Molecular Addition Compounds. 15. Synthesis, Hydroboration, and Reduction Studies of New, Highly Reactive *tert*-Butyldialkylamine−Borane Adducts

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Two series of *tert*-butyldialkylamines have been prepared and examined for borane complexation. The complexing ability of each amine in the two series examined decreases in the order shown. First series: *t*-BuN$(CH_2CH_2)_2O$ **1a** > *t*-$BuNEt_2$ **1b** > *t*-$BuNPr^n{}_2$**1c** > *t*-BuN$(CH_2CH_2OMe)_2$ **1d** ≫ *t*-$BuNBu^i{}_2$ **1e**. Second series: *t*-$BuNBu^iMe$ **2a** > *t*-$BuNPr^iMe$ **2b** > *t*-$BuNBu^iEt$ **2c** > *t*-$BuNBu^iPr^n$ **2d** ≫*t*-$BuNPr^iEt$ **2e**. The reactivity of the corresponding borane adducts toward 1-octene increases in the reverse order. The following amines form highly reactive liquid borane adducts hydroborating 1-octene in tetrahydrofuran at room temperature in less than 1 h: *t*-BuN$(CH_2CH_2OMe)_2$, *t*-$BuNBu^iEt$, and *t*-$BuNPr^iMe$. The limit of borane complexation among the amines examined is reached for *t*-$BuNBu^i{}_2$ exchanging borane neither with BMS nor with BH_3−THF. Among the various borane adducts prepared, the more promising borane adducts, *t*-Bu$(CH_3OCH_2CH_2)_2N-BH_3$ (**7**), *t*-$BuMePr^iN-BH_3$ (**8**), and *t*-$BuEtBu^iN-BH_3$ (**9**), were selected for complete hydroboration and reduction studies. Hydroboration studies with the new, highly reactive trialkylamine−borane adducts **7**−**9** and representative olefins, such as 1-hexene, styrene, β-pinene, cyclopentene, norbornene, cyclohexene, 2-methyl-2-butene, α-pinene, and 2,3-dimethyl-2-butene, in tetrahydrofuran, dioxane, *tert*-butyl methyl ether, *n*-pentane, and dichloromethane, at room temperature (22 ± 3 °C) were carried out. The reactions are faster in dioxane, requiring 1−2 h for the hydroboration of simple, unhindered olefins to the trialkylborane stage. Moderately hindered olefins, such as cyclohexene and 2-methyl-2-butene, give the corresponding dialkylboranes rapidly, with further slow hydroboration. However, the more hindered olefins, α-pinene and 2,3-dimethyl-2-butene, give stable monoalkylboranes very rapidly, with further hydroboration proceeding relatively slowly. The hydroborations can also be carried out conveniently in other solvents, such as THF, *tert*-butyl methyl ether, and *n*-pentane. A significant rate retardation is observed in dichloromethane. Regioselectivity studies of 1-hexene and styrene using these amine−borane adducts show selectivities similar to that of BH_3−THF. The rates and stoichiometry of the reaction of *t*-$BuMePr^iN-BH_3$ in tetrahydrofuran with selected organic compounds containing representative functional groups were also examined at room temperature. The reductions of esters, amides, and nitriles, which exhibit a sluggish reaction at room temperature, proceed readily under reflux conditions in tetrahydrofuran and dioxane and without solvent (at 85−90 °C). The carrier amines can be recovered by simple acid−base manipulations in good yield and readily recycled to make the borane adducts.

Borane−amine adducts are important reducing agents with a multitude of applications in organic synthesis and industrial processes.[4] They have a wide range of reactivities, are soluble in various solvents including hydrocarbons, and often show low sensitivity to moisture and air. In contrast, their use as hydroborating agents is of limited scope due to the formation of strong borane complexes, rendering the reactivity toward olefins lower than that of the adducts with ethers and sulfides.[5] Recently, we[6] and others[7] developed a number of new, highly reactive borane adducts with *N*,*N*-dialkylanilines, alkyldiisopropylamines, and *N*-silylamines as demonstrated by their success in hydroborating 1-octene in tetrahydrofuran at room temperature in less than 1 h. For the first time, aliphatic amines have been shown to be useful borane carriers for hydroboration. Their poten-

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Table 1. Borane Adducts with *t*-BuNR$_2$

	exchange,[a] %		amine−BH_3				
						hydroboration of 1-octene[e]	
amine	BH_3−SMe_2	BH_3−THF	state[b] (mp, °C)	$[BH_3]$[c] M	^{11}B NMR[d] (δ)	in THF[f]	neat
t-BuN(CH_2CH_2)$_2$O (**1a**)	100	100			−16.88	6 h	
t-BuNEt$_2$ (**1b**)	85	100			−14.89	6 h	
t-BuNPr$^n_2$ (**1c**)	70	100			−14.13	3 h	
t-BuN(CH_2CH_2OMe)$_2$ (**1d**)	50	95	liquid	4.5	−14.26	30 min	1 h
t-BuNBu$^i_2$ (**1e**)	0	0					

[a] Amine mixed with BH_3−SMe_2 or 1 M BH_3−THF in 1:1 molar ratio at room temperature and analyzed by ^{11}B NMR at equilibrium. [b] At 0 °C. [c] Estimated by hydrolysis in 2.00 M HCl−glycerol−water (2:1:1) and measuring the hydrogen evolved. [d] From the exchange with BH_3−SMe_2. [e] 5% excess of 1-octene, room temperature. [f] 3.00 M solution of 1-octene and 1.00 M in BH_3.

Table 2. Borane Adducts with *t*-BuNRR′

	exchange,[a] %		amine−BH_3				
						hydroboration of 1-octene[e]	
amine	BH_3/SMe_2	BH_3/THF	state[b] (mp, °C)	$[BH_3]$,[c] M	^{11}B NMR[d] (δ)	in THF[f]	neat
t-BuNBu^{i}Me (**2a**)	73	100			−14.15	20 h	
t-BuNPr^{i}Me (**2b**)	50	90	liquid	5.3	−16.23	30 min	3 h
t-BuNBu^{i}Et (**2c**)	33	73	liquid	4.4	−14.71	20 min	2 h
t-BuNBu^{i}Pr^n (**2d**)	24	71			−14.10	20 min	
1,2,2,6,6-pentamethylpiperidine	8	51	(78−80)		−16.04	20 min	
t-BuNPr^{i}Et (**2e**)	0	32	liquid	5→3	−14.14[g]	15 min	1 h

[a] Amine mixed with BH_3−SMe_2 or 1.00 M BH_3−THF in 1:1 molar ratio at room temperature and analyzed by ^{11}B NMR at equilibrium. [b] At 0 °C. [c] Estimated by hydrolysis in 2.00 M HCl−glycerol−water (2:1:1) and measuring the hydrogen evolved. [d] From the exchange with BH_3−SMe_2. [e] 5% excess of 1-octene, room temperature. [f] 3.00 M solution of 1-octene and 1.00 M in BH_3. [g] From the exchange with BH_3−THF, since no exchange occurred with BMS.

