Hydroboration. 89. Preparation of DIBborane, a Sterically Hindered Monoalkylborane. Comparison with Thexylborane

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DIBborane ($DibBH_2$) is prepared in quantitative yield by the reaction of BH_3·THF or BH_3·SMe_2 with 2,4,4-trimethyl-2-pentene (diisobutylene-2 ≡ Dib-2) at 0 or 25 °C, respectively. DIBborane exists as a symmetrically bridged dimer in THF, as seen by IR and ^{11}B NMR, and reacts with water or methanol to liberate hydrogen quantitatively to form the corresponding boronic acid or dimethylboronate ester. Both DIBborane and thexylborane react with a variety of bases, $S(CH_3)_2$, pyridine, $N(CH_3)_3$, TMED, and NEt_3, to give the corresponding addition compounds. The stability of the adducts was investigated spectroscopically (IR, ^{11}B NMR) and by the rate of reaction with olefins (1-octene, α-pinene) and methanol. The results reveal that with the stronger, less sterically demanding bases, the reaction is essentially complete. With the weaker, more sterically demanding bases, a definite equilibrium is involved. The results show that both thexylborane and DIBborane establish the bases in the same order: $S(CH_3)_2 < NEt_3 < TMED < N(CH_3)_3 <$ Pyr. The DIBborane adducts are more reactive than the corresponding thexylborane adducts, indicating DIBborane to be the weaker Lewis acid. Clearly, DIBborane is a sterically demanding monoalkylborane readily available by hydroboration of a relatively inexpensive olefin.

Introduction

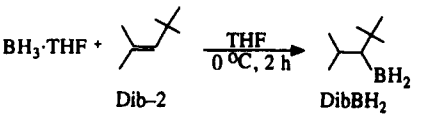
The hydroboration of simple olefins with BH_3·THF or BH_3·SMe_2 proceeds rapidly past the monoalkylborane stage (RBH_2) to the trialkylborane stage (R_3B).[2-5] However, moderately hindered olefins proceed to the dialkylborane stage (R_2BH).[6] For example, hydroboration of 2-methyl-2-butene produces disiamylborane (Sia_2BH). With more hindered olefins, such as tetramethylethylene (TME), the hydroboration proceeds to the monoalkylborane stage, producing thexylborane ($ThxBH_2$).[6,7] Thexylborane has been extensively studied and found to be a highly useful reagent for various syntheses, including selective hydroborations and reductions.[8] In addition, bis(thexylborane)-*N,N,N',N'*-tetramethylethylenediamine (2 $ThxBH_2$·TMED) has been prepared and reacts with olefin with the facile displacement of TME to form the corresponding bis(monoalkylborane)·TMED adducts in nearly quantitative yield.[9] This provides entry into a whole new series of less hindered monoalkylborane adducts previously unavailable by hydroboration. In view of the useful chemistry provided by $ThxBH_2$, it appears desirable to explore other highly sterically hindered monoalkylboranes available by direct hydroboration.

Earlier hydroboration studies[6,7] indicated that the reaction of Dib-2 with borane produced a new, highly sterically hindered monoalkylborane; namely, $DibBH_2$. These studies had largely been conducted in diglyme solvent or on a vacuum line. It was desirable to establish a convenient synthesis of $DibBH_2$ starting with BH_3·THF or BH_3·SMe_2.

In this paper we discuss how $DibBH_2$ has been conveniently prepared, characterized, and derivatized. Hydrolysis and methanolysis rates have been studied and compared to $ThxBH_2$. The stability of $DibBH_2$ complexes with Lewis bases and the reactivity of these complexes have been explored relative to $ThxBH_2$.

Results and Discussion

Preparation of $DibBH_2$. BH_3·THF was reacted with 2,4,4-trimethyl-2-pentene (Dib-2) in a 1:1 molar ratio in THF at 0 °C to produce quantitatively $DibBH_2$ in 2 h (eq 1). Olefin uptake was followed by GC and the residual



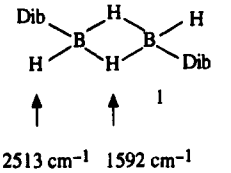
(1)

hydride determined by the hydrolysis of reaction aliquots using a gas buret. In similar fashion, Dib-2 can be hydroborated with BH_3·SMe_2 (BMS) in a 1:1 molar ratio in THF or pentane at 25 °C to give $DibBH_2$ quantitatively in 2 h (eq 2). Room temperature is used in the BMS

$$BH_3{\cdot}SMe_2 + \text{Dib-2} \xrightarrow[25\ ^\circ C,\ 2\ h]{THF} DibBH_2 \qquad (2)$$

reaction since the hydroboration of Dib-2 at 0 °C is only 74% complete in 2 h and 88% complete in 24 h.

Characterization of $DibBH_2$. IR spectroscopy reveals that $DibBH_2$ exists as a dimer (1) in THF solution.



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(8) Negishi, E.; Brown, H. C. *Synthesis* **1974**, *2*, 77.
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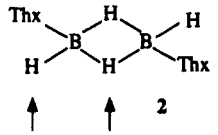
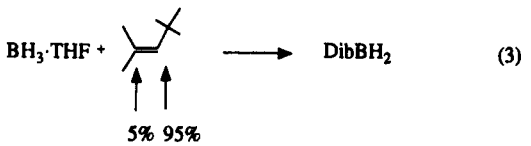
Terminal Dib–B–H stretching is observed at 2513 cm^{-1}, and B–H–B bridge stretching is seen at 1592 cm^{-1}. Steric factors should require the large Dib groups to occupy a trans orientation in the bridged dimer similar to the $ThxBH_2$ dimer (2) previously studied.[7]



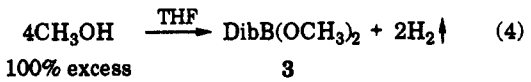
The ^{11}B NMR spectrum of 1 in THF (1.0 M) showed a broad hextet at +24.0 ppm, indicative of a bridged dimeric species similar to the $ThxBH_2$ dimer (+24.2 ppm). For convenience, $DibBH_2$ and $ThxBH_2$ are often depicted as monomers.

