than Mo, and the electrochemical data also supports this claim. The calculations as well as the spectra indicate that the buildup of negative charge on the carbonyl oxygen is increased for W compounds relative to Mo compounds, and the head-to-tail coupling of $W_2(\mu\text{-CO})$ to $[W_2(\mu\text{-CO})]_2$ compounds is easily rationalized in view of these observations. Thus, these calculations on a series of related compounds have allowed for the correlation of our experimental data, improved our insight into the chemical bonding and reactivity, and stimulated our imagination for future experimentation.

The stepwise reaction involving $W{\equiv}W + C{\equiv}O \rightarrow W_2(\mu\text{-CO})$ followed by $2W_2(\mu\text{-CO}) \rightarrow [W_2(\mu\text{-CO})]_2$ converts $W{\equiv}W$ and $C{\equiv}O$ triple bonds first into double bonds and then into single bonds. Formally the ditungsten center is oxidized $(W{\equiv}W)^{6+} \rightarrow (W{=}W)^{8+} \rightarrow (W{-}W)^{10+}$, and the carbonyl moiety is reduced. This C—O reduction requires the cooperative effects of two ditungsten centers. We believe that the reaction does not stop here, but by further reaction between $(W{\equiv}W)^{6+}$ and $[W_2(\mu\text{-CO})]_2$, the C—O bond of the former carbon monoxide molecule is cleaved to give carbido (C^{4-}) and oxo (O^{2-}) tungsten alkoxide clusters. These matters are currently under investigation. In this regard we note that we have recently observed a facile $C{\equiv}O$ bond cleavage reaction between $(i\text{-PrO})_3W_2(\mu\text{-CSiMe}_3)_2$ and $C{\equiv}O$ leading to the formation of $(i\text{-PrO})_4W(\mu\text{-}\sigma,\pi\text{-CCSiMe}_3)(\mu\text{-CSiMe}_3)W(O\text{-}i\text{-Pr})(=O)$. This represents the first example of the stoichiometric cleavage of $C{\equiv}O$ in a homogeneous reaction at room temperature.[29]

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Registry No. I (M = Mo, R = H), 103671-07-4; I (M = W, R = H), 103671-08-5; I (M = W, R = *t*-Bu), 95674-36-5; I (M = Mo, T = *t*-Bu), 66775-48-2; II (M = W, R = CH_2-*t*-Bu), 95674-37-6; II (M = Mo, R = CH_2-*t*-Bu), 83437-05-2; II (M = Mo, R = Pr-*i*), 83437-00-7; IIIa (R = Pr-*i*), 85956-37-2; IIIb (R = H), 103671-11-0; IIIb (R = CH_2-*t*-Bu), 103692-70-2; IIIb (R = Pr-*i*), 95674-38-7; $Mo_2(OH)_6(NH_3)_2(\mu\text{-CO})$, 103671-09-6; $W_2(OH)_6(NH_3)_2(\mu\text{-CO})$, 103671-10-9.

(29) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1771.

Organoboranes. 47. An Extremely Facile Elimination of Alkenes from Dialkylhaloboranes. A Comparative Rate Study with Related Trialkylboranes

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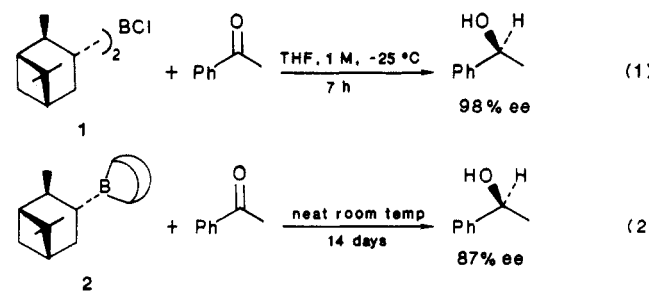
Dialkylhaloboranes reduce benzaldehyde at a rate much faster than does trialkylboranes. Whereas Ipc_2BCl reduces 2 equiv of benzaldehyde at room temperature almost instantaneously, the related trialkylborane Ipc_2B-*n*-Hex requires approximately 6 days. Sia_2BCl, 2-$MeCpn_2BCl$, Car_2BCl and Ipc_2BBr also reduce benzaldehyde rapidly, but 2-$MeChx_2BCl$ reacts relatively slowly. A cyclic mechanism with a "boat-like" transition state is proposed, which can account for the major differences in the rates of reduction among the various dialkylhaloboranes.