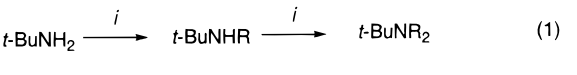
tial advantages over traditional carriers, such as tetrahydrofuran or dimethyl sulfide, for large-scale applications have been pointed out. We also demonstrated that borane complexation depends strongly on the steric requirements of the amine. The results obtained with alkylisopropylamines prompted us to examine *tert*-butyldialkylamines, with the objective of developing borane adducts meeting the following requirements: (1) hydroboration of 1-octene in tetrahydrofuran at room temperature in less than 1 h and (2) liquid adduct of high borane concentration, stable at room temperature, and soluble in representative solvents.

Results and Discussion

Two series of amines, **1a**−**e** and **2a**−**e**, with increasing steric bulk of the alkyl groups within each series were selected for the study. 1,2,2,6,6-Pentamethylpiperidine was also included for comparison.

t-BuNR$_2$	*t*-BuNRR^1
1a R = −$CH_2CH_2OCH_2CH_2$−	**2a** R = Me, R^1 = Bu^i
1b R = Et	**2b** R = Me, R^1 = Pr^i
1c R = Pr^n	**2c** R = Et, R^1 = Bu^i
1d R = −CH_2CH_2OMe	**2d** R = Pr^n, R^1 = Bu^i
1e R = Bu^i	**2e** R = Et, R^1 = Pr^i

Synthesis of Amines. The amines **1a**−**d** having two primary unbranched alkyl groups were prepared by the alkylation of *tert*-butylamine, following routine procedures (eq 1).



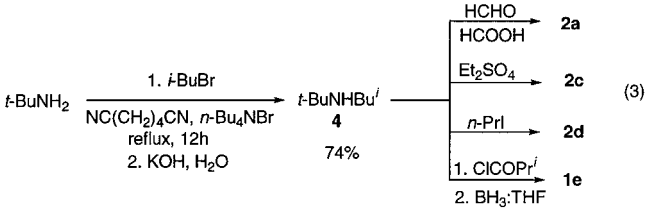
(1)

1a: *i* = $(ClCH_2CH_2)_2O$; **1b**: *i* = Et_2SO_4
1c: *i* = IPr^n

The amino ether **1d** was obtained by methylation of *tert*-butyldiethanolamine with dimethyl sulfate in the presence of a phase transfer catalyst (eq 2).

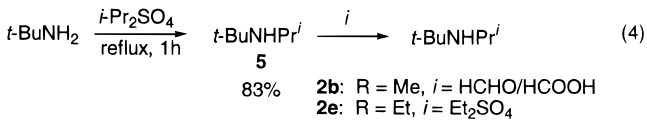
(2)

Alkyl-*tert*-butylisobutylamines **1e** and **2a**,**c**,**d** were prepared from a common intermediate, *t*-BuNHBu^i, **4**, as shown in eq 3. The alkylation of *tert*-butylamine with isobutyl bromide is very slow. Only 3% of **4** was formed after 24 h at reflux. Fortunately, a small amount of tetraalkylammonium iodide dissolved in adiponitrile markedly accelerates the reaction, and **4** is obtained in good yield in a reasonable time (eq 3).



(3)

Introduction of the second isobutyl group on **4** by direct alkylation is difficult. No product was obtained after refluxing **4** with isobutyl iodide for 24 h. Consequently, **1e** was prepared by acylation−reduction (eq 3). Similarly, alkyl-*tert*-butylisopropylamines **2b**,**e** were prepared from a common intermediate, *t*-BuNHPr^i, **5**, according to eq 4.



(4)

Although **5** is commercially available, it is costly. The synthesis shown in eq 4 is simple, employing low-cost starting materials. Alternatively, **5** can be prepared by

the alkylation of *tert*-butylamine with isopropyl bromide in the presence of tetraalkylammonium iodide and by other methods.[8,9]

Borane−Amine Adducts. The complexing ability of amines toward borane was tested by the exchange with BMS (borane−methyl sulfide) and BH_3−THF (borane−tetrahydrofuran) mixed in a 1:1 molar ratio. The amount of borane taken by an amine in the equilibrium was determined by ^{11}B NMR and is shown in Tables 1 and 2. Values for the exchange with BH_3−THF, a 1 M solution, should be considered qualitative since THF is in considerable excess. As revealed by the exchange experiments, dialkyl-*tert*-butylamines **1a**−**c** having two primary unbranched alkyl groups, take more than 50% of borane from BMS and 100% from BH_3−THF (Table 1). The lower complexing ability of *t*-BuNEt$_2$, as compared to *N*-*tert*-butylmorpholine suggested that substituting 2-methoxyethyl groups for ethyl groups might result in weaker borane complexation. Previously, it was also observed that diisopropyl(2-methoxyethyl)amine forms a weaker adduct with borane than did diisopropylethylamine.[7] Indeed, the amino ether **1d** takes only 50% of borane from BMS. The adduct hydroborates 1-octene in THF at room temperature in 30 min and under neat conditions in 1 h. It is a liquid, 4.5 M in borane, meeting well our requirements. The reactivity of borane adducts with **1a**−**d** toward 1-octene increases in the following order:

$$\mathbf{1a}\text{−}BH_3 \approx \mathbf{1b}\text{−}BH_3 < \mathbf{1c}\text{−}BH_3 \ll \mathbf{1d}\text{−}BH_3$$

Higher reactivity of the borane adduct with *t*-BuNPr$^n_2$, as compared to *t*-BuNEt$_2$, indicates the sensitivity of the systems to even minor differences in the steric requirements of the amines.

In the series of alkyl-*tert*-butylisobutylamines, the methyl derivative **2a** takes 73% of borane from BMS, giving a relatively strong adduct, which hydroborates 1-octene only very slowly (Table 2). The ethyl and *n*-propyl derivatives **2c**,**d** give highly reactive adducts, meeting our requirements. The limit of borane complexation is reached with *t*-BuNBu$^i_2$, **1e**. This amine does not only fail to take borane from BMS but also fails to take it from BH_3−THF! This is the most hindered amine for borane complexation among the amines examined in the present study.

Similarly, as observed for the dialkylisopropylamines, the substitution of the isopropyl group for the isobutyl group in the series decreases the complexing ability of amines. Thus, the methyl derivative **2b** takes 50% of borane from BMS as compared to 73% for **2a**. The adduct of **2b** is a liquid, 5.3 M, in borane, hydroborating 1-octene in THF at room temperature in less than 1 h. The ethyl derivative **2e** forms a weaker adduct, losing borane upon storage.

It was interesting to examine 1,2,2,6,6-pentamethylpiperidine, **6**, in comparison with the *N*-methyl derivatives **2a** and **2b**. The exchange with BMS and BH_3−THF reveals the complexing order **2a** > **2b** > **6**, as might be expected considering the increasing steric bulk of the alkyl groups attached to the nitrogen atom. Despite its high steric hindrance, **6** takes as much as 51% of borane from BH_3−THF. Regrettably, for the purpose of this study its borane adduct is a solid. The ^{11}B NMR spectrum of a solution in diethyl ether shows only one signal (quartet) at δ −15.8. In deuterated chloroform, a mixture of free amine and the adduct (40:60) was observed by ^1H NMR.