In order to establish the position of the boron atom in $DibBH_2$, an alkaline hydrogen peroxide oxidation was carried out to produce 95% secondary Dib-ol and 5% tertiary Dib-ol as seen by GC. Therefore, $DibBH_2$ must consist of two structural isomers which arise from placement of the boron atom mainly, but not exclusively, on the less substituted carbon of the double bond (eq 3).



(3)

$DibBH_2$ reacts with methanol to liberate the theoretical amount of hydrogen within 30 min at 25 °C to form dimethyl DIBboronate ester (3) in quantitative yield (eq 4). ^1H NMR examination of the methanolyzed products,



(4)

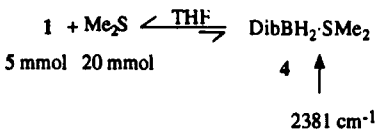
after evaporation of THF and excess methanol, provides a convenient method for determining the quantities $RR'BOCH_3$ and $RB(OCH_3)_2$. In all cases examined, the methoxy protons of monomethoxydialkylboranes appeared downfield (δ 3.64–3.96) relative to those of dimethoxymonoalkylboranes (δ 3.50–3.62). Thus, without completely isolating these compounds, their identity and quantities (relative to an internal standard) could be readily determined. The ^1H NMR spectrum (CCl_4) showed only one methoxy peak at δ 3.52 (s, 6 H) for the methanolyzed reaction depicted in eq 4. In addition, GC analysis (SE-30) showed only a single sharp product peak. Alkaline hydrogen peroxide oxidation of 3 produced secondary Dib-ol/tertiary Dib-ol in a ratio of 94:6, as seen by GC. These data are consistent with the complete formation of 3 arising from the previous quantitative preparation of $DibBH_2$.

Stability of $DibBH_2$ in THF. $DibBH_2$ was stored as a standard solution (1.04 M) under nitrogen at both 0 and 25 °C. Analyses were performed at various time intervals to determine whether hydride loss, isomerization, or disproportionation (i.e., dimer redistribution) had occurred. $DibBH_2$ is stable at 0 °C for at least 18 days. With longer storage times at 0 °C, slight isomerization and some hydride loss were noted. Storage at 25 °C shows extensive isomerization and slight hydride loss after only 8 days. No disproportionation was noted under any of the conditions studied.

Methanolysis of $DibBH_2$ and Comparison with $ThxBH_2$. $DibBH_2$ (1.0 M) was reacted with 100% excess methanol at 0 °C in THF and the H_2 evolution measured continuously (eq 4). The results are given in Table I and compared with the methanolysis results for $ThxBH_2$. The results show that the complete methanolysis of $DibBH_2$ is much slower than that of $ThxBH_2$ at 0 °C.

$DibBH_2$ (1.0 M) was also hydrolyzed with 100% excess H_2O at 0 °C in THF to form quantitatively $DibB(OH)_2$ (DIBboronic acid) in 20 min while $ThxBH_2$ underwent complete hydrolysis within 10 min. These results, as well as the methanolysis results, indicate $DibBH_2$ to be a weaker Lewis acid than $ThxBH_2$.

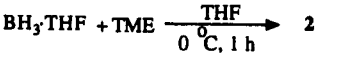
Formation of $DibBH_2$·SMe_2 and Comparison with $ThxBH_2$·SMe_2. $DibBH_2$ dimer (1) (5 mmol) was prepared (eq 1) and treated with 100% excess Me_2S in THF at 25 °C for 1 h (eq 5). Longer reaction times revealed no differences. Solution IR showed that an equilibrium



(5)

existed with mainly 1 present. However, some $DibBH_2$·complex absorption was seen at 2381 cm^{-1} consistent with the formation of 4. The ^{11}B NMR displayed a broadened triplet at −8.19 ppm corresponding to 4, as well as a broad hextet at +24.0 ppm, corresponding to the formation of a much greater amount of 1.

For comparison, the $ThxBH_2$ dimer (2) was prepared[10] (eq 6) and treated with 100% excess Me_2S in THF at 25 °C for 1 h (eq 7). The IR spectrum of the solution showed



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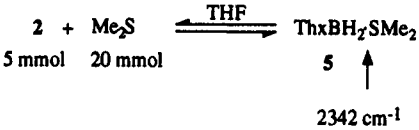
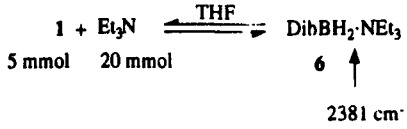


(7)

that an equilibrium existed with both $ThxBH_2$ dimer (2) and $ThxBH_2$·SMe_2 (5) present in significant amounts. The ^{11}B NMR of the reaction mixture gave a triplet at −1.82 ppm and a broad hextet at +24.2 ppm corresponding to 5 and 2, respectively.

Formation of $DibBH_2$·NEt_3 and Comparison with $ThxBH_2$·NEt_3. $DibBH_2$ dimer (1) (5 mmol) was reacted with Et_3N in THF at 25 °C for 1 h (eq 8). The IR spectrum



(8)

of the solution indicated a substantial amount of 6 in equilibrium with 1. The ^{11}B NMR spectrum showed a triplet at −5.60 ppm corresponding to 6 and a broad hextet at +23.8 ppm (1). A much greater amount of the $DibBH_2$·complex was present with Et_3N than was found

(10) Zweifel, G.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *85*, 2066.

with Me_2S, revealing that Et_3N was a stronger base than Me_2S in the $DibBH_2$ series.

The reaction mixture (eq 8) (1.0 M in boron) (10 mmol) was treated with 1-octene (10 mmol) and α-pinene (10 mmol) for 1 h at 25 °C in THF in separate experiments to determine the relative reactivity of the mixture under standard hydroboration conditions. Both reactions were quenched with 100% excess methanol at 25 °C for 1 h and analyzed by GC (SE-30) for unreacted olefin relative to an internal standard (*n*-hexadecane). During the standard 1-h reaction period, 100% 1-octene and 80% α-pinene reacted, but substantial amounts of Dib-2 appeared via dehydroboration in the α-pinene case, but not in the hydroboration of 1-octene.