The synthesis of optically active secondary alcohols by the asymmetric reduction of prochiral ketones using chiral organoboron and borohydride reagents has been an active field of study in the recent past.[3] We recently achieved excellent optical yields in the asymmetric reductions of prochiral aromatic ketones with diisopinocampheylchloroborane, Ipc_2BCl (1), readily prepared by the reaction of dry hydrogen chloride in diethyl ether (Et_2O) with diisopinocampheylborane, which in turn is obtained by the hydroboration of α-pinene with BMS.[4] The extremely rapid rate of reduction of ketones by Ipc_2BCl as compared to the trialkylborane *B*-3-pinanyl-9-borabicyclo[3.3.1]nonane, *B*-Ipc-9-BBN [2; Aldrich, Alpine-Borane][5] (eq 1 and 2) attracted our attention, and we undertook a study of the comparative rates of reduction of carbonyls using related dialkylhaloboranes and trialkylboranes.



Treatment of Ipc_2BCl (1) with 1 equiv of benzaldehyde at 25 °C resulted in the instantaneous elimination of 1 mol

(1) Postdoctoral research associate on Grant DAAG 850062 from the United States Army Research Office.
(2) Postdoctoral Research Associate on Grant CHE 8414171 from the National Science Foundation.
(3) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 2.
(4) Chandrasekharan, J.; Ramachandran, P. V.; Brown, H. C. *J. Org. Chem.* **1985**, *50*, 5446.
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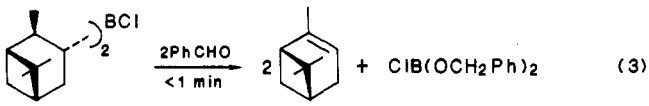
Table I. Reaction of Dialkylhaloboranes and Trialkylboranes with Benzaldehyde at 25 °C

reagent	solv	time for elimination of 1 equiv of alkene, min	time for elimination of 2 equiv of alkene, min
Ipc_2BCl (1)	THF	<1	<1
Ipc_2B-*n*-Hex (3)	THF	<1	8640
Ipc_2B-*exo*-Nb (4)	THF	15	12960
Sia_2BCl (5)	CH_2Cl_2	<1	270
2-$MeChx_2BCl$ (6)	THF	1320	∞[a]
2-$MeCpn_2BCl$ (7)	THF	<1	300
Car_2BCl (8)	THF	<1	15
Car_2B-*n*-Hex (9)	THF	<1	10080
Ipc_2BBr (10)	THF	<1	45

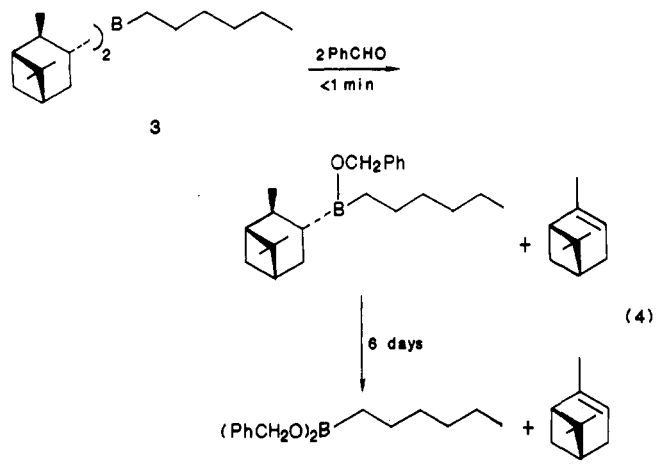
[a] A second mole of 1-methylcyclohexene was not eliminated, even on refluxing in CH_2Cl_2 for several hours.