Detailed Hydroboration Studies. The above initial studies clearly demonstrated that borane adducts of amines **1d, 2b**, and **2c** are more reactive toward hydroboration of 1-octene. Encouraged by these observations and in order to establish the complete potential of these new borane adducts, detailed hydroboration studies of the borane adducts of *tert*-butylbis(2-methoxyethyl)-amine (**1d**), *tert*-butyl-*N*-methyl-*N*-isopropylamine (**2b**), and *tert*-butyl-*N*-ethyl-*N*-isobutylamine (**2c**) were undertaken. The borane adducts were prepared by passing a slight excess of diborane gas into the neat amine at 0−5 °C (eq 5). The concentration of the adsorbed borane was established by hydrolysis of an aliquot, using 2.00 M HCl−glycerol−water mixture, measuring the hydrogen evolved.

$$t\text{-BuR}^1\text{R}^2\text{N:} \xrightarrow[0\text{-}5^\circ\text{C}]{B_2H_6\ (\text{excess})} t\text{-BuR}^1\text{R}^2\text{N:BH}_3 \qquad (5)$$

1d R^1 = Me, R^2 = Pr^i	**7** R^1 = Me, R^2 = Pr^i
2b R^1 = Et, R^2 = Bu^i	**8** R^1 = Et, R^2 = Bu^i
2c $R^1 = R^2 = -CH_2CH_2OCH_3$	**9** $R^1 = R^2 = -CH_2CH_2OCH_3$

The adducts thus obtained, maintained under nitrogen, are stable at room temperature indefinitely. The stability of solutions of these adducts in THF, *tert*-butyl methyl ether, and dioxane were also studied. Solutions of the adduct in solvents (2.00 M in BH_3) were sealed in NMR tubes and monitored using ^{11}B NMR at intervals. The adducts **8** and **9** did not show any new peaks in the ^{11}B NMR spectra other than that given by the adducts during 6 months of observation. In THF, the adduct **8** developed small amounts (2−4%) of solvent-cleaved products after two months, but no further increase in this solvent-cleaved product was noted in the next 4 months.

Hydroboration of Olefins in Tetrahydrofuran. Hydroboration of representative mono-, di-, tri-, and tetrasubstituted olefins with the adducts **7**, **8**, and **9** was conducted in THF at room temperature. To establish the rate and stoichiometry, the reactions were carried out in solutions that were 0.50 M in BH_3 and 1.50 M in olefin. The procedure followed was to add the THF solution of the olefin (3 equiv) to the amine−borane (1 equiv) in THF at 0 °C, stirring the mixture further at room temperature (22 ± 3 °C). The progress of the hydroboration was conveniently followed by taking out aliquots at intervals, hydrolyzing with 3.00 M HCl−glycerol−THF (2:1:0.2), and measuring the hydrogen evolved. The reactions were also followed by ^{11}B NMR, monitoring a decreasing amine−borane signal and an increasing alkylborane signal.

Hydroborations are relatively faster with the adduct **7**, which hydroborated simple unhindered olefins, such as 1-hexene, styrene, and β-pinene to the trialkylborane stage within 1 h. The other adducts (**8** and **9**) required ~2 h for hydroboration to the trialkylborane stage. Hydrolysis of aliquots of the reaction mixture does not evolve any hydrogen, confirming complete utilization of borane. The moderately hindered 2-methyl-2-butene gave disiamylborane after 1 h (^{11}B NMR, δ ppm, +31.1), with further hydroboration slower. Cyclohexene forms dicyclohexylborane rapidly in ~1 h (^{11}B NMR, δ, ppm, +51.5 after methanolysis), and 2.84 hydride equivalents are

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Table 3. Hydroboration of Representative Olefins with *t*-Bu(CH$_3$OCH$_2$CH$_2$)$_2$N−BH$_3$ in Selected Solvents at Room Temperature[a]

	dioxane		THF		*tert*-butyl methyl ether		*n*-pentane		dichloromethane	
olefin	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized
1-hexene	1.00	3.00	1.00	3.00	1.50	3.00	1.00	3.00	18	3.00
					1.00	2.78			1.00	0.53
styrene	1.00	3.00	1.00	3.00	1.50	3.00	1.00	3.00	18	3.00
					1.00	2.90			1.00	0.46
β-pinene	1.00	3.00	1.00	3.00	2.00	3.00	1.00	3.00	18	3.00
					1.00	2.74				
cyclopentene	1.00	3.00	1.50	3.00	2.50	3.00	1.50	3.00	15	3.00
					1.00	2.71	1.00	2.85		
norbornene	1.00	3.00	2.00	3.00	2.50	3.00	2.00	3.00	15	3.00
					1.00	2.62	1.00	2.75		
cyclohexene	24	2.95	24	2.84	24	2.85	24	2.95	18	2.95
	0.66	2.00	1.16	2.00	1.00	2.00	0.83	2.00		
2-methyl-2-butene	24	2.95	24	2.93	24	2.93	24	2.93	24	2.93
	0.58	2.00	0.83	2.00	0.91	2.00	2.00	2.00		
α-pinene	24	2.00	24	1.89	24	1.88	24	1.57	48	1.78
	0.33	1.00	0.40	1.00	0.40	1.00	0.41	1.00	24	1.18
2,3-dimethyl-2-butene	24	1.80	24	1.73	24	1.69	24	1.70	24	1.70
	0.33	1.00	0.66	1.00	0.75	1.00	0.83	1.00		

[a] Reactions were carried out using amine−borane **7** (5 mmol) and an olefin (15 mmol) in a total volume of 10 mL solution.

Table 4. Hydroboration of Representative Olefins *t*-BuMePr^{i}N−BH$_3$ in Selected Solvents at Room Temperature[a]

	dioxane		THF		*tert*-butyl methyl ether		*n*-pentane		dichloromethane	
olefin	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized
1-hexene	1.50	3.00	2.00	3.00	2.00	3.00	2.00	3.00	1.00	2.70
	1.00	2.93	1.00	2.86	1.00	2.88	1.00	2.37	48	1.85
styrene	2.00	3.00	2.00	3.00	2.00	3.00	2.00	3.00	48	1.88
	1.00	2.88	1.00	2.86	1.00	2.90	1.00	2.03		
β-pinene	2.00	3.00	3.00	3.00	2.50	3.00	2.00	3.00	48	2.00
	1.00	2.85	1.00	2.85	1.00	2.78	1.00	2.40		
cyclopentene	2.00	3.00	3.00	3.00	3.00	3.00	2.00	3.00	48	2.39
	1.00	2.88	1.00	2.78	1.00	2.76	1.00	2.40		
norbornene	2.00	3.00	3.00	3.00	3.00	3.00	2.50	3.00	48	2.47
	1.00	2.85	1.00	2.76	1.00	2.73	1.00	2.28		
cyclohexene	24	2.95	24	2.88	24	2.90	24	2.95	48	2.38
	0.91	2.00	0.91	2.00	1.25	2.00	1.16	2.00		
2-methyl-2-butene	24	2.95	24	2.85	24	2.88	24	2.95	48	2.50
	0.91	2.00	1.00	2.00	1.16	2.00	3.66	2.00		
α-pinene	24	2.00	24	1.78	24	1.59	24	1.65	48	1.55
	0.58	1.00	0.50	1.00	0.40	1.00	0.66	1.00		
2,3-dimethyl-2-butene	24	1.64	24	1.38	24	1.47	24	1.57	48	1.65
	0.50	1.00	0.58	1.00	0.91	1.00	0.91	1.00		