For comparison, the $ThxBH_2$ dimer (2), treated with Et_3N in THF at 25 °C for 1 h, produces $ThxBH_2{\cdot}NEt_3$ as an undissociated addition complex, as previously reported (eq 9).[11] Examination of the solution by IR showed no

$$\underset{5\text{ mmol}}{2} + \underset{20\text{ mmol}}{Et_3N} \xrightarrow[25\,^{\circ}C,\,1\text{ h}]{\text{THF}} \underset{7}{ThxBH_2{\cdot}NEt_3} \quad (9)$$

2381 cm^{-1}

free terminal Thx–B–H or bridging B–H–B stretching absorptions characteristic of 2. Only the $ThxBH_2$·complex was seen at 2381 cm^{-1}. The ^{11}B NMR spectrum showed only a triplet at −4.60 ppm consistent with the complete formation of 7. The addition complex 7 is reported to be unstable in the absence of excess Et_3N and, consequently, has not been isolated.[11]

Reaction of 7 (10 mmol) with 1-octene (10 mmol) and α-pinene (10 mmol), as described previously, showed 100% 1-octene and 75% α-pinene uptake in 1 h at 25 °C. A significant amount of TME appeared via dehydroboration during the α-pinene reaction only. Thus, the behavior of $ThxBH_2{\cdot}NEt_3$ in the hydroboration of 1-octene and α-pinene parallels the behavior of $DibBH_2{\cdot}NEt_3$.

Formation of $DibBH_2$·TMED and Comparison with $ThxBH_2$·TMED. $DibBH_2$ dimer (1) (5 mmol) was treated with a half-molar amount of TMED (5 mmol) in THF at 25 °C for 1 h (eq 10). IR examination of the solution

$$\underset{5\text{ mmol}}{1} + \underset{5\text{ mmol}}{(H_3C)_2N{-}CH_2CH_2{-}N(CH_3)_2} \rightleftharpoons[\text{THF}] \underset{8}{DibBH_2{\cdot}TMED} \quad (10)$$

2370 cm^{-1}

indicated that 8 was present in equilibrium with a significant amount of 1. Increasing the reaction time to 24 h at 25 °C (eq 10) did not decrease 1 to any significant extent. In addition, only a trace of bis($DibBH_2$)·TMED was observed.

$DibBH_2$ dimer (1) was then treated with an equimolar amount of TMED in THF at 25 °C for 1 h, and the complete formation of $DibBH_2$·TMED (8) was observed (eq 11). IR

$$\underset{5\text{ mmol}}{1} + \underset{10\text{ mmol}}{TMED} \xrightarrow[25\text{ °C},\,1\text{ h}]{\text{THF}} \underset{8}{DibBH_2{\bullet}TMED} \quad (11)$$

examination of the solution confirmed the complete formation of 8 with only addition complex hydride observed at 2370 cm^{-1}. The ^{11}B NMR spectrum showed only a broad triplet at −1.74 ppm consistent with the formation of 8.

$DibBH_2$·TMED (1.0 M) (10 mmol) was treated with 1-octene (10 mmol) and α-pinene (10 mmol) in THF at 25 °C for 1 h in separate experiments. The uptake of 100% 1-octene with only 5% dehydroboration of Dib-2 was noted, while 20% α-pinene reacted with the liberation of 20% Dib-2. The primary products found are formed as shown in eqs 12 and 13, respectively.

$$\underset{8}{} + \text{1-octene} \xrightarrow[25\,^{\circ}C,\,1\text{ h}]{\text{THF}} Dib{-}B(H)(n\text{-}C_8H_{17}) + TMED \quad (12)$$

$$\underset{8}{} + \alpha\text{-pinene} \xrightarrow[25\,^{\circ}C,\,1\text{ h}]{\text{THF}} IpcBH_2{\cdot}TMED + Dib\text{-}2 \quad (13)$$

For comparison, $ThxBH_2$ dimer (2) was treated with a half-molar equivalent of TMED in THF at 25 °C for 1 h (eq 14). A quantitative yield of 2 $ThxBH_2$·TMED (9) resulted. The IR spectrum of the solution established

$$\underset{5\text{ mmol}}{2} + \underset{5\text{ mmol}}{TMED} \xrightarrow[25\,^{\circ}C,\,1\text{ h}]{\text{THF}} \underset{9}{ThxBH_2{\cdot}TMED{\cdot}H_2BThx} \quad (14)$$

2326-2273 cm^{-1}

that an undissociated $(ThxBH_2)_2$·TMED complex had been cleanly formed. Only a broad multiplet at +0.77 ppm was seen in the ^{11}B NMR spectrum, consistent with 9. 2 $ThxBH_2$·TMED is a stable, isolatable solid, readily characterized by ^1H NMR. Thus, the stronger Lewis acidity of $ThxBH_2$ relative to $DibBH_2$ was again evident.

The $ThxBH_2$ dimer (2) was next treated with an equimolar amount of TMED in THF at 25 °C for 1 h (eq 15). The IR spectrum of the solution established that an

$$\underset{5\text{ mmol}}{2} + \underset{10\text{ mmol}}{TMED} \xrightarrow[25\text{ °C},\,1\text{ h}]{\text{THF}} \underset{10}{ThxBH_2{\bullet}TMED} \quad (15)$$

undissociated $ThxBH_2$·complex had been formed with hydride absorption only at 2326–2273 cm^{-1}. The ^{11}B NMR spectrum showed only a broad triplet at +1.31 ppm, consistent with the formation of 10. The ^1H NMR spectrum supported the quantitative formation of 10 with essentially no free TMED seen in the reaction media (eq 15).

$ThxBH_2$·TMED (1.0 M) (10 mmol) was treated with 1-octene (10 mmol) and α-pinene (10 mmol) in THF at 25 °C for 1 h. With 1-octene, 100% reacted and no dehydroboration of TME was seen. With α-pinene, 20% reacted with 15% TME dehydroborated.