of α-pinene. Utilization of 2 equiv of benzaldehyde resulted in the rapid elimination of 2 mol of α-pinene (eq 3), whereas, in the case of **2**, only 1 mol of α-pinene can be eliminated.[6]



(3)

Since the direct comparison of **1** and **2** may not be appropriate, we prepared a trialkylborane corresponding more closely to the structure of **1**, *B*-*n*-hexyldiisopinocampheylborane, Ipc_2B-*n*-Hex (**3**), and studied its rate of reaction with benzaldehyde. The first α-pinene unit eliminated almost immediately on the addition of 2 equiv of benzaldehyde with the second unit undergoing displacement much more slowly, requiring approximately 6 days (eq 4).



(4)

This apparent huge difference in the reactivities of Ipc_2BCl and Ipc_2BR toward benzaldehyde was unexpected and encouraged a more detailed study of the phenomenon. Accordingly, we undertook to synthesize a number of R_2BX (X = halogen) and R_2BR' derivatives and compared their reactions with benzaldehyde.

Pertinent to the present study is a related one recently described by Midland and Zderic involving a detailed examination of the kinetics of the reaction of benzaldehyde with various *B*-alkyl-9-BBN derivatives.[7]

Results and Dicussion

Diisopinocampheylchloroborane reacts rapidly with 2 equiv of benzaldehyde in THF (1 M) at 25 °C, eliminating both of the α-pinene units almost instantaneously. A yellow coloration was observed on the addition of benzaldehyde to the reagent **1**, and the color disappears almost immediately. The yellow color is believed to be due to a complex formation between the carbonyl oxygen and the boron atom of the reagent.[8] The rate of elimination of α-pinene was too fast to be measured by the gas chromatographic methods we utilized. However, analysis by GC showed a 100% elimination of α-pinene.

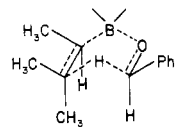


Figure 1. Transition-state model for the reduction of benzaldehyde with Sia_2BCl.

On the other hand, treatment of *B*-*n*-hexyldiisopinocampheylborane (**3**) with 2 equiv of benzaldehyde under similar conditions caused the displacement of 1 equiv of α-pinene almost immediately, whereas the second equivalent was completely eliminated only within 6 days. In this case also a yellow color was observed on mixing the reagent, with the color vanishing much more slowly.

To achieve a better understanding of the characteristics of the reaction, we modified the dialkylhaloborane and trialkylborane by changing the alkyl group and halogen atom and studied the rate of elimination of the corresponding olefin by GC analysis, assumed to be equal to the rate of reduction of benzaldehyde. Aliquots were removed and quenched with sodium methoxide at periodic intervals and analyzed for the olefin content. In the case of low boiling olefins, the rate of the reaction was monitored by the disappearance of benzaldehyde. Simultaneously, aliquots were withdrawn, quenched with methanol, and checked by ^{11}B NMR spectroscopy for the completion of the reaction. The times required for complete elimination of the olefin are presented in Table I.

In order to make certain that this decreased reactivity of Ipc_2B-*n*-Hex is general, we synthesized *B*-*exo*-norbornyldiisopinocampheylborane, Ipc_2B-*exo*-Nb (**4**), and studied its characteristics in the rate of reduction. In this case, the first α-pinene unit was eliminated in 15 min, whereas the second α-pinene required approximately 9 days. The delay in the elimination of both α-pinene units, as compared to that in the case of **3**, may be due to the increased steric hindrance afforded by the more bulky norbornyl group, as compared to the less bulky *n*-hexyl group, decreasing complexation between the boron and the carbonyl oxygen, presumed to be an important aspect in the cyclic mechanism proposed for these reductions.[8b]

With an aim to understand whether the pinanyl group in Ipc_2BCl plays any special role in the fast rate of re-