[a] Reactions were carried out using amine−borane **8** (5 mmol) and an olefin (15 mmol) in a total volume of 10 mL solution.

utilized in 24 h (^{11}B NMR, *δ*, ppm, +81.0 after methanolysis corresponding to the formation of tricyclohexylborane). However, the more hindered α-pinene consumes one hydride rapidly in 30 min, but then the reaction continues only slowly, with the hydride utilization increasing to 1.89, 1.78, and 1.71 in 24 h for the adducts **7**, **8**, & **9**, respectively, at room temperature, indicating incomplete formation of Ipc$_2$BH. This is also confirmed by ^{11}B NMR, which gave two peaks after methanolysis at +32 (minor, due to IpcB(OMe)$_2$) and +53 (major, due to Ipc$_2$BOMe). Further substitution on the olefin, i.e., the tetrasubstituted 2,3-dimethyl-2-butene, results in further lowering of the hydride uptake. Here also, addition of the first hydride is very fast, giving thexylborane (^{11}B NMR, *δ* ppm, +24). The olefin/BH$_3$ ratio then rises to 1.73, 1.38, and 1.69 after 24 h for the adducts **7**, **8**, and **9**, respectively, at room temperature (^{11}B NMR *δ* ppm +24 and +81, after methanolysis +31 and +53). The order of reactivity of these adducts toward representative olefins in THF is **7** > **9** > **8** (Tables 3−5).

Hydroboration of Olefins in Other Solvents. Hydroborations with the adducts **7**−**9** were also conducted in solvents, such as dioxane, *tert*-butyl methyl ether, *n*-pentane, and dichloromethane. In dioxane, the adducts showed an enhanced reactivity when compared to their solutions in tetrahydrofuran. Thus, in dioxane **7** and **9** hydroborate unhindered mono- and disubstituted olefins to the corresponding trialkylborane stage within 1 h. Enhanced reactivity is also observed for hindered olefins. For example, α-pinene is cleanly hydroborated to the Ipc$_2$-BH stage. This is also confirmed by ^{11}B NMR observation, which reveals the exclusive presence of Ipc$_2$BOMe after methanolysis (*δ* ppm +53). The reactivity of the adduct **8** toward representative olefins was slightly lower. Thus the adduct **8** required 2 h to hydroborate simple unhindered olefins, such as 1-hexene, styrene, and cyclopentene, to the trialkylborane stage. However, in the case of hindered α-pinene, the adduct cleanly hydroborated to the Ipc$_2$BH stage. In *tert*-butyl methyl ether and *n*-pentane the reactivity of the borane−amine adducts **7**−**9** is similar to that observed in THF. In dichloromethane, a remarkable retardation of the rates of hydroboration is observed. Only with the adduct **7** was the hydroboration of simple unhindered olefins is com-

Table 5. Hydroboration of Representative Olefins with *t*-BuEtBu^{i}N−BH_3 in Selected Solvents at Room Temperature[a]

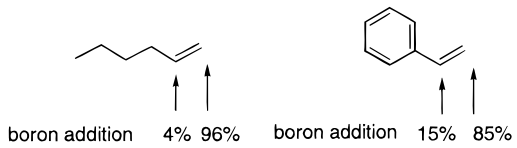
	dioxane		THF		*tert*-butyl methyl ether		*n*-pentane		dichloromethane	
olefin	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized	time (h)	hydrides utilized
1-hexene	1.00	3.00	2.00	3.00	1.00	3.00	1.00	3.00	48	1.91
			1.00	2.95						
styrene	1.00	3.00	2.00	3.00	1.00	3.00	1.00	3.00	48	1.85
			1.00	2.86						
β-pinene	1.00	3.00	3.00	3.00	1.50	3.00	1.50	3.00	48	1.97
			1.00	2.83	1.00	2.93	1.00	2.76		
cyclopentene	1.00	3.00	3.00	3.00	2.00	3.00	2.00	3.00	48	2.69
			1.00	2.85	1.00	2.83	1.00	2.52		
norbornene	1.00	3.00	3.00	3.00	2.00	3.00	2.50	3.00	48	2.74
			1.00	2.74	1.00	2.83	1.00	2.40		
cyclohexene	24	2.93	24	2.84	24	2.95	24	2.92	48	2.80
	0.58	2.00	1.16	2.00	0.91	2.00	0.91	2.00		
2-methyl-2-butene	24	2.95	24	2.88	24	2.88	24	2.93	48	2.87
	0.58	2.00	1.16	2.00	0.91	2.00	2.83	2.00		
α-pinene	24	2.00	24	1.71	24	1.59	24	1.65	48	1.66
	0.33	1.00	0.33	1.00	0.33	1.00	0.33	1.00		
2,3-dimethyl-2-butene	24	1.74	24	1.69	24	1.47	24	1.57	48	1.71
	0.33	1.00	0.33	1.00	0.66	1.00	0.50	1.00		

[a] Reactions were carried out using amine-borane **9** (5 mmol) and an olefin (15 mmol) in a total volume of 10 mL solution.

plete in 18 h, whereas, with the adducts **8** and **9**, the hydroborations were not complete even after 48 h at room temperature and the ^{11}B NMR studies showed the presence of starting amine−borane. This unusual rate retardation may be due to interaction of the solvent, dichloromethane, with the amine−borane, as reported earlier.[7d]

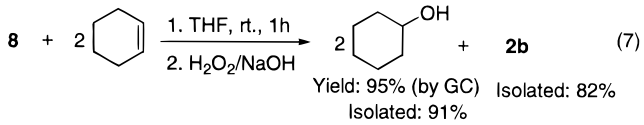
Summarizing all the solvents, the following order of reactivity with change of solvent in the hydroboration of representative olefins with **7**−**9** was noted: dioxane > tetrahydrofuran ≈ *tert*-butyl methyl ether ≈ *n*-pentane ≫ dichloromethane. Tables 3−5 summarize the results of these hydroboration studies with the adducts **7**−**9** in various solvents.

Regioselectivity of Hydroboration. Regioselectivity studies for 1-hexene and styrene with **7**−**9** were carried out in THF. 1-Hexene and styrene were hydroborated using 1 equiv of amine−borane for 3 equiv of an olefin. All the reactions were followed by ^{11}B NMR. The intermediate organoboranes were oxidized with H_2O_2/NaOH, and the product alcohols were analyzed by GC. The regioselectivities of hydroboration of 1-hexene and styrene with **7**−**9** are similar to those reported for BH_3−THF.[10] Thus, the hydroboration of 1-hexene formed the 1- and 2-hexanols in a ratio of 96:4. Similarly, with styrene, 1- and 2-phenylethanols were formed in a ratio of 85:15.



(6)

Hydroboration−Oxidation of Olefins. To further establish the synthetic applicability of these new highly reactive amine−borane adducts, hydroboration−oxidation of olefins was also studied. Hydroboration−oxidation of cyclohexene with **8** in THF gave cyclohexanol in quantitative yields (96% by GC, 91% isolated, eq 7). The carrier amine (**2b**) was recovered using acid−base manipulations in 82% yield and can be used again for the preparation of borane adducts.