Formation of $DibBH_2{\cdot}N(CH_3)_3$ and Comparison with $ThxBH_2{\cdot}N(CH_3)_3$. $DibBH_2$ dimer (1) was treated with $(CH_3)_3N$ in THF at 25 °C for 1 h (eq 16). Examination

$$\underset{5\text{ mmol}}{1} + \underset{20\text{ mmol}}{(CH_3)_3N} \xrightarrow[25\,^{\circ}C,\,1\text{ h}]{\text{THF}} \underset{11}{DibBH_2{\cdot}N(CH_3)_3} \quad (16)$$

2353 cm^{-1}

of the solution IR showed that an undissociated $DibBH_2$·complex was formed quantitatively, even with only a stoichiometric amount of $(CH_3)_3N$ (10 mmol). The ^{11}B NMR showed a slightly broadened triplet at −1.94 ppm,

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

consistent with 11. Reaction of 11 (10 mmol) under standard conditions with 10 mmol of 1-octene and α-pinene in separate experiments gave 17% and 5% olefin uptake, respectively. Thus, the formation of a very strong or "tight" addition complex is evident.

The behavior of $ThxBH_2$ dimer (2) with $(CH_3)_3N$ in THF at 25 °C for 1 h is similar (eq 17). Indeed, the

$$\underset{5\text{ mmol}}{2} + \underset{20\text{ mmol}}{(CH_3)_3N} \xrightarrow[25\ ^{o}C,\ 1\ h]{THF} \underset{12}{ThxBH_2{\cdot}N(CH_3)_3} \qquad (17)$$

2381-2326 cm^{-1}

stretching absorptions for 12 matched identically the values observed in an earlier study.[7] The ^{11}B NMR of 12 exhibits a triplet at +1.72 ppm. Reaction of 12 with 1-octene and α-pinene showed 0% olefin uptake in THF at 25 °C after 1 h in both cases.

Formation of $DibBH_2$·Pyridine and Comparison with $ThxBH_2$·Pyridine. $DibBH_2$ dimer (1) was treated with pyridine in THF at 25 °C for 1 h (eq 18). Examination

$$\underset{5\text{ mmol}}{1} + \underset{20\text{ mmol}}{N\bigcirc} \xrightarrow[25\ ^{o}C,\ 1\ h]{THF} \underset{13}{DibBH_2{\cdot}Pyr} \qquad (18)$$

2336-2262 cm^{-1}

of the IR spectrum of the solution showed that undissociated $DibBH_2$·complex (13) formed. Reaction of 1 (5 mmol) with an equimolar amount of pyridine (10 mmol) formed 13 quantitatively, even at −78 °C.[12] The ^{11}B NMR showed a broadened triplet at −6.08 ppm.

Reaction of 13 under the standard conditions with 1-octene and α-pinene gave 6% and 0% olefin uptake, respectively.

$ThxBH_2$ dimer (2) was treated with pyridine in THF at 25 °C for 1 h (eq 19). Solution IR absorptions found for 14 matched identically with the absorptions previously reported for this addition complex.[11] The ^{11}B NMR spectrum of 14 showed a triplet at −0.48 ppm.

$$\underset{5\text{ mmol}}{2} + \underset{20\text{ mmol}}{N\bigcirc} \xrightarrow[25\ ^{o}C,\ 1\ h]{THF} \underset{14}{ThxBH_2{\cdot}Pyr} \qquad (19)$$

2330 cm^{-1}

The reaction of 14 (10 mmol) with 1-octene (10 mmol) and α-pinene (10 mmol) in THF at 25 °C for 1 h in separate experiments revealed 0% olefin uptake in both cases. Thus, the relative basicity of $(CH_3)_3N$ versus pyridine could not be determined from the hydroboration data in the $ThxBH_2$ series. However, methanolysis data readily distinguish differences in their stabilities. Reaction of 14 with 100% excess methanol in THF at 0 °C showed no hydrogen evolution for at least 6 h, whereas under the same conditions, 12 exhibited complete hydrogen evolution after 30 min. Moreover, the $ThxBH_2$·Pyr complex 14 failed to evolve hydrogen, even at 25 °C (30 min). Thus, pyridine was clearly the strongest base in the series examined.

The order of complexing agent basicity is identical in both the $ThxBH_2$ and $DibBH_2$ series and is ranked as follows: $Me_2S < Et_3N < TMED < Me_3N < Pyr$. In every case $ThxBH_2$ forms the more stable, less reactive addition complex with the representative bases compared to $DibBH_2$. This means that $DibBH_2$ is the weaker Lewis acid, possibly because of greater steric requirements. The relative stabilities of the various $DibBH_2$ and $ThxBH_2$ addition complexes, as determined by spectroscopy (IR, ^{11}B NMR), hydroboration, and methanolysis are summarized in Tables II and III, respectively.

(12) Unpublished observation of Dr. Bakthan Singaram.

Table I. Rate of Methanolysis of $DibBH_2$ and $ThxBH_2$ (10 mmol) in THF at 0 °C with CH_3OH (40 mmol)

	$DibBH_2$		$ThxBH_2$	
time (min)	H_2 evolved (mmol)	yield (%)	H_2 evolved (mmol)	yield (%)
<0.3			10.0	50
1	0.6	3		
5	3.8	19	15.6	78
10	6.4	32		
15	8.6	43	19.3	96
19	10.0	50	19.6	98
27	12.1	60		
32			19.8	99
48	15.2	76		
99	17.8	89		
180	20.0	100		

Conclusions

DIBborane ($DibBH_2$) is prepared in quantitative yield by treating 1 equiv of BH_3·THF or $BH_3{\cdot}S(CH_3)_2$ with 1 equiv of Dib-2 (2,4,4-trimethyl-2-pentene) in THF at 0 or 25 °C, respectively, for 2 h. Oxidation of DIBborane to the corresponding alcohols shows two isomers present. Approximately 94–95% of the boron is attached to the less hindered secondary position (2,2,4-trimethyl-3-pentylborane), and 5–6% is attached to the more hindered tertiary position (2,4,4-trimethyl-2-pentylborane). DIBborane exists as a symmetrically bridged dimer, as seen by IR and ^{11}B NMR spectroscopy. It reacts with water or methanol to liberate hydrogen quantitatively and forms the corresponding boronic acid or dimethyl boronate ester. Both DIBborane and thexylborane react with a variety of bases, $S(CH_3)_2$, NEt_3, TMED, $N(CH_3)_3$, and pyridine, to give the corresponding addition compounds. The stability of the adducts has been investigated both spectroscopically (IR, ^{11}B NMR) and by the rate of reaction of the adducts with various olefins (1-octene, α-pinene) and with methanol under standardized conditions. The results reveal that with the stronger, less sterically demanding bases, the reaction was essentially complete. With the weaker, more sterically demanding bases, an equilibrium mixture is produced. The ^{11}B NMR shifts for the various $ThxBH_2$ and $DibBH_2$ addition compounds are indicative of their relative reactivity toward olefins and methanol. In all cases, the reactivity of $DibBH_2$·complex is greater than that of the corresponding $ThxBH_2$·complex. The correlation of ^{11}B NMR shifts with the observed reactivity within either the $ThxBH_2$ series or the $DibBH_2$ series is less reliable. The results for both the thexylborane and DIBborane series establish the bases in the same order: $S(CH_3)_2 < NEt_3 < TMED < N(CH_3)_3 < Pyr$. Comparison of the chemical reactivity of the corresponding thexylborane and DIBborane adducts shows DIBborane to be the weaker Lewis acid.

Experimental Section

General Comments. All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[3] The spectra were obtained from samples in an inert atmosphere.[3] The ^{11}B NMR chemical shifts are in δ ppm relative to $BF_3{\cdot}OEt_2$ with

Table II. Relative Stabilities of $DibBH_2$ Addition Compounds As Determined by Spectroscopy (IR, ^{11}B NMR), Hydroboration, and Methanolysis (10 mmol Scale)

	ligand[a]				
analyses	SMe_2	NEt_3	TMED	NMe_3	
IR	E[b]	E[b,c]	C[d]	C	C
1-octene reacted,[e] (%)	100	100	100	17	6
α-pinene reacted,[e] (%)		80	20	5	0
^{11}B NMR,[f] δ	−8.19 (br t) +24.0 (br hextet)	−5.60 (t) +24.0 (br hextet)	−1.74 (br t)	−1.94 (br t)	−6.08 (br t)
$T_{1/2}$ methanolysis[g] (min)	19	0.25	0.30	10[h]	60[h]

[a] A Lewis base (20 mmol) was added to $DibBH_2$ (1.0 M) (10 mmol) in THF at 25 °C and stirred for 1 h. [b] E = equilibrium mixture. [c] Greater amount of addition compound seen than in SMe_2 case. [d] C = complete addition compound formation. [e] Olefin (10 mmol) was added to $DibBH_2$·complex (1.0 M) (10 mmol) at 25 °C for 1 h before quenching with 100% excess methanol. [f] All shifts are relative to BF_3·EE. [g] $T_{1/2}$ = time in minutes required to liberate half of the theoretical amount of hydrogen present upon addition of 100% excess methanol at 0 °C. [h] $T_{1/2}$ at 25 °C.

Table III. Relative Stabilities of $ThxBH_2$ Addition Compounds As Determined by Spectroscopy (IR, ^{11}B NMR), Hydroboration, and Methanolysis (10 mmol scale)

	ligand[a]				
analyses	SMe_2	NEt_3	TMED	NMe_3	
IR	E[b]	C[c]	C	C	C
1-octene reacted,[d] (%)	100	100	100	0	0
α-pinene reacted,[d] (%)	100	75	20	0	0
^{11}B NMR,[e] (δ)	−1.82 (t) +24.2 (br hextet)	−4.60 (t)	+1.31 (t)	+1.72 (t)	−0.48 (t)
$T_{1/2}$ methanolysis[f] (min)	<0.30	0.50	10	18[g]	stable[h]

[a] A Lewis base (20 mmol) was added to $ThxBH_2$ (1.0 M) (10 mmol) in THF at 25 °C and stirred for 1 h. [b] E = equilibrium mixture. [c] C = complete formation of addition compound. [d] Olefin (10 mmol) was added to $ThxBH_2$·complex (1.0 M) (10 mmol) at 25 °C for 1 h before quenching with 100% excess methanol. [e] All shifts are relative to BF_3·EE. [f] $T_{1/2}$ = time in minutes needed to liberate half of the theoretical amount of hydrogen present upon addition of 100% excess methanol at 0 °C. [g] $T_{1/2}$ at 25 °C. [h] No H_2 evolved after 6 h at 0 °C or 30 min at 25 °C.

chemical shifts downfield from BF_3·OEt_2 as positive. The chemical shifts are in δ relative to Me_4Si for ^1H NMR spectra. GC analyses were carried out on SE-30 and CW-20M columns using TC detectors.

Materials. The preparation of BH_3·THF[3] was carried out as reported previously. BH_3·SMe_2 (BMS) was obtained from the Aldrich Chemical Co. as the neat complex (10 M). 9-BBN was obtained from the Aldrich Chemical Co. as a powder (98%). Tetrahydrofuran (THF) was predried over calcium hydride and then distilled from lithium aluminum hydride (LAH) and stored under N_2. Pentane was stirred over concentrated sulfuric acid, decanted, extracted with saturated potassium carbonate solution, and washed with distilled water. It was then distilled from LAH and stored under N_2. The olefin, 2,3-dimethyl-2-butene (TME), was obtained from Aldrich (99+%), distilled from LAH, and stored in the cold room (−2 °C) under N_2. The olefin, 2,4,4-trimethyl-2-pentene (Dib-2) (98%), obtained from Aldrich was purified as described below. Straight-chain hydrocarbons (used as internal standards for GC analyses) were obtained from the Phillips Petroleum Co. in 99+% purity and used directly. Methanol (reagent spectro grade) was obtained from the J. T. Baker Chemical Co. and stored under N_2 over 3-Å molecular sieves. Benzene (spectro grade) (used as internal standard for ^1H NMR) was obtained from the Mallinckrodt Chemical Works and stored under N_2 over 5-Å molecular sieves. The olefins, 1-octene and α-pinene, were obtained as reagent-grade chemicals from Chemical Samples and Dragoco, respectively. These olefins were distilled from LAH and stored under N_2. Dimethyl sulfide was obtained from the Aldrich Chemical Co. (98%) and stored under N_2 over 5-Å molecular sieves. Pyridine (certified ACS) was obtained from the Fisher Scientific Co. and stored under N_2 over 4-Å molecular sieves. *N,N,N′,N′*-Tetramethylethylenediamine (TMED) (99%) was obtained from the Aldrich Chemical Co. and distilled from calcium hydride under N_2. Trimethylamine (anhydrous) was obtained from the Eastman Kodak Co. and used directly. Triethylamine was obtained from Matheson, Coleman, and Bell. It was dried over sodium hydroxide and then distilled under N_2 from 3% naphthyl isocyanate (98%; Aldrich Chemical Co.) in order to remove primary and secondary amine impurities.

Purification of 2,4,4-Trimethyl-2-pentene (Dib-2). An oven-dried, 1-L, two-necked flask containing a magnetic stirring bar, septum inlet, and a connecting tube leading to a mercury bubbler was flushed with nitrogen. The flask was then charged with 695 mL (500 g, 4460 mmol) of 2,4,4-trimethyl-2-pentene (98%). The 2% impurity present was 2,4,4-trimethyl-1-pentene, as seen by GC (10% SE-30), and confirmed by coinjection with an authentic sample. In a nitrogen atmosphere (glove bag), 12.04 g of 9-BBN (98.6 mmol) was weighed into a 200-mL tared flask. The 9-BBN powder was then added to the diisobutylene mixture at 0 °C via a gooseneck sidearm adaptor under nitrogen. The ice bath was removed immediately after complete addition of the 9-BBN and the flask allowed to warm to 25 °C with stirring. Virtually all of the 9-BBN dissolved after 1–2 h with stirring at 25 °C. The clear solution turned pale yellow, and stirring was continued overnight. The Dib-2 was distilled at 104–105 °C (750 mm); n^{20}_D 1.4160 (found), n^{20}_D 1.4159 (lit.). GC (SE-30) showed Dib-2 to be essentially 100% pure. No trace of Dib-1 was seen. The 9-BBN had selectively hydroborated the less hindered terminal olefin.

Preparation of $DibBH_2$ in THF from BH_3·THF. A 50-mL flask equipped with a septum inlet and magnetic stirring bar was flushed with nitrogen and charged with 3.54 mL of THF, 0.81 mL (0.572 g, 5.00 mmol) of *n*-octane (internal standard for GC), and 4.08 mL of BH_3·THF (2.45 M, 10.0 mmol). The mixture was cooled to 0 °C, and 1.57 mL (1.12 g, 10.0 mmol) Dib-2 was added dropwise over 10 min with stirring. Aliquots were taken at various time intervals and hydrolyzed in a 1:1:1 mixture of H_2O/glycerol/THF at 25 °C via a 250-mL gas buret to determine the amount of residual hydride. Additional aliquots were also taken and quenched in excess methanol and analyzed by GC (10% SE-30) for residual Dib-2. The reaction was virtually quantitative after 2 h at 0 °C.

Preparation of $DibBH_2$ from BH_3·SMe_2. The following procedure is representative. A 50-mL flask equipped with a septum inlet and magnetic stirring bar was flushed with nitrogen and charged with 7.43 mL of THF and 1.00 mL (10.0 mmol) of BH_3·$S(CH_3)_2$ (10.0 M). The mixture was stirred at 25 °C, and 1.57 mL (1.12 g, 10.0 mmol) of Dib-2 was added dropwise over

10 min. Aliquots were taken at various time intervals and hydrolyzed at 25 °C in H_2O/glycerol/THF (1:1:1) via a 50-mL gas buret to determine the amount of residual hydride. The reaction for the formation of $DibBH_2$ was complete in 2 h at 25 °C.

Preparation of $ThxBH_2$ in THF from BH_3·THF. The following procedure is representative. A 50-mL flask equipped with a septum inlet and magnetic stirring bar was flushed with nitrogen and charged with 4.73 mL of THF and 4.08 mL of BH_3·THF (2.45 M, 10.0 mmol). The mixture was cooled to 0 °C with stirring, and 1.19 mL (0.842 g, 10.0 mmol) TME was added dropwise over 10 min. The reaction was allowed to proceed for 1–2 h at 0 °C. The stoichiometry studies and methanolysis reaction were previously reported.[6,7]

Oxidation of $DibBH_2$ to the Corresponding Alcohols. $DibBH_2$ (10 mmol) was prepared as described previously using 1.0 mL (0.763 g, 3.37 mmol) of *n*-hexadecane as internal GC standard and employing a water condenser. To the reaction mixture at 25 °C was added 3.4 mL of 3 M NaOH (10.2 mmol) and 5.0 mL of EtOH (95%) as cosolvent. The reaction mixture was vigorously stirred for 15 min to ensure complete hydrolysis of all active hydride. Next, 1.2 mL of 30% H_2O_2 (12 mmol) was added dropwise with stirring over 15–20 min. Upon complete addition of peroxide, the reaction mixture was stirred at 50–55 °C for an additional 1–2 h to ensure complete oxidation. The reaction mixture was then cooled to 25 °C, and 5.6 g K_2CO_3 (anhydrous) was added slowly with vigorous stirring to salt out the aqueous layer. The two phases were then allowed to separate (5 min). An aliquot of the organic phase was taken and placed in a vial over anhydrous $MgSO_4$ for 15–30 min. The solid $MgSO_4$ was centrifuged down and a GC analysis (10% CW-20M) carried out. The analysis showed 9.4–9.5 mmol of 2,2,4-trimethyl-3-pentanol (94–95% yield) and 0.5–0.6 mmol of 2,4,4-trimethyl-2-pentanol (5–6% yield). The compounds were identified by coinjection with authentic samples.

Hydrolysis of $DibBH_2$ in THF at 0 °C. The following procedure is representative. A 50-mL flask equipped with a septum inlet, water condenser, and magnetic stirring bar was attached to a gas meter through a dry ice/2-propanol tap (−78 °C) and flushed with nitrogen. The flask was cooled to 0 °C with stirring and charged with 10.0 mmol of $DibBH_2$ (1.0 M) in THF. While the mixture stirred, 0.72 mL (40 mmol) of distilled water was quickly added. The hydrogen evolution was measured continuously over time.

Methanolysis of $DibBH_2$ in THF at 0 °C. The following procedure is representative. A 50-mL flask equipped with a septum inlet, water condenser, and magnetic stirring bar was attached to a gas meter through a dry ice/2-propanol trap (−78 °C) and flushed with nitrogen. The flask was cooled to 0 °C with stirring and charged with 10.0 mmol of $DibBH_2$ (1.0 M) in THF. While stirring, 1.6 mL (40 mmol) of methanol was quickly added. The hydrogen evolution was measured continuously over time. The results are summarized in Table I. The $DibB(OCH_3)_2$ purity by GC (SE-30) was 99+%.

Isolation of $DibB(OCH_3)_2$. To 20.0 mmol of $DibBH_2$ (1.0 M) at 0 °C in THF was added 3.2 mL (80 mmol) of methanol. The reaction mixture was allowed to warm to 25 °C and stir for 1 h. Distillation under nitrogen provided an 85% yield of $DibB(OCH_3)_2$: bp 93–94 °C (60 mm); n^{20}_D 1.4228; ^{1}H NMR (CCl_4, TMS) δ 0.94 (t, 15 H), 1.84 (doublet of heptet, 1 H), 2.65 (broad d, 1 H), 3.52 (s, 6 H); IR (1.0 M, THF solution) 1370–1290 cm^{-1} (s); mass spectrum *m/e* 186 (p^+, very weak), 171 ($p^+ - 15$, weak), 73 (base peak). Anal. Calcd for $C_{10}H_{23}BO_2$: C, 64.52; H, 12.48; B, 5.81. Found: C, 64.75; H, 12.47; B, 5.82. Oxidation of 1 mmol of the distilled product as previously described yielded 0.94 mmol (94%) of 2,2,4-trimethyl-3-pentanol and 0.6 mmol (6%) of 2,4,4-trimethyl-2-pentanol.

Reaction of $DibBH_2$ with $(CH_3)_2S$ in THF at 25 °C. The following procedure is representative. $DibBH_2$ (10 mmol) (1.0 M) was prepared as described previously from BH_3·THF. To the stirred reaction mixture at 0 °C was quickly added 1.47 mL (1.24 g, 20.0 mmol) of $(CH_3)_2S$. The reaction temperature was immediately allowed to warm to 25 °C, and stirring was continued for 1 h. Methanolysis was carried out as described previously for $DibBH_2$.

Reaction of $DibBH_2$ with Et_3N in THF at 25 °C. The following procedure is representative. $DibBH_2$ (10 mmol) (1.0 M) was prepared as described previously from BH_3·THF using *n*-hexadecane as GC internal standard. To the stirred reaction mixture at 0 °C was quickly added 2.79 mL (2.02 g, 20.0 mmol) of Et_3N. The reaction temperature was immediately allowed to warm to 25 °C, and stirring was continued for 1 h. Methanolysis was carried out as described previously for $DibBH_2$. Alternatively, hydroboration of the reaction mixture was carried out by quickly adding 1.57 mL (1.12 g, 10.0 mmol) of 1-octene at 25 °C for 1 h. After 1 h, the reaction mixture was quenched at 25 °C for 1 h with 1.6 mL (40 mmol) of methanol and GC (10% SE-30) analysis carried out.

Reaction of $DibBH_2$ with TMED in THF at 25 °C. The following procedure is representative. $DibBH_2$ (10 mmol) (1.0 M) was prepared as described previously. To the stirred reaction mixture at 0 °C was quickly added 1.58 mL (1.16 g, 10.0 mmol) of TMED. The reaction temperature was immediately allowed to warm to 25 °C. Stirring was continued for 1 h. Methanolysis was carried out as described previously for $DibBH_2$. Alternatively, hydroboration was carried out by adding 1.59 mL (1.36 g, 10.0 mmol) of α-pinene at 25 °C for 1 h. After 1 h, the reaction mixture was quenched at 25 °C for 1 h with 1.6 mL (40 mmol) of methanol and GC (10% SE-30) analysis carried out. Analysis showed 8.0 mmol of α-pinene unreacted (80%) and 2.0 mmol (20%) of Dib-2 via dehydroboration.

Isolation of $DibBH_2$·TMED. To 10.0 mmol of $DibBH_2$ (1.0 M) at 0 °C in THF was added 1.58 mL (1.16 g, 10.0 mmol) of TMED. The reaction mixture was allowed to warm to 25 °C and stir for 1 h. After the mixture was stirred, the THF was evaporated (25 °C/12 mmHg/2 h) using a water aspirator and $DibBH_2$·TMED was left behind as a white solid. The solid was recrystallized from 5 mL of pentane under nitrogen at −25 °C. The pentane layer was decanted away via a double-ended needle,[3] and the white solid was dried at 25 °C (12 mmHg) for 2 h. $DibBH_2$·TMED was recovered in 90% yield: mp 92–95 °C; ^{1}H NMR ($CDCl_3$, TMS) δ 0.12 (small hump, 1 H), 0.95–1.05 (s, d, 15 H),1.83 (m, 1 H), 2.22 (s, 6 H), 2.50 (s, 6 H), 2.60–3.20 (m, 4 H); IR (1.0 M in THF solution) 2370 cm^{-1} (s); ^{11}B NMR (relative to BF_3·EE) δ −1.74 (broad t). Anal. Calcd for $C_{14}H_{35}BN_2$: C, 69.41; H, 14.56; B, 4.46; N, 11.56. Found: C, 69.20; H, 14.61; B, 4.22; N, 11.29. The compound appeared very stable when exposed to air.

Isolation of $ThxBH_2$·TMED. To 10.0 mmol of $ThxBH_2$ (1.0 M) at 0 °C in THF was added 1.58 mL (1.16 g, 10.0 mmol) of TMED. The reaction mixture was allowed to warm to 25 °C and stir for 1 h. After 1 h at 25 °C, the THF was evaporated (25 °C/12 mmHg/1 h) using a water aspirator. A clear, viscous liquid remained. Distillation under nitrogen provided $ThxBH_2$·TMED in 92% yield: bp 38–40 °C (12 mmHg); n^{20}_D 1.4240; ^{1}H NMR ($CDCl_3$, TMS) δ 0.83–0.93 (s, d, 12 H), 1.08–1.60 (m, 1 H), 2.25 (s, 6 H), 2.63 (s, 6 H), 2.65–3.00 (m, 4 H); ^{11}B NMR (relative to BF_3·EE) +1.38 ppm (t); IR (1.0 M in THF solution) 2326–2273 cm^{-1} (s). Anal. Calcd for $C_{12}H_{31}BN_2$: C, 67.29; H, 14.59; B, 5.05; N, 13.08. Found: C, 67.34; H, 14.54; B, 4.95; N, 12.90. The liquid, prior to distillation, flamed in moist air after prolonged exposure.

Isolation of Bis($ThxBH_2$)·TMED. Thexylborane (10.0 mmol) was prepared from BH_3·$S(CH_3)_2$ according to the literature procedure.[13] To this product 5.0 mmol of TMED (0.79 mL) was added to form the bis addition compound. Removal of methyl sulfide under reduced pressure (12 mmHg) provided the adduct as a semisolid: 1.46 g, (93% yield). It was then purified by recrystallization from *n*-pentane at −50 °C: mp 43–45 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 12 H), 0.87 (d, J = 6 Hz, 12 H), 1.47 (septet, J = 6 Hz, 2 H), 2.63 (s, 12 H), 3.22 (s, 4 H); ^{11}B NMR δ +0.77.

Reaction of $DibBH_2$ with $(CH_3)_3N$ in THF at 25 °C. The following procedure is representative. $DibBH_2$ (10 mmol) (1.0 M) was prepared as described previously. To the stirred reaction mixture at 0 °C was added 500 mL of $(CH_3)_3N$ (20.0 mmol) via a gas-tight 250-mL syringe. The reaction temperature was immediately allowed to warm to 25 °C. Stirring was continued for 1 h. Methanolysis and hydroboration were carried out as described previously.

(13) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1392.

Isolation of $DibBH_2 \cdot N(CH_3)_3$. To 10.0 mmol of $DibBH_2$ (1.0 M) at 0 °C in THF was added 250 mL of $(CH_3)_3N$ (10.0 mmol) via a gas-tight 250-mL syringe. The reaction mixture was allowed to warm to 25 °C and stir for 1 h. After stirring, the THF was evaporated (25 °C/12 mmHg/1 h) using a water aspirator. $DibBH_2 \cdot N(CH_3)_3$ was left behind as a white solid. The solid was recrystallized from 5 mL of pentane under nitrogen at −25 °C. The pentane layer was decanted away via a double-ended needle, and the white solid was dried at 25 °C/12 mmHg/2 h. $DibBH_2 \cdot N(CH_3)_3$ was recovered in 90% yield: mp 58–60 °C; IR (1.0 M in THF) 2353 cm^{-1} (s); ^{11}B (relative to $BF_3 \cdot EE$) δ −1.94 (slightly broadened triplet). Anal. Calcd for $C_{11}H_{28}BN$: C, 71.35; H, 15.24; B, 5.84; N, 7.56. Found: C, 71.24; H, 15.34; B, 6.07; N, 7.27. The compound appeared to be stable in air.

Reaction of $DibBH_2$ with Pyridine in THF at 25 °C. The following procedure is representative. $DibBH_2$ (10 mmol) (1.0 M) was prepared as described previously. To the stirred reaction mixture at 0 °C was added 0.81 mL (0.791 g, 10.0 mmol) of pyridine. The reaction temperature was immediately allowed to warm to 25 °C, and stirring was continued for 1 h. Methanolysis and hydroboration were carried out as described previously.

Isolation of $DibBH_2$-Pyridine. To 10.0 mmol of $DibBH_2$ (1.0 M) at 0 °C in THF was added 0.81 mL (0.791 g, 10 mmol) of pyridine. The reaction mixture was allowed to warm to 25 °C and stir for 1 h. After stirring for 1 h at 25 °C, the THF was evaporated (25 °C/12 mmHg/1 h) using a water aspirator. The white solid which remained was recrystallized from 5 mL of pentane under N_2 at −25 °C. The pentane layer was decanted off via a double-ended needle, and the white solid was dried at 25 °C/12 mmHg/2 h. $DibBH_2$-pyridine was recovered in 90% yield: mp 51–52 °C; ^1H NMR ($CDCl_3$, TMS) δ 0.45 (small hump, 1 H), 0.84–0.98 (t, 15 H), 1.99 (m, 1 H), 7.44 (m, 2 H), 7.89 (m, 1 H), 8.69 (doublet of doublets, 2 H); ^{11}B NMR (relative to $BF_3 \cdot EE$) δ −0.68 (broad triplet); IR (1.0 M in THF) 2336–2262 (s), 1381–1361 (w), 769 (m), 695 cm^{-1} (m). Anal. Calcd for $C_{13}H_{24}BN$: C, 76.11; H, 11.79; B, 5.27; N, 6.83. Found: C, 75.93; H, 12.01; B, 5.11; N, 6.80. The compound appeared to be very stable in air.

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