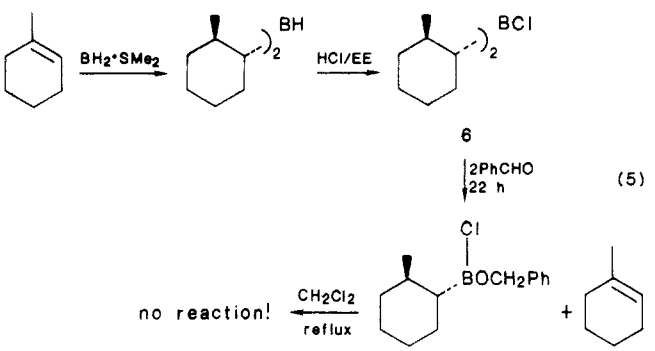
(6) Treatment of **2** with 2 or more equiv of benzaldehyde leaves the cyclooctyl group unaffected.

(7) Midland, M. M.; Zderic, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 525.

(8) (a) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352. (b) Mikhailov, B. M.; Bubnov, Yu. N.; Kiselev, V. G. *J. Gen. Chem. USSR (Engl. Transl.)* **1966**, *36*, 65.

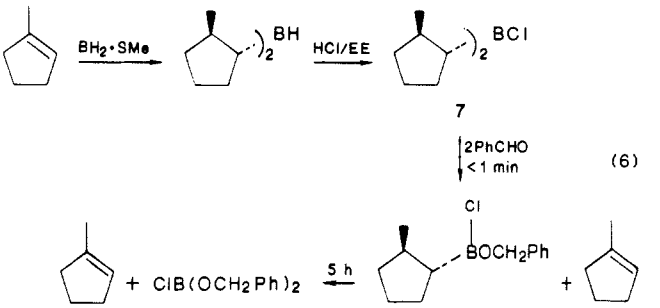
duction of carbonyls, we changed the alkyl group and studied the reduction of benzaldehyde by using disiamylchloroborane, Sia_2BCl (**5**). Although the first alkene unit was displaced almost immediately, unlike the behavior of **1**, the second molecule was eliminated only within 4.5 h. The decreased rate for the elimination of the second unit becomes clear when we consider the proposed "boat-like" cyclic transition state for the reduction of carbonyls using both the *B*-3-pinanylborabicyclo[3.3.1]-nonane derivatives,[7] as well as the R_2BCl compounds,[9] where the C–H and C–B bonds undergoing rupture are expected to be syn coplanar (Figure 1). Such a transition state for **5** would encounter an eclipsed conformation between the methyls of the adjacent carbons. But in the case of **1**, the conformation of the pinane ring favors the "boat-like" transition state and the H–C–C–B bonds lie in the same plane. Thus, both the electronic effect of the halogen and the conformational effect of the alkyl unit play their respective roles, adding up to the observed fast rate of reduction using **1**. It must be noted that Midland and Zderic observed that Alpine-Borane **2** reduces carbonyls faster than other *B*-alkyl-9-BBN reagents.[7]

The importance of the structure of the alkyl group in the dialkylhaloborane is made clear by studying the reduction characteristics of bis(*trans*-2-methylcyclohexyl)-chloroborane, 2-$MeChx_2BCl$ (**6**). For elimination to occur from **6**, the cyclohexyl group must assume an unfavorable boat conformation enabling the H–C–C–B bonds to be in the same plane. In fact, when 2 equiv of benzaldehyde were added to **6**, elimination of even the first olefin unit was slow, requiring 22 h. This is the only case in the compounds we studied where the first unit underwent displacement slowly. Moreover, to our surprise, we observed that the second unit was not eliminated, even on refluxing in CH_2Cl_2 for several hours (eq 5).