(7)

Similar hydroborations were also carried out with borane adducts **7** and **9**, and the product cyclohexanol was isolated in 92% and 90.5% yields, respectively. Since the basic carrier amine was present in the reaction mixture after hydroboration, oxidation of the organoborane with hydrogen peroxide was also examined without the usual addition of sodium hydroxide. The oxidation was instantaneous; however, the yield of cyclohexanol was slightly lower (91% by GC). In the case of styrene, the yield of 1- and 2-phenylethanols was even less (85% by GC) and the isomeric ratio was 79:21. Apparently, the oxidation is not complete under these conditions. It was made complete by the addition of 20 mol % excess carrier amine after hydroboration was complete. The hydroboration can be conveniently carried out in a variety of solvents. However, for water immiscible solvents, such as *n*-pentane, ethyl ether, and *tert*-butyl methyl ether, either ethanol or THF should be added to facilitate oxidation with hydrogen peroxide.

Selective Reductions

Most of the literature reported studies on reducing properties of known amine−borane adducts are limited to high-temperature reductions and reductions under acidic conditions.[4a,5f] The amine−boranes reported in the literature so far fail to reduce ketones at room temperature. However, the presence of Lewis acids such as BF_3·OEt_2 or oxazaborolidines facilitates the reduction of ketones with amine−boranes, such as *N*,*N*-diethylaniline−borane at room temperature.[4a,11−14] On the other

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Table 6. Reaction of *t*-BuMePr^{i}N−BH_3 with Representative Alcohols at a Molar Ratio of 1.33:1 in THF at Room Temperature

	t-BuMePr^{i}N−BH_3			
compound[a]	time (min)	hydrogen equiv evolved	hydride equiv used	hydride equiv used for reduction
benzyl alcohol	5	1.00	1.00	0.00
1-butanol	5	1.00	1.00	0.00
2-pentanol	10	1.00	1.00	0.00
2-methyl-2-butanol	15	1.00	1.00	0.00
phenol	30	1.00	1.00	0.00

[a] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution (0.25 M in compound and 1.00 M in hydride).

hand, borane reagents have been proven to be reagents of choice for many organic functional group reductions. To establish further the synthetic potential of the new, highly reactive amine−boranes, reduction studies of the representative organic functional groups at room temperature was undertaken. For these detailed studies, from the three adducts, *tert*-butyl-*N*-methyl-*N*-isopropylamineborane (**8**), which contains the higher percentage of borane, was selected.

Rate and Stoichiometric Studies. The procedure adopted was to add 6.25 mmol of the organic compound to 8.3 mmol of amine−borane in sufficient THF to give 25 mL of solution. This makes the reaction mixture 0.33 M in "BH_3" (1.00 M hydride) and 0.25 M in compound. The compound was added at 0 °C and stirred further at room temperature (contents maintained at room temperature, ∼20 °C). Aliquots are removed at appropriate intervals and analyzed for residual hydride by hydrolysis using glycerol−3.00 N HCl−THF (1:1:0.2) and measuring the hydrogen evolved. This establishes both the rate and the stoichiometry of the reaction. The reactions are also cross-checked either by ^{11}B NMR analysis or GC analysis.

Alcohols. Alcohols reacted with **8** rapidly and liberated hydrogen quantitatively. No further reaction was observed. Table 6 shows the reactivity of various alcohols with amine−boranes. The rate of hydrogen evolution for the alcohols decreases in the order primary > secondary > tertiary. This is in agreement with the usual interpretation that the acidity of the hydroxylic hydrogen in these alcohols decreases in this order.[15] However, the slow reactivity of phenol may be attributed to the weaker basic character of the oxygen atom which may oppose the formation of a prior addition complex (eq 8).

$$\mathrm{ROH} + \mathrm{BH_3} \longrightarrow \mathrm{R\text{-}O(H)B(H)_2H} \longrightarrow \mathrm{R\text{-}OBH_2} + \mathrm{H_2} \qquad (8)$$

To further understand the reactivity of these alcohols toward amine−boranes, another set of experiments was carried out by using 3 equiv of alcohol for 1 equiv of amine−borane. Reaction of **8** with 3 equiv of simple unhindered hydroxy compounds, such as 1-butanol and benzyl alcohol, was very fast and gave trialkoxyborane (^{11}B NMR, +18.2, singlet). Moderately hindered 2-pentanol took a relatively long time to react completely.

Table 7. Reaction of *t*-BuMePr^{i}N−BH_3 with Representative Aldehydes and Ketones at a Molar Ratio of 1.33:1 in THF at Room Temperature

	t-BuMePr^{i}N−BH_3	
compound[a]	time (h)	hydride equiv for reduction
caproaldehyde	1.00	1.00
benzaldehyde	0.50	1.00
2-hexanone	1.00	1.00
acetophenone	0.50	0.51
	1.00	0.77
	2.50	1.00
benzophenone	0.50	0.03
	3.00	0.17
	6.00	0.36
	18	0.93
	24	1.00

[a] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution 0.25 M in compound and 1.00 M in hydride.

Hindered tertiary alcohols gave only dialkoxyborane (^{11}B NMR, +26, doublet).

Aldehydes and Ketones. The aldehydes and ketones examined all consumed one hydride, indicating reduction to the alcohol stage. Caproaldehyde, benzaldehyde, and 2-hexanone were reduced rapidly within 1 h. In the case of acetophenone and benzophenone the reactions were slower, which may be due to the combined steric and electronic effects exerted by the phenyl group. The results are summarized in Table 7.

For better synthetic utility, reductions were also tried using 2 equiv of compound for 1 equiv of amine−borane. However, under these molarity conditions the reactions require more time to go to completion than observed above. For example, using adduct **8**, benzaldehyde took 2 h for complete reaction and acetophenone 18 h. The reduction of benzaldehyde with **8** under these conditions was carried out on a preparative scale and the benzyl alcohol was isolated in 80% yield, while the amine was recovered in 89% yield. Similarly, the reduction of acetophenone gave 1-phenylethanol in 91% yield, and *tert*-butyl-*N*-methyl-*N*-isopropylamine was recovered in 86% yield.

Carboxylic Acids, Anhydrides, and Acid Chlorides. The reaction with caproic acid is very fast, whereas the reaction with benzoic acid is somewhat slower. Both reactions consume ∼3 hydride equiv, one for hydrogen evolution and two for the reduction to the alcohol stage. ^{11}B NMR studies for the reduction of caproic acid with **8** shows a peak at +18.5 and traces of unreacted amine−borane are also indicated. Among the other acyl derivatives, only acetic anhydride was reduced to the alcohol stage, taking 3.8 hydride equiv from **8** out of the expected 4 for complete reduction.[16] The ^{11}B NMR analysis shows trialkoxyborane (+18.1, singlet) as a major peak. The other anhydrides such as succinic anhydride and phthalic anhydride formed a precipitate, which did not dissolve even after 48 h. Hydride analysis revealed very little hydride uptake. The ^{11}B NMR of the THF solution showed only the presence of amine−borane in solution. Hydrolysis with water and the usual workup of the reaction mixture gives unreacted anhydride in major amounts. Under the standard conditions, both the aliphatic and aromatic acid chlorides, caproyl chloride and

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Table 8. Reaction of *t*-BuMePr^{i}N−BH$_3$ with Representative Carboxylic Acid and Acyl Derivatives at a Molar Ratio of 1.33:1 in THF at Room Temperature

	t-BuMePr^{i}N−BH$_3$			
compound[a]	time (h)	hydrogen equiv evolved	hydride equiv used	hydride equiv for reduction
caproic acid	1.50	1.00	3.00	2.00
benzoic acid	0.25	1.00	1.02	0.02
	6.00	1.00	3.00	2.00
acetic anhydride	0.25	0.00	0.55	0.55
	2.00	0.00	2.21	2.21
	6.00	0.00	3.34	3.34
	24	0.00	3.80	3.80
succinic anhydride	precipitate formed			
phthalic anhydride	precipitate formed			
caproyl chloride	24	0.00	0.26	0.26
benzoyl chloride	24	0.00	0.22	0.22

[a] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution 0.25 M in compound and 1.00 M in hydride.

Table 9. Reaction of *t*-BuMePr^{i}N−BH$_3$ with Representative Esters at a Molar Ratio of 1.33:1 in THF at Room Temperature

	t-BuMePr^{i}N−BH$_3$	
compound[a]	time (h)	hydride equiv for reduction
ethyl butyrate	0.50	0.03
	2.00	0.13
	4.00	0.21
	24	0.33
	72	0.53
methyl caproate	0.50	0.00
	2.00	0.11
	8.00	0.23
	24	0.42
	48	0.61
	96	0.64
methyl benzoate	0.50	0.03
	1.00	0.03
	2.00	0.03
	24	0.06
	48	0.12

[a] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution 0.25 M in compound and 1.00 M in hydride.

benzoyl chloride, fail to react even after prolonged periods of time (Table 8).

Esters. Both aliphatic and aromatic esters fail to react with **8** under the present conditions. Very little hydride uptake was noted even after 72 h. The ^{11}B NMR analysis showed exclusively unreacted amine−borane. Table 9 summarizes the results.

Amines, Imines, and Amides. *n*-Hexylamine liberates only 0.11 equiv of hydrogen upon the reaction with **8** over 24 h. The resulting solution, after 24 h, was found to contain *n*-hexylamine−borane (60%), reagent amine−borane (29%), and borane−THF (10%) complexes as revealed by ^{11}B NMR (δ −19.9, −14.1, and −1.1 respectively), indicating the presence of an equilibrium mixture. Imines are reduced to the corresponding amines rapidly with the uptake of one hydride, and the resulting amine−boranes were in equilibrium with the reagent amine−borane. *N*-Phenylbenzylimine takes a relatively longer time for the reduction (∼8 h), which may be attributed to the presence of phenyl groups on both sides of the imine functionality.

Table 10. Reaction of *t*-BuMePr^{i}N−BH$_3$ with Representative Amines, Imines, and Amides at a Molar Ratio of 1.33:1 in THF at Room Temperature

	t-BuMePr^{i}N−BH$_3$			
compound[a]	time (h)	hydrogen equiv evolved	hydride equiv used	hydride equiv for reduction
n-hexylamine	0.50	0.03	0.03	0.00
	1.00	0.08	0.08	0.08
	24	0.11	0.11	0.11
N-butylbenzylimine	0.50	0.00	0.89	0.89
	1.00	0.00	1.00	1.00
N-phenylbenzylimine	0.50	0.00	0.41	0.41
	2.00	0.00	0.79	0.79
	4.00	0.00	0.92	0.92
	8.00	0.00	1.00	1.00
caproamide	0.50	1.32	1.45	0.13
	1.00	1.35	1.65	0.30
	18	1.35	2.22	0.87
	24	1.35	2.25	0.90
	48	1.35	2.25	0.90
benzamide	0.50	1.14	1.15	0.01
	1.00	1.19	1.21	0.02
	4.00	1.31	1.56	0.25
	18	1.31	2.04	0.73
	36	1.31	2.32	1.01
	72	1.31	2.40	1.09
N-methylbenzamide	0.50	0.61	0.64	0.04
	1.00	0.68	0.74	0.06
	4.00	0.85	1.54	0.69
	8.00	0.85	1.99	1.14
	24	0.85	2.22	1.37
	48	0.85	2.45	1.60
N,*N*-dimethylcaproamide	0.50	0.00	0.26	0.26
	1.00	0.00	1.01	1.01
	3.00	0.00	2.00	2.00
N,*N*-dimethylbenzamide	0.50	0.00	0.15	0.15
	1.00	0.00	0.21	0.21
	4.00	0.00	0.85	0.85
	8.00	0.00	1.40	1.40
	24	0.00	2.00	2.00

[a] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution 0.25 M in compound and 1.00 M in hydride.

Primary amides are reduced very slowly, exhibiting only about 50% reduction even after long hours. The reactions evolve hydrogen (1.3 equiv) rapidly, with further reduction slow, though the presence of unreacted amine−borane in the reaction medium is observed by ^{11}B NMR. In the case of the secondary amide, *N*-methylbenzamide, rapid hydrogen (0.85 equiv) evolution is also observed, with the formation of a white precipitate and only slow further reaction. On the other hand, the rates of reaction of tertiary amides is considerably faster, exhibiting hydride uptake of two required for reduction to the amine stage.[16] Table 10 summarizes the results.

Nitriles and Nitro Compounds. Nitriles react very slowly with **8**, and the reaction fails to proceed to completion. Only 1.68 equiv of hydride was consumed even after 96 h, whereas 2 hydride equiv is required for reduction to the amine stage.[16,17]

A detailed account of more rapid reductions at higher temperatures, with isolation of the products, is discussed in the following text.

Nitro compounds such as nitromethane and nitrobenzene failed to react under the present conditions. This inertness of borane toward the nitro group is presumably due to the very weakly basic properties of this group. The

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Table 11. Reaction of *t*-BuMePr^{i}N−BH_3 with Representative Nitriles and Nitro Compounds at a Molar Ratio of 1.33:1 in THF at Room Temperature

	t-BuMePr^{i}N−BH_3	
compound[a]	time (h)	hydride equiv for reduction
heptanenitrile	2.00	0.00
	12	0.19
	24	1.16
	48	1.33
	96	1.56
benzonitrile	2.00	0.00
	12	0.19
	24	0.59
	48	1.11
	72	1.52
	96	1.68
nitromethane	1.00	0.00
	24	0.00
nitrobenzene	24	0.00

[a] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution 0.25 M in compound and 1.00 M in hydride.

reduction studies with the nitriles and the nitro compounds are presented in Table 11.

Epoxides. The reaction of epoxides is slow. With simple 1,2-propylene oxide, the hydride uptake is almost one after 24 h, but the usual workup and GC analysis reveals only 30% of propanols. Similar results are also realized with styrene oxide. It consumes 2 hydride equiv after 24 h, though only one hydride is required for reduction, and the usual workup gave only small amounts of 1- or 2-phenylethanols. These observations were similar to those reported for BH_3−THF, and it was also known that presence of sodium borohydride or boron trifluoride markedly changes the reaction of epoxides with diborane.[18] However, in the present study, no further efforts were made to improve the reactivity of epoxides with **8**.

Reaction of 8 with Esters, Amides, and Nitriles at Reflux Temperatures. The reduction of some functional groups, such as esters, amides, nitriles, etc., are sluggish at room temperature. However, BH_3−THF[19] and BMS[20] have proven to be the reagents of choice for these reductions over any complex metal hydride.[21−24] To further establish the potential of this new, reactive amine−borane adduct and in a bid to find an alternative for BH_3−THF and BMS, it was decided to examine whether a modest increase in the temperature would facilitate the reduction. Thus, reductions with **8** toward esters, amides, and nitriles were also examined in tetrahydrofuran and dioxane at reflux temperature and also without solvent at 85−90 °C.

Esters. The reductions of ethyl undecanoate, methyl caproate, and methyl benzoate with **8** in THF and dioxane at reflux temperatures were studied. It was established from previous experiments at room temperature that esters require 2 hydride equiv for the reduction to the alcohol stage. Accordingly, reductions were carried out in 1:1.5 amine−borane/ester molar ratio using 10% excess hydride to ensure complete reaction. The procedure adopted was to add 12.5 mmol of ester to a solution of 9 mmol of amine−borane in 21.6 mL of the solvent, reacting the mixture under reflux. Aliquots were taken out at intervals, worked up, and checked for the presence of the starting ester by GC analysis. The reactions were also cross-checked by ^{11}B NMR analysis. The results are presented in Table 12.

Table 12. Reduction of Representative Esters, Nitriles, and Amides with *t*-BuMePr^{i}N−BH_3 in Tetrahydrofuran and Dioxane at Reflux and without Solvent

	t-BuMePr^{i}N−BH_3 time (h)		
compound	THF	dioxane	neat[a,b]
ethyl undecanoate[c]	0.50	0.25	0.25
methyl caproate[c]	0.50	0.25	0.25
methyl benzoate[c]	2.50	0.50	10
n-heptanenitrile[d]	2.00	0.50	
benzonitrile[d]	6.00	0.50	
caproamide[e]	10	2.00	
benzamide[e]	12	2.00	
N-methylbenzamide[f]	10	1.00	
N,*N*-dimethylcaproamide[g]	0.25	0.25	
N,*N*-dimethylbenzamide[g]	0.50	0.25	

[a] Amine-borane in 30% excess was taken to compensate the loss of diborane in heating. [b] At 85−90 °C. [c] 12.5 mmol of compound was added to 9.1 mmol of amine−borane (10% excess of hydride) in 25 mL solution (0.5 M in compound). [d] 6.25 mmol of compound was added to 8.3 mmol of amine−borane (25 mmol of hydride) in 25 mL of solution 0.25 M in compound and 1.00 M in hydride. [e] 6.25 mmol of compound was added to 9 mmol of amine−borane (10% excess) in 25 mL of solution in THF or dioxane. [f] 6.25 mmol of compound was added to 13.7 mmol of amine−borane (10% excess) in 25 mL solution of THF or dioxane. [g] 6.25 mmol of compound was added to 11.6 mmol of amine−borane (10% excess) in 25 mL solution of THF or dioxane.

In dioxane, the reductions are very fast. Aliphatic esters are reduced in 15 min, and methyl benzoate is reduced in 30 min. In THF, the reductions are relatively slower, perhaps because of the somewhat lower refluxing temperature. Thus, **8** reduced ethyl undecanoate to 1-undecanol in 0.5 h. The difference is more pronounced for aromatic esters, requiring 2.5 h for the reduction of methyl benzoate to the corresponding alcohol.

Reductions without solvent were carried out by mixing the amine−borane adduct **8** with esters and heating to 85−90 °C. Under these conditions, aliphatic esters reduce rapidly within 15 min. However, methyl benzoate reacts much slower, and some loss of diborane was observed leading to incomplete reduction. This was also confirmed by ^{11}B NMR, which showed the presence of only trialkoxyborane, with absence of amine−borane, confirmed by GC analysis which showed the presence of unreacted ester. The reactions could be forced to completion by taking an excess of **8**.

Nitriles. Reductions of *n*-heptanenitrile and benzonitrile were carried out with **8**. From studies at room temperature, it was established that nitriles consume 2 hydride equiv to give the corresponding borazine derivative, which can be hydrolyzed to the product amine (eq 9).[17]

Accordingly, reactions were carried out by adding 9 mmol amine−borane (10% excess) and 8.3 mmol nitrile to THF or dioxane and refluxing the mixture. The reactions were followed by taking aliquots at intervals and GC analysis for the remaining nitrile after workup. The results are presented in Table 12. As follows from

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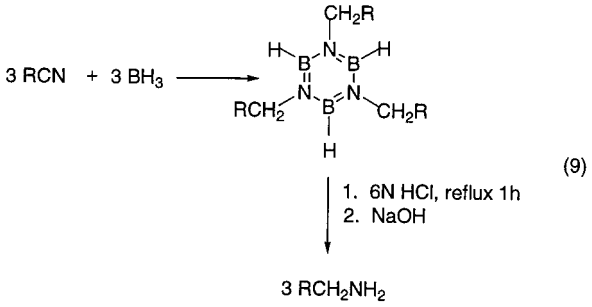

(9)

the results, in THF the aliphatic nitrile is reduced faster than the aromatic one. In dioxane, the reductions are faster, being complete in 30 min for both nitriles. Reductions of nitrile in neat condition were not studied because loss of diborane during the reaction was observed leading to incomplete reduction.

Amides. Reductions of primary, secondary, and tertiary amides using **8** in THF and dioxane at reflux temperature were followed by ^{11}B NMR, hydrolysis of aliquots at intervals, and GC examination for unreacted amide. The product of the reduction is an amine that forms a relatively stable borane−amine, so that 1 mol of borane reagent is required per mole of amine product. Accordingly, tertiary amides require five hydrides, secondary six, and primary four hydrides.[25] The reductions gave quantitative yields of amine products (by GC). The results are presented in Table 12.

In refluxing THF, reactions with primary amides evolve hydrogen (2 equiv) rapidly and further reduction is slow. *N*-Methylbenzamide, a secondary amide, evolves hydrogen (1 equiv) rapidly; here also, further reaction is slow. In both cases, reduction to the amine stage requires 10 h of refluxing in THF. Tertiary amides are reduced rapidly in 0.5 h, giving the corresponding borane adducts as products. In dioxane, the reductions are faster, being complete in 2 h for the slowest reacting primary amides and in only 15 min for the tertiary amides.

Isolation of the Products. In case of reduction of aldehydes, ketones, acids, esters, etc., the product alcohols are readily separated by simple acid−base manipulations. When the product is a water-soluble alcohol, it can be easily isolated by either distillation or column chromatography.

Two procedures for the isolation of product amines obtained from imines, nitriles, and amides can be used. The first procedure is used when the product amine and the carrier amine differ in boiling points or polarities. The reduction product, the amine−borane, is hydrolyzed with 6.00 M hydrochloric acid, and the mixture of both amines obtained by treatment of the acidic phase with sodium hydroxide is separated by distillation or column chromatography. The second procedure is applied when the product amine is strongly complexed with borane (as in the case with less hindered amines, e.g., *N*-methylbenzylamine and *N*,*N*-dimethylbenzylamine), the reaction product is treated with dilute hydrochloric acid. Under these conditions, the product borane−amine complex is stable. The more hindered carrier amine is extracted into the acidic aqueous phase, separated, and recovered by alkalization. The product amine can be liberated from its borane adduct by the addition of boron trifluoride−etherate.

Conclusion

This study has demonstrated that several *tert*-butyldialkylamines are convenient borane carriers for hydroboration. The complexing ability of amines can be varied in a predictable manner by a proper choice of alkyl groups. Stable, highly reactive liquid adducts of **1d**, **2b**, and **2c** have been prepared. Simple procedures for the synthesis of the majority of amines examined have been worked out. As the result of this and our previous studies,[6] a group of new, highly reactive borane−amine adducts has become available for the first time. The present study also clearly demonstrates the synthetic potential of the new, highly reactive amine−borane adducts *tert*-butyl-bis(2-methoxyethyl)amine-borane (**7**), *tert*-butyl-*N*-methyl-*N*-isopropylamine-borane (**8**), and *tert*-butyl-*N*-ethyl-*N*-isobutylamine-borane (**9**). Simple unhindered olefins can be hydroborated to the trialkylborane stage rapidly, whereas hindered olefins can be partially hydroborated to the mono- or dialkylborane stage. The hydroborations can be carried out conveniently in a variety of solvents. The amine−borane adduct shows enhanced reactivity in dioxane but low reactivity in dichloromethane. The present study also indicates that the reactivity of these borane adducts toward representative olefins is similar to that of BMS, so the accumulated data on the rates and stoichiometry of hydroboration with these reagents can be used to predict the hydroboration results with **7**−**9**. In the great majority of cases, the hydroboration products were oxidized using hydrogen peroxide/sodium hydroxide to give the corresponding alcohols in quantitative yields, without any interference by the amine. This study also demonstrates that **8** can substitute for borane−dimethyl sulfide (BMS) in the reduction of various functional groups. Aldehydes, ketones, acids, imines, and tertiary amides are reduced conveniently at room temperature. Functional groups that show sluggish reactivity at room temperature, such as esters, primary and secondary amides, and nitriles, can be readily reduced in tetrahydrofuran or dioxane under reflux conditions.

In refluxing dioxane, the reductions of esters, amides, and nitriles are complete in 15 min to 2 h. The reductions are faster than with BMS in refluxing THF, even when dimethyl sulfide is removed from the reaction mixture.[25] The borane carrier amines **1d**, **2b**, and **2c** can be readily recovered from the hydroboration or reduction products by simple acid−base manipulations, distillation, or column chromatography and can be easily recycled for the preparation of the borane adduct. Consequently, the borane adducts **7**, **8**, and **9** described in the present study can serve as eco-friendly substitutes for the currently popular hydroborating−reducing agents borane−dimethyl sulfide and borane−tetrahydrofuran.

Experimental Section

Manipulations and reactions with air-sensitive compounds were carried out under nitrogen atmosphere. Glassware was oven-dried for several hours, assembled while hot, and cooled in a stream of dry nitrogen gas. Techniques for handling air-sensitive compounds described elsewhere were followed.[26] ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on either a 200 or 300 MHz multinuclear NMR spectrometer. The ^{11}B NMR

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chemical shifts are in δ relative to $BF_3 \cdot Et_2O$. GC analyses were performed on a chromatograph (catharometer) equipped with the following columns: a 12 ft × 0.125 in. packed with 10% SE 30 on Chromosorb W 100−120 mesh; 6 ft × 0.125 in, 15% Carbowax 20M on Chromosorb W; 9 ft × 0.125 in, 3% OV-17 on Chromosorb-G; SPB-5 (0.25 μm × 30 m) capillary column. Optical rotations were measured on a polarimeter. Hydride analysis studies were carried out using the gasimeter. Microanalyses were performed at the Microanalytical Laboratory, Purdue University.

Materials. *N-tert*-Butylmorpholine,[27] **1a**, and diisopropyl sulfate[28] were prepared according to the literature. *N-tert*-Butyldiethanolamine (Fluka) and other starting amines (Aldrich) were commercial products. All solvents were purified according to literature procedures and stored under nitrogen. Tetrahydrofuran and dioxane were freshly distilled from benzophenone ketyl before use. All olefins were distilled from a small amount of lithium aluminum hydride and stored under nitrogen. All compounds except amides were commercial samples and were used as obtained. Amides used in this study were prepared following literature procedures[29] and were fully analyzed before use.

Borane−Amine Adducts. General Procedure. Diborane generated as described elsewhere[30,31] was passed into a neat amine (50 mmol) at 0 °C and placed in a bubbler provided with a sintered glass tip and a magnetic stirring bar. Excess of diborane not absorbed by the amine was absorbed in a following bubbler containing tetrahydrofuran (10 mL) over mercury and cooled in ice−water. A mercury bubbler was connected to the exit. Diborane was passed into the amine until the concentration of borane in the THF in the following bubbler was ~1.0 M. The borane−amine adduct was stirred overnight at room temperature prior to disconnecting the bubblers and then analyzed for active hydride by a standard procedure[32] using a 2.00 M hydrochloric acid−glycerol−water (2:1:1) hydrolysis solution.

***tert*-Butylisobutylamine 4.** A mixture of *tert*-butylamine (11.0 g, 0.15 mol), isobutyl bromide (13.7 g, 0.1 mol), adiponitrile (10.8 g, 0.1 mol), and tetrabutylammonium iodide (1.85 g, 5 mmol) was refluxed with stirring for 12 h. Aqueous 5.00 M potassium hydroxide (30 mL, 0.15 mmol) was added, and the mixture was extracted with *n*-pentane. Three layers were formed. Adiponitrile (middle layer) was recovered. The pentane solution was dried over anhydrous magnesium sulfate, and the product isolated by distillation: 9.56 g, (74%), bp 45−47 °C/40 mmHg.[33,34]

***tert*-Butylisopropylamine 5. By Alkylation of *tert*-Butylamine with Diisopropyl Sulfate.** The mixture of *tert*-butylamine (14.6 g, 0.2 mol) and diisopropyl sulfate (18.2 g, 0.1 mol) was refluxed for 1 h with stirring. The temperature increased from 58 to 83 °C. Two phases formed. Aqueous 5.00 M potassium hydroxide (50 mL, 0.25 mol) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic solutions were combined and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 9.55 g (83%), bp 98−100 °C/760 mmHg (lit.[8] bp 99−99.5 °C).

By Alkylation of *tert*-Butylamine with Isopropyl Bromide. A mixture of *tert*-butylamine (11.0 g, 0.15 mol), isopropyl bromide (12.3 g, 0.1 mol), adiponitrile (10.8 g, 0.1 mol), and tetrabutylammonium iodide (1.85 g, 5 mmol) was refluxed with stirring for 30 h. The temperature of the mixture increased from 53 to 78 °C. Aqueous 5.00 M potassium hydroxide (30 mL, 0.15 mmol) was added, and the mixture was extracted with *n*-pentane. Three layers were formed. Adiponitrile (middle layer) was recovered. The pentane solution was dried over anhydrous magnesium sulfate, and *tert*-butylisopropