3 in pentane at 0 °C (1.0 M $BHCl_2$ and 0.5 M in alkyne). Five minutes after the addition of $BHCl_2 \cdot EE$, a small aliquot was analyzed for the residual alkyne by GC. It was found that all the alkyne had disappeared from the reaction mixture. Aliquots (2 ml) were analyzed for residual hydride at 15 min and 1 h after the addition of $BHCl_2 \cdot EE$. Afterwards, the reaction mixture was brought to 25 °C and analyzed for residual hydride in a 2-ml aliquot withdrawn after 1 h at 25 °C. The results are given in Table IX. All the alkyne underwent hydroboration within 5 min. More than 92% hydride underwent reaction in 1 h at 0 °C in both cases. The reaction went virtually to completion at the end of 1 h at 25 °C. The quantitative disappearance of the alkyne and the hydride from the reaction mixture indicates that complete dihydroboration of the alkyne has taken place. ^1H NMR spectrum of the crude product, obtained by removing the solvent, did not show the presence of vinyl protons in the product. This means that the triple bond in the alkyne was completely hydroborated (dihydroboration). Since it is known that in the dihydroboration of alkynes the major product has the two boron atoms on the same carbon atom,[23] the product in the dihydroboration of 1-hexyne with $BHCl_2$ will have the structure **1** (eq 14). The crude product from the dihydrobo-

Table IX. Dihydroboration of Alkynes with $BHCl_2 \cdot EE$ in the Presence of BCl_3 in Pentane (0.5 M Alkyne, 1.0 M $BHCl_2$)

Alkyne	Time, h	Aliquot, ml	Alkyne reacted, mmol	Hydride reacted, mmol	Hydride used/ alkyne used	Dihydroboration product, %[b]
1-Hexyne	0.25	2.0	1.00	1.72	1.72	72
	1.00	2.0	1.00	1.84	1.84	84
	1.00[a]	2.0	1.00	1.96	1.96	96
3-Hexyne	0.25	2.0	1.00	1.76	1.76	76
	1.00	2.0	1.00	1.92	1.92	92
	1.00[a]	2.0	1.00	1.96	1.96	96

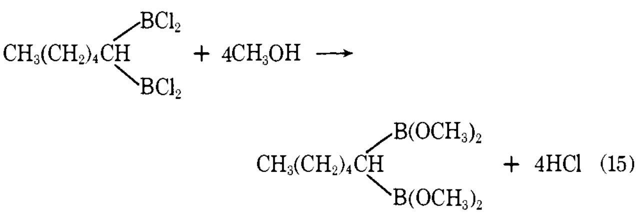
[a] The reaction was carried out at 0 °C for 1 h, followed by 1 h at 25 °C. [b] Expected yield.



$$CH_3(CH_2)_3C{\equiv}CH + 2BHCl_2 \longrightarrow CH_3(CH_2)_3CH_2CH(BCl_2)_2 \quad (14)$$

1

ration of 1-hexyne with $BHCl_2$ was methanolyzed, and the ^1H NMR spectrum of the methanolyzed product was taken. The spectrum showed a single at δ 3.55 due to $B(OCH_3)_2$ protons (12 H) and a broad multiplet between δ 0.7 and 1.8 due to the alkyl protons (12 H). This indicates that the methanolysis product has the structure **2** (eq 15).



$$CH_3(CH_2)_4CH(BCl_2)_2 + 4CH_3OH \longrightarrow CH_3(CH_2)_4CH[B(OCH_3)_2]_2 + 4HCl \quad (15)$$

2

No additional effort was made to characterize the products from the dihydroboration of alkynes with $BHCl_2$. The 1,1-diboraalkanes and their derivatives would prove to be useful intermediates for synthesizing organometallic and organic compounds.[23-25]

Experimental Section

Materials and analytical techniques used in this work were the same as those used in the study of the hydroboration with BH_2Cl etherates reported previously.[4] The same equipment was also used for spectral measurements. The only additional material used in this study was *n*-pentane, Phillips '66 Petroleum Co., 99% pure, dried over Type 4A molecular sieves. Solutions of $LiBH_4$ and BCl_3 in EE used in this work also were prepared according to the procedure described previously.[4]

Preparation of BCl_3 Solution in Pentane. The experimental setup was the same as in the preparation of BCl_3 solution in EE, described in the experimental section of the previous report.[4] Dry pentane (500 ml) was used instead of diethyl ether. The solution prepared in this way was 2.22 M in BCl_3. The solution was stored in a cold room where the strength maintained over several months. During the course of the work, stock solutions of different strengths were prepared and used at different times.

Preparation of BCl_3 Solution in Tetrahydropyran (THP). The same experimental setup as in the above was used. Freshly double-distilled dry THP (500 ml) was used in place of pentane. The strengths of the solutions prepared at various times varied from 2 to 4 M. Always freshly prepared solutions of BCl_3 in THP were used.

Preparation of $BHCl_2$.Solution in Diethyl Ether. In a 1-l. round-bottom flask, oven dried, equipped with a rubber stoppled side arm, and a connecting tube attached to a mercury bubbler, was taken, under an atmosphere of nitrogen at 0 °C, 600 mmol of BCl_3 in EE (420 ml). $LiBH_4$ (200 mmol) in EE (148 ml) was slowly added to it while stirring the contents at 0 °C. (The reagents were introduced into the flask through the rubber stopple using large hypodermic syringes.) Stirring was continued at 0 °C for 4 h after the addition of $LiBH_4$ was over. On keeping the reaction mixture still for a few hours, the LiCl settled, leaving clear supernate of $BHCl_2$ in EE. An aliquot of the clear solution was analyzed for the hydride content by hydrolyzing and measuring the hydrogen evolved. The chloride was estimated by hydrolyzing an aliquot and titrating the HCl produced with $NaHCO_3$ using methyl orange indicator. The solution was found to be 1.4 M in hydride and 2.82 M in chloride ($\overline{Cl}/\overline{H}$ = 2.02, expected Cl/H = 2.00). Therefore the solution was 1.4 M in $BHCl_2$. The ^{11}B NMR spectrum of the solution indicated that it is >95% pure. (Symmetrical doublet at −8.05 ± 0.1 relative to BF_3·EE with J_{BH} = 164 Hz. Proton heteronuclear spin decoupling produced a singlet. Trace quantity of BH_2Cl and BCl_3 could be seen in the decoupled spectrum.) The solution under nitrogen was stored in a cold room where it was found to remain unchanged for several months (virtually no change in strength during several months).

Table X. Analysis of Neat $BHCl_2 \cdot EE$ Reagent

Sample no.	Aliquots used for analysis, ml	Hydride, mmol	Chloride, mmol	Estimated $BCl_3 \cdot EE$ present, mol %
I	1.0	6.66	14.10	4
II	1.0	6.60	14.35	6

Preparation of Neat $BHCl_2$·EE. A clean 500-ml round-bottom flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled under a stream of nitrogen. The flask was immersed in an ice bath. Then 350 mmol of $BHCl_2$ in EE (250 ml) and 35 mmol of BCl_3 in EE (25 ml) were introduced into the flask and stirred for 15 min at 0 °C. The excess EE was removed under vacuum (15 mm) using a water aspirator at 25 °C. The preparation of EE was continued until constant weight of the flask and the contents were realized (6–8 h). The neat $BHCl_2$·EE thus obtained was.a colorless liquid. The reagent was analyzed for the hydride content by hydrolyzing an aliquot and measuring the hydrogen gas evolved. The chloride was analyzed by hydrolysis and followed by the titration of the HCl produced with $NaHCO_3$ using methyl orange indicator. Two different samples of $BHCl_2$·EE prepared according to this procedure gave the analysis given in Table X. The neat reagent prepared was generally 6.6 M in $BHCl_2$·EE and contained about 4–6 mol % of BCl_3·EE as impurity. The ir spectrum of neat $BHCl_2$·EE showed strong absorption at 2542 cm^{-1} (B–H stretching). ^1H NMR spectrum of the sample in CCl_4 gave a quartet at δ 4.45 (4 H) and a triplet at δ 1.35 (6 H). ^{11}B NMR spectrum of the neat sample displayed a doublet (somewhat distorted due to the overlap of the BCl_3·EE resonance) at −8.0 ± 0.2 ppm (relative to BF_3·EE) with J_{BH} = 163 Hz. Proton heteronuclear spin decoupling gave a large singlet due to $BHCl_2$·EE and a smaller singlet at lower field due to BCl_3·EE. The reagent is miscible with benzene, CCl_4, and EE, but not with pentane or other saturated hydrocarbons. The material did not remain stable at room temperature for more than 2 days. Therefore, it was stored in a cold room where it was found to remain unchanged for a few weeks. (However, it must be mentioned here that one sample which had been stored in the cold room was found to have deteriorated when examined after 10 weeks.)

Preparation of Stock Solution of $BHCl_2$ in THF–THP Mixture. The experimental setup was the same as that used in the preparation of $BHCl_2$ solution in EE. BH_3 (516 mmol) in THF[26] (170 ml) was introduced into the flask first. Then 1032 mmol of BCl_3 in

THF (25 ml) was slowly added to the flask while stirring at 0 °C. After stirring for 1 h, the mixture was stored in a cold room for overnight. The next morning the strength of the solution was determined as in the case of $BHCl_2$·EE. The strength was 3.6 M in $BHCl_2$ ($\overline{\mathrm{Cl}}/\overline{\mathrm{H}} = 2.02$, expected $\overline{\mathrm{Cl}}/\overline{\mathrm{H}} = 2.0$). The stock solution was 60% THP and 40% THF by volume. In the cold room, the solution was found to remain stable to loss of hydride. (Virtually there was no measurable change in hydride concentration after 8 months.) ^{11}B NMR spectrum of the solution indicated it to be >95% pure (symmetrical doublet at −7.0 ± 0.05 ppm relative to BF_3·EE with $J_{BH} = 162$ Hz; proton heteronuclear spin decoupling produced a singlet). Stock solutions of different strengths were prepared and used at different times during the course of the work.

Rate of Reaction of 1-Hexene with $BHCl_2$ in EE. A clean 100-ml flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled under a stream of nitrogen. The reaction flask was immersed in an ice bath. EE (166 ml), 10 mmol of 1-hexene (1.26 ml), and 10 mmol of *n*-octane (1.63 ml, internal standard for GC analysis) were introduced into the flask through the rubber stopple using hypodermic syringes. $BHCl_2$ (10 mmol) in EE (5.45 ml) was added, and the reaction mixture was stirred at 0 °C. Aliquots were withdrawn and analyzed for the residual 1-hexene by GC after destroying the chloroborane using aqueous NaOH at 0 °C. The reaction was very slow. Only 31% 1-hexene reacted in 24 h.

For the reaction at 25 °C, a water bath at room temperature was used. For the reaction at reflux, the reagents were mixed at 25 °C and then heated to reflux using a heating mantle while stirring the reaction mixture.

Rate of Reaction of 1-Hexene with Neat $BHCl_2$·EE at 25 °C. A clean 100-ml flask, dried in an oven, equipped with a side arm fitted with a rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled to 25 °C under a stream of nitrogen by immersing in a water bath. Then 20 mmol of neat $BHCl_2$·EE (3.03 ml), 20 mmol of *n*-octane (3.26 ml as internal standard for GC analysis), and 20 mmol of 1-hexene (2.52 ml) were introduced through the rubber stopple using hypodermic syringes. The mixture was stirred at 25 °C and aliquots were withdrawn at intervals and analyzed by GC for residual 1-hexene after destroying the chloroboranes in the aliquot using aqueous NaOH at 0 °C. Toward the end of the reaction, a white solid started depositing on the sides of the flask. This might be BCl_3·EE.

Rate of Reaction of 1-Octene with $BHCl_2$·EE in Benzene Solution at 25 °C. A clean 100-ml flask, dried in an oven, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled to 25 °C under a stream of nitrogen by immersing in a water bath. 1-Octene (5 mmol, 0.785 ml), 2.5 mmol of *n*-decane (0.488 ml, internal standard for GC analysis), and 2.93 ml of benzene were introduced through the stopple using hypodermic syringes. The mixture was stirred at 25 °C, and 5 mmol of $BHCl_2$·EE (0.8 ml) was added, and stirring was continued at 25 °C. Aliquots were withdrawn at intervals and analyzed for residual 1-octene by GC after destroying the chloroboranes using aqueous NaOH at 0 °C. 1-Octene (97%) underwent reaction in 6 h.

Analysis of Methanolysis Products of Reaction of 1-Butene with Neat $BHCl_2$·EE at 25 °C. A clean 100-ml flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and connected to a mercury bubbler through a connecting tube with a stopcock closing the mouth of the flask, was cooled under a stream of nitrogen. The flask was immersed in a bath at 25 °C. Neat $BHCl_2$·EE (20 mmol, 3.03 ml) and 4 mmol of tridecane (0.975 ml, internal standard for GC analysis) were introduced into the flask through the stopple using a hypodermic syringe. The stopcock was closed and 20 mmol of 1-butene was added to the flask as gas using a gas syringe.[27] The mixture was stirred at 25 °C for 10 h. The stopcock was opened, and 4 ml of methanol was added to methanolyze the reaction products. After stirring for 15 min at 25 °C, 7 ml of Et_3N was added to neutralize the HCl produced by the methanolysis of chloroboranes. The mixture was diluted with 10 ml of EE, and the clear supernate was analyzed by GC for *n*-$BuB(OCH_3)_2$ and *n*-Bu_2BOCH_3 on SE-30 column. *n*-Bu_2BOCH_3 (8.9 mmol) and 1.41 mmol of *n*-$BuB(OCH_3)_2$ were obtained corresponding to a total yield of 96% butyl groups.

Analysis of the Methanolysis Products of the Reaction of 1-Butene with $BHCl_2$·EE in Benzene Solution at 25 °C. The experimental setup and procedure were the same as in the above experiment. In the flask were taken 4.10 ml of benzene and 0.5 mmol of tridecane (0.122 ml, internal standard for GC analysis). $BHCl_2$·EE (5 mmol, 0.8 ml) was added and stirred at 25 °C. Then as in the above experiment, 5 mmol of 1-butene was added as gas, and the reaction mixture was stirred for 6 h at 25 °C. Methanol (3 ml) was used for methanolysis, and 5 ml of Et_3N was used for neutralizing the HCl. Analysis was done exactly as in the above experiment. *n*-Bu_2BOCH_3 (2.60 mmol) was obtained (104%). Only traces of *n*-$BuB(OCH_3)_2$ were detected.

Rate of Reaction of Representative Olefins with $BHCl_2$·EE in the Presence of BCl_3 in Pentane. The experiment using 1-octene is described as the typical example. A clean 100-ml flask, dried in an oven, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in a stream of nitrogen. The flask was immersed in an ice bath. *n*-Pentane (5.43 ml), 5 mmol of 1-octene (0.785 ml), 2.5 mmol of *n*-decane (0.488 ml, internal standard for GC analysis), and 5 mmol of BCl_3 in pentane (2.5 ml) were introduced into the flask through the rubber stopple using hypodermic syringes. The mixture was stirred vigorously at 0 °C and 5 mmol of $BHCl_2$·EE (0.8 ml) was slowly added. (BCl_3·EE started depositing on the sides of the flask while $BHCl_2$·EE was being added. The solution was 0.5 M in $BHCl_2$ and 1-octene. This dilute reagent concentration was used because stirring with a magnetic stirrer was easier under this dilution due to the solid formation.) Aliquots were withdrawn at 5 and 15 min after the addition of $BHCl_2$·EE. After 15 min at 0 °C, the reaction mixture was brought to 25 °C, and stirring was continued vigorously at this temperature. Another aliquot was withdrawn after 15 min at 25 °C. All the aliquots were analyzed for residual 1-octene by GC (SE-30) after destroying the chloroboranes using aqueous NaOH at 0 °C. The experiment was repeated using the other olefins.

Analysis of the Methanolysis Products of the Reaction of Butene with $BHCl_2$·EE in the Presence of BCl_3 in Pentane. The experiment using 1-butene is described as a typical example. A clean 100-ml flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and connected to a mercury bubbler through a connecting tube with a stopcock closing the mouth of the flask, was cooled in an ice bath under a stream of nitrogen. *n*-Pentane (6.4 ml), 0.5 mmol of tridecane (0.122 ml, internal standard for GC analysis), and 5 mmol of BCl_3 in pentane (2.5 ml) were introduced into the flask through the rubber stopple using hypodermic syringes. The mixture was stirred at 0 °C. 1-Butene (5 mmol) was added to the flask as gas using a gas syringe,[27] after closing the stopcock on the connecting tube. The mixture was stirred for 15 min at 0 °C to let the gas dissolve in pentane. Neat $BHCl_2$·EE (5 mmol, 0.8 ml) was then slowly added at 0 °C while vigorously stirring the contents of the flask. After 15 min at 0 °C, the flask was brought to 25 °C, and stirring was continued for another 15 min at this temperature. The reaction mixture was then methanolyzed by adding 3 ml of CH_3OH (after opening the stopcock). Five minutes after this, 5 ml of Et_3N was added to neutralize the HCl formed by the methanolysis of chloroboranes. The supernate was analyzed by GC (SE-30 Column B) for *n*-$BuB(OCH_3)_2$ and *n*-Bu_2BOCH_3. *n*-$BuB(OCH_3)_2$ (4.5 mmol) and 0.29 mmol of *n*-Bu_2BOCH_3 were obtained, corresponding to a total yield of 101% based on butyl groups. The experiment was repeated using *cis*-2-butene and isobutylene and analyzed for the corresponding alkylboron compounds.

Directive Effect in the Hydroboration of 1-Hexene and Styrene with $BHCl_2$·EE in the Presence of BCl_3 in Pentane. A clean 100-ml flask, dried in an oven, equipped with a side arm fitted with a rubber serum stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled in a stream of nitrogen. The flask was immersed in an ice bath and charged with 11.2 ml of *n*-pentane, 10 mmol of 1-hexene (1.26 ml), 5 mmol of *n*-octane (0.815 ml, internal standard for GC analysis), and 10 mmol of BCl_3 in pentane (5 ml). $BHCl_2$·EE (10 mmol, 1.52 ml) was then slowly added, while the reaction mixture was being stirred vigorously. After 15 min at 0 °C, the ice bath was replaced by a water bath at 25 °C, and vigorous stirring was continued at 25 °C for 15 min. The stirring was then stopped, and 10 ml of the clear supernate was transferred using a hypodermic syringe into another flask equipped and set up exactly as the reaction flask. EtOH (20 ml), 6 ml of 3 N NaOH, and 2 ml of 30% H_2O_2 were then added to the second flask and stirred at 25 °C for 1 h for oxidizing the organoboron compound. The oxidation was completed by heating the flask at 50 °C for 30 min. The organic layer was then analyzed by GC (Carbowax column) for 1-hexanol and 2-hexanol. Total yield of the alcohols was 99.4%, which consisted of 99.7% 1-hexanol and 0.3% 2-hexanol.

The experiment was repeated using 10 mmol of styrene instead of 1-hexene. In this case, after oxidation, the reaction mixture was analyzed for 2-phenylethanol and 1-phenylethanol. The total yield of the alcohols in this case was 98.6%, containing 96.3% 2-phenylethanol and 3.7% 1-phenylethanol.

Synthesis of Alkyldichloroboranes and Dimethyl Alkylboronates. The syntheses of cyclopentyldichloroborane and dimethyl cyclopentylboronate are described as typical examples. A clean 300-ml round-bottom flask, oven dried, equipped with a side arm fitted with a rubber serum stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in an ice bath under a stream of nitrogen. The flask was charged with 127 ml of pure dry pentane, 100 mmol of cyclopentene (7.8 ml), and 100 mmol of BCl_3 in pentane (50 ml). The mixture was stirred at 0 °C for 5 min. $BHCl_2$·EE (100 mmol, 15.1 ml) was slowly added over a period of 15 min while vigorously stirring the contents of the flask. Stirring was continued for 15 min at 0 °C after the addition of $BHCl_2$·EE was over. The ice bath was then replaced by a water bath at 25 °C, and stirring was continued for another 15 min at this temperature. The contents of the flask were then cooled to 0 °C, and the pentane solution of the cyclopentyldichloroborane was syphoned into another flask kept under nitrogen through a glass tube fitted with a fritted disk under a positive pressure of nitrogen, leaving the solid BCl_3·EE in the reaction flask. The BCl_3·EE in the flask was washed twice with pentane at 0 °C, and the washings were collected with the main solution in the second flask. The pentane was then removed using a water aspirator, and the cyclopentyldichloroborane was purified by distillation at 136–138 °C at atmospheric pressure (751 mm). The product was obtained in 79% yield. The purity of the product was checked by methanolysis, followed by the analysis of the dimethyl cyclopentylboronate by ^{1}H NMR.

For the synthesis of dimethyl cyclopentylboronate, the above method was followed. After stirring at 25 °C for 15 min, the reaction mixture was cooled to 0 °C and 50 ml of methanol was added slowly while stirring. Stirring was continued for 30 min at 0 °C after the addition of methanol. The pentane, HCl, the excess methanol, and the $B(OCH_3)_3$ (produced by the methanolysis of BCl_3) were removed using a water aspirator, and the dimethyl cyclopentylboronate was distilled at 76–78 °C at 40 mm. The product was obtained in 76% yield. The material was identified by ^{1}H NMR.

A series of alkyldichloroboranes and dimethyl alkylboronates were synthesized by this procedure.

Rate of Reaction of 1-Hexyne with $BHCl_2$ (1:1) in THF–THP Mixture. The experimental setup was the same as in the previous experiments for rate measurements. $BHCl_2$ (30 mmol) in THF–THP mixture (10.8 ml) and 30 mmol of *n*-octane (4.89 ml, internal standard for GC analysis), and 10.86 ml of THF were introduced into the flask. 1-Hexyne (30 mmol, 3.45 ml) was then added, and the mixture was stirred at 0 or 25 °C, as the case may be. (The reaction mixture is 1.0 M in reactants.) Aliquots (1 ml) were withdrawn at intervals and analyzed for residual hydride (hydrolyzing and measuring the hydrogen evolved) and for residual 1-hexyne by GC (after destroying the chloroboranes using aqueous NaOH at 0 °C). The reaction was very slow (only 18% reaction in 24 h at 0 °C and 75% reaction in 48 h at 25 °C).

Rate of Reaction of 1-Hexyne with $BHCl_2$ (1:1) in EE. The experimental setup and procedure were exactly as in the previous case. $BHCl_2$ (8 mmol) in EE (9.2 ml) and 4 mmol of *n*-octane (0.65 ml, internal standard for GC analysis) were introduced into the flask. 1-Hexyne (8 mmol, 0.92 ml) was then added, and the reaction mixture was stirred at 0 or 25 °C, as desired. The solution was 0.75 M in reactants. Aliquots were withdrawn at intervals and analyzed for residual 1-hexyne by GC (after destroying the chloroboranes using aqueous NaOH at 0 °C). The reaction was very slow (only 15% reaction in 24 h at 0 °C and 90% reaction in 72 h at 25 °C).

Table XI. Stability of 1-Hexyne in the Presence of BCl_3 in Pentane (0.5 M in 1-Hexyne and BCl_3)

Time	1-Hexyne remaining, %	Time	1-Hexyne remaining, %
1 min	98	1.0 h	90
5 min	98	1.0 h[a]	79
15 min	96	18.0 h[b]	63

[a] The mixture was stirred at 0 °C for 1 h, followed by 1 h at 25 °C.
[b] The mixture was stirred at 0 °C for 1 h, followed by 18 h at 25 °C.

Reaction of 1-Hexyne with Neat $BHCl_2$·EE (1:1) in Pentane at 25 °C. The reaction flask was set up as in the previous experiment. 1-Hexyne (10 mmol, 1.15 ml), 5 mmol of *n*-octane (0.814 ml, internal standard for GC analysis), and 6.5 ml of pentane were introduced into the flask. $BHCl_2$·EE (10 mmol, 1.6 ml) was then added, and the reaction mixture was stirred at 25 °C. Aliquots were withdrawn at intervals and analyzed for residual 1-hexyne by GC after destroying the chloroboranes using aqueous NaOH at 0 °C. The reaction was slow, but 95% 1-hexyne reacted in 12 h.

The experiment was repeated without using *n*-octane. After 12 h of reaction, 3 ml of methanol was added and stirred for 15 min. The pentane and excess methanol were pumped off using a water aspirator. The ^{1}H NMR spectrum of the residue indicated that it is a mixture of the *B*-methoxy derivatives of the dialkenylchloroborane, alkenyldichloroborane, and also the dihydroboration product. The major component was the *B*-methoxy derivative of the expected alkenyldichloroborane.

Stability of 1-Hexyne in the Presence of BCl_3 in Pentane. To the reaction flask, set up as described in the previous experiment, were introduced 10 mmol of 1-hexyne (1.15 ml), 5 mmol of *n*-octane (0.814 ml, internal standard for GC analysis), 13 ml of pentane, and 10 mmol of BCl_3 in pentane (5 ml), and the mixture was stirred at 0 °C (0.5 M in 1-hexyne and BCl_3). Aliquots were withdrawn at intervals and analyzed for 1-hexyne by GC after destroying the BCl_3 using aqueous NaOH at 0 °C. After 1 h at 0 °C, the mixture was brought to 25 °C and analysis was continued for 1-hexyne in aliquots withdrawn at intervals. The results are given in Table XI. The results show that 1-hexyne is not significantly destroyed by BCl_3 during short periods of contact at 0 °C in pentane, but considerable destruction of 1-hexyne does occur over long periods of contact with BCl_3 at 25 °C.

Reaction of Alkynes with $BHCl_2$·EE in the Presence of BCl_3 in Pentane. The experiment using 1-hexyne is described as a typical example. The reaction flask was set up as in the previous experiment. The flask was cooled to 0 °C. Pentane (5.725 ml), 5 mmol of 1-hexyne (0.575 ml), 2.5 mmol of *n*-octane (0.407 ml, internal standard for GC analysis), and 5 mmol of BCl_3 in pentane (2.5 ml) were introduced into the flask. $BHCl_2$·EE (5 mmol, 0.8 ml) was immediately added to the flask while stirring the contents of the flask vigorously at 0 °C. As soon as the $BHCl_2$·EE was added, solid BCl_3·EE started depositing on the sides of the flask. Fifteen minutes after the addition of $BHCl_2$·EE, an aliquot of the solution was withdrawn and analyzed for residual 1-hexyne by GC after destroying the chloroboranes using aqueous NaOH at 0 °C. Afterward, the reaction mixture was brought to 25 °C and stirred vigorously for 1 h at 25 °C. Another aliquot was withdrawn and analyzed for the residual 1-hexyne. The residual hydride in another aliquot withdrawn at this time was analyzed by hydrolyzing and measuring the hydrogen evolved. The experiment was repeated using 5 mmol of 3-hexyne in place of 1-hexyne.

Synthesis of Alkenyldichloroboranes. The synthesis of *trans*-1-hexenyldichloroborane is described as a typical example. A clean 200-ml flask, oven dried, equipped with a side arm fitted with a rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in an ice bath under a stream of nitrogen. 1-Hexyne (77 mmol, 8.85 ml, 10% excess), 85 ml of pentane, and 70 mmol of BCl_3 in pentane (35 ml) were introduced into the flask. While stirring vigorously at 0 °C, 70 mmol of $BHCl_2$·EE (11.2 ml) was slowly added when solid BCl_3·EE started depositing on the sides of the flask. Stirring was continued for 15 min at 0 °C, followed by 1 h at 25 °C. The contents of the flask were cooled to 0 °C, and the pentane solution of *trans*-1-hexenyldichloroborane was syphoned into another dry flask kept under nitrogen through a glass tube fitted with a fritted disk, leaving the solid $BCl_3 \cdot EE$ in the reaction flask. The $BCl_3 \cdot EE$ in the reaction flask was washed twice with pentane at 0 °C, and the washings were added to the main solution in the second flask. Pentane was then removed using a water aspirator and the product was distilled at 66–68 °C at 18 mm over an 8 in. Vigreaux column (to prevent frothing over). The *trans*-1-hexenyldichloroborane was obtained in 69% yield, which was identified by ^1H NMR. The *cis*-3-hexenyldichloroborane was synthesized (83% yield, bp 56–58 °C at 17 mm) and identified in exactly the same way starting with 3-hexyne.

The corresponding *B*-dimethoxy derivatives were prepared by adding a drop of methanol to a drop of the alkenyldichloroborane in CCl_4, taken in an NMR tube (5 mm o.d.). The *B*-dimethoxy derivatives were identified by ^1H NMR of the sample [$B(OCH_3)_2$ proton resonance at δ 3.58].

Dihydroboration of Alkynes with $BHCl_2 \cdot EE$ in the Presence of BCl_3 in Pentane. The experiment using 1-hexyne is described as the typical example. A 100-ml reaction flask was set up as described in the previous experiment. Pentane (2.825 ml), 5 mmol of 1-hexyne (0.575 ml), and 10 mmol of BCl_3 in pentane (5 ml) were introduced into the flask. While stirring vigorously at 0 °C, 10 mmol of $BHCl_2 \cdot EE$ (1.6 ml) was slowly added. Within 5 min after the addition of $BHCl_2$, a small aliquot was withdrawn and analyzed for any residual 1-hexyne by GC after destroying the chloroboranes using aqueous NaOH at 0 °C. Aliquots (2 ml) were withdrawn at 15 min and 1 h at 0 °C and analyzed for residual hydride by hydrolyzing and measuring the hydrogen evolved. Afterwards, the reaction mixture was brought to 25 °C and stirred vigorously for 1 h. A 2-ml aliquot was withdrawn at this time and analyzed for residual hydride. The experiment was repeated using 3-hexyne in place of 1-hexyne.

At the end of 1 h at 25 °C, 5 ml of methanol was added to the 1-hexyne reaction mixture and stirred for 15 min. The pentane and other volatile materials were removed using a water aspirator, and the ^1H NMR spectrum of the crude product was examined. The spectrum displayed a singlet at δ 3.55 (12 H) due to $B(OCH_3)_2$ protons and a broad multiplet between δ 0.7 and 1.8 (12 H) due to alkyl protons.

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The Palladium(II) Catalyzed Olefin Carbonylation Reaction. The Stereochemistry of Methoxypalladation[1]

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Abstract: The reaction of carbon monoxide with *cis*- and *trans*-2-butene at 2–3 atm in methanol in the presence of a catalytic amount of palladium(II) chloride and copper(II) chloride as reoxidant yielded, in the initial stages of the reactions, methyl *threo*- and *erythro*-3-methoxy-2-methylbutanoate, respectively. These results demonstrated that stereospecific trans methoxypalladation is the exclusive reaction pathway. Addition of equimolar amounts of sodium acetate to the reaction mixture completely changed the course of the reaction. Carbonylation of *trans*-2-butene gave exclusively *dl*-dimethyl 2,3-dimethylsuccinate while *cis*-2-butene afforded only the meso diastereomer. Stereospecific cis carbomethoxypalladation was therefore the exclusive reaction pathway.

The addition of nucleophiles to monoolefin–transition metal complexes is an important type of synthetic reaction.[3-6] Whereas the nucleophilic addition to a diolefin complex produces a stable σ-bonded enyl complex, the analogous σ-bonded complex from reaction of a monoolefin is generally unstable and decomposes because of the absence of chelation. In the case of the diolefins, the stereochemistry of the addition with a variety of nucleophiles is trans.[7-10] It has been argued,[11-13] however, that the chelating diolefins are atypical, and the stereochemical results cannot be extended to monoolefins since approach of an external nucleophile from the cis side presents steric problems. The trans stereochemistry has also been attributed to the inability of the chelating diolefins to rotate 90° from the position perpendicular to the square plane of the metal complex to a position which would favor cis addition of the metal and a ligand attached to it.[14] In the Wacker process, the kinetics of oxidation of olefins suggest, but do not require, the cis hydroxypalladation of olefins.[11,15]

The addition–elimination reaction of olefins presents a dichotomy of mechanistic results in that many of the reactions are consistent with either a cis addition, cis elimina-