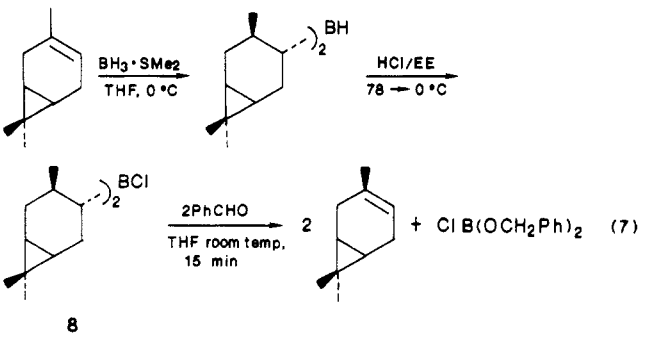
In bis(*trans*-2-methylcyclopentyl)chloroborane, 2-$MeCpn_2BCl$ (**7**), the conformation of the cyclopentyl unit favors a B–C–C–H coplanarity suited for elimination with benzaldehyde. The fast reaction of **7** with benzaldehyde is considered to support the proposed requirement for coplanarity of the B–C–C–H moiety. Two equivalents of benzaldehyde achieved the elimination of the first alkene unit instantaneously, with the second equivalent undergoing displacement in 5 h (eq 6). Midland observed a similar rate difference in the reaction of benzaldehyde with *B-trans*-2-methylcyclohexyl-9-BBN and *B-trans*-2-methylcyclopentyl-9-BBN, the former being much slower than the latter.[7]

According to this interpretation, both Ipc_2BCl and 2-$MeCpn_2BCl$ possess the favorable B–C–C–H coplanarity, which facilitates the reaction. How, then, can we account for the large difference in the rates of reaction of these two



derivatives? The Ipc moiety possesses a *cis*-1-Me moiety, in which the methyl group is strongly strained by the adjacent *gem*-dimethyl groups.[10] No such strain is present in 2-$MeCpn_2BCl$. We believe that it is the driving force provided by the relief of this strain which so strongly facilitates the reactions of Ipc_2BCl.

The above argument was tested by reacting bis(4-isocaranyl)chloroborane, 4-Car_2BCl (**8**). The isocaranyl moiety is believed to be forced into the boat conformation by the *gem*-dimethylcyclopropyl unit.[7] Moreover, elimination relieves modest strain between the 3-methyl and *gem*-dimethyl groups. Indeed, as expected, treatment of **8** with 2 equiv of benzaldehyde results in an almost instantaneous elimination of the first Δ^3-carene unit, followed by the second one in 0.25 h (eq 7).



The much faster elimination of alkenes from dialkylhaloboranes, as compared to trialkylboranes, was once again demonstrated by comparing the rate of elimination of Δ^3-carene from 4-Car_2BCl with that from *B*-*n*-hexylbis(4-isocaranyl)borane, 4-Car_2B-*n*-Hex (**9**). The latter was much slower. Treatment with 2 equiv of benzaldehyde eliminated the first Δ^3-carene immediately, but the second one was displaced only in 7 days (eq 8).

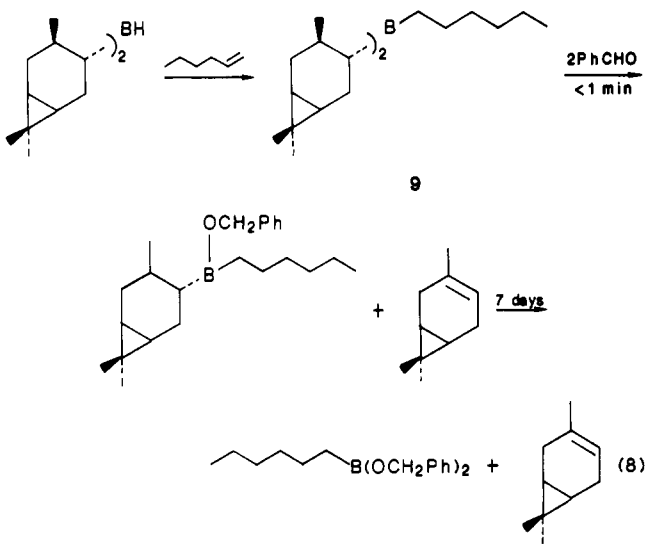
The effect of the halogen atom in these reductions was studied by changing the halogen atom of Ipc_2BCl. Substituting bromine for chlorine in **1** did not affect the reactivity significantly. Diisopinocampheylbromoborane, Ipc_2BBr (**10**), prepared from Ipc_2BH and hydrogen bromide in Et_2O, was treated with 2 equiv of benzaldehyde. The reaction proceeded to eliminate 80% of the α-pinene immediately, with complete elimination occurring in 0.75 h. Although the reaction was modestly slower, compared to that of the chloro derivative, it was still very much faster than that of the trialkylborane **3**.

The effect of the change from chlorine to bromine in Ipc_2BX was contrary to our expectations. It has been demonstrated that the Lewis acidity of BX_3 increases as we go down the halogen group in the periodic table. BBr_3 is a better Lewis acid than BCl_3.[11] Consequently, we had anticipated that the reaction of benzaldehyde with Ipc_2BBr

(9) Brown, H. C.; Chandrasekharan, J.; Ramachandran, P. V. *J. Org. Chem.* **1986**, *51*, 3394.

(10) Midland, M. M.; Petre, J. E.; Zderic, S. A.; Kazubski, A. *J. Am. Chem. Soc.* **1982**, *104*, 528.

(11) (a) Brown, H. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1956**, *78*, 2173. (b) Brown, H. C.; Chandrasekharan, *J. Organometallics* **1983**, *2*, 1261.



would be considerably faster than that of Ipc_2BCl. But we observed the reverse. We cannot, at present, give any definite reason for this difference between the anticipated and observed behavior of Ipc_2BCl and Ipc_2BBr. Possibly the greater steric requirements of bromine compared to chlorine play a role in the reversal of the anticipated reactivities.

B-Ipc-9-BBN is an excellent reagent for the asymmetric reduction of acetylenic ketones,[12] but it encounters difficulties with more hindered ketones.[13] We were originally persuaded to try Ipc_2BCl as a reducing agent because we thought the presence of the chlorine substituent would enhance complexation of the carbonyl oxygen to the boron and permit the successful asymmetric reduction of such hindered ketones. Such complexation is believed to be involved in the mechanism used by **2** to achieve chiral reductions.[7,12] Indeed, we observed that **1** reduces prochiral aromatic and α-tertiary ketones with ease and high asymmetric induction.[4] Even pinacolone with the bulky *tert*-butyl group on one side of the carbonyl undergoes reduction with **1** within 12 days, resulting in an optical yield of 95% for the alcohol. A similar reaction with **2** was only 60% complete in 40 days and the alcohol was racemic, indicating that the reaction involved a dehydroboration, followed by achiral reduction of the ketone by the 9-BBN.[5] Reaction at very high pressures as 6000 atmospheres did not help![13] Indeed, we have found it possible to reduce various α-tertiary alkyl ketones with **1** in 12 h, achieving high enantiomeric excess.[9]

Conclusion

We have shown that increasing the Lewis acidity of boron enhances the rate of reductions of carbonyl compounds considerably. We had already shown the importance of this aspect in obtaining alcohols of high enantiomeric excess in the reduction of prochiral ketones. The present study gives some hints for the future modifications of such asymmetric boron reagents by proper manipulation of the steric and electronic environments. We are currently studying various boron reagents for asymmetric reductions. Moreover, we have achieved a very simple and general method for upgrading the optical purities of terpenes, which are proving so valuable as chiral auxiliaries.[14]

Experimental Section

The organoboranes were always handled with extreme care under an atmosphere of prepurified nitrogen.[15] All glassware, syringes, and needles were oven-dried at 130 °C before use, assembled hot, and cooled under nitrogen. ^{11}B NMR were recorded in a Varian FT-80A spectrometer. All GC analyses were carried out with a Varian Aerograph Series 1200 gas chromatograph using a $^1/_8$ in. × 12 ft column packed with 10% SP-2100 on Chromosorb W (80–100 mesh) or 5% Carbowax 1540 on Chromosorb W (80–100 mesh).

Materials. α-Pinene, 1-methylcyclopentene, 1-methylcyclohexene, 2-methyl-2-butene, norbornene, and 1-hexene were obtained from Aldrich Chemical Co. Δ^3-Carene was obtained as a gift from Dr. S. N. Mehra of the Camphor and Allied Products, Bareilly, India. All of the alkenes were distilled over LAH before use. BMS was obtained as a neat liquid from Aldrich Chemical Co. and standardized by using known procedure.[15] THF was distilled over benzophenone ketyl and stored under nitrogen atmosphere in an ampule. CH_2Cl_2 was distilled over P_2O_5. The internal standards were kept over 5-Å molecular sieves under nitrogen atmosphere and used as such.

Ipc_2BCl (**1**) was prepared from Ipc_2BH and HCl in ethyl ether, as reported by us earlier.[4] Sia_2BCl (**5**), 2-MeChx_2BCl (**6**), 2-MeCpn_2BCl (**7**), and Car_2BCl (**8**) were all prepared by using a similar procedure by treating the corresponding dialkylboranes with the calculated amount of HCl in Et_2O. Ipc_2BBr (**10**) was prepared by a similar procedure using Ipc_2BH and HBr in Et_2O. The trialkylboranes Ipc_2B-*n*-Hex (**3**), Ipc_2B-*exo*-Nb (**4**), and Car_2B-*n*-Hex (**9**) were prepared according to a reported procedure[16] using Ipc_2BH, the corresponding alkene, and 15% excess of the terpene at −25 °C. The excess terpene was pumped off at high vacuum to provide the pure compounds.

The purities of the compounds were checked by ^{11}B NMR spectroscopy, and all of them gave a singlet. Following are the chemical shifts in Et_2O solution in δ relative to $BF_3\text{-}Et_2O$ at 0.00: **1**, 74.00; **3**, 80.00; **4**, 80.00; **5**, 78.00; **6**, 78.00; **7**, 78.00; **8**, 79.00; **9**, 84.00; **10**, 80.00.

The reagents were used as such for the reaction with benzaldehyde.

Procedure. To a solution of 5 mmol of R_2BCl in THF (1 M in the reagent, overall) in an oven-dried, nitrogen-cooled reaction flask fitted with a connecting tube was added 10 mmol of benzaldehyde. An appropriate internal standard was then added. Aliquots (0.1 mL) were withdrawn at periodic intervals and quenched with sodium methoxide (2 equiv so as to destroy the HCl evolved during quenching). The mixture was extracted with ether and analyzed for the olefin eliminated by GC using a $^1/_8$ in. × 12 ft 5% Carbowax 1540 on Chromosorb W (80–100 mesh) column or a $^1/_8$ in. × 12 ft 10% SP-2100 on Chromosorb W (80–100 mesh) column. The time required for the elimination of 1 equiv and 2 equiv of olefin are presented in Table I. Simultaneously, aliquots were quenched with methanol and ^{11}B NMR spectra were recorded for comparison of the rate of elimination.

In the case of the trialkylboranes, aliquots were withdrawn, diluted with ether, and analyzed by GC for the olefin eliminated.

In the case of Sia_2BCl (**5**), aliquots were withdrawn at periodic intervals, quenched with methanol, and analyzed on a $^1/_8$ in. × 12 ft SP-2100 column on Chromosorb W (80–100 mesh) for excess benzaldehyde.

All of the experiments were repeated to demonstrate their reproducibility.

Acknowledgment. We gratefully acknowledge support from the United States Army Research Office (Grant DAAG 850062) and the National Science Foundation (Grant CHE 8414171) in this research. We also wish to acknowledge helpful discussions with Professor M. M. Midland.

(12) Midland, M. M.; Tramontano, A.; Kazubski, A.; Graham, R. S.; Tsai, D. J. S.; Carbin, D. B. *Tetrahedron* **1984**, *40*, 1371.
(13) Midland, M. M.; McLoughlin, J. I. *J. Org. Chem.* **1984**, *49*, 1316.
(14) In a separate experiment, we isolated the α-pinene from Ipc_2BCl and observed a rotation of $[\alpha]^{22}_D$ +51.3°, i.e., 99.4% ee.
(15) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975; Chapter 9.
(16) Brown, H. C.; Desai, M. C.; Jadhav, P. K. *J. Org. Chem.* **1982**, *47*, 5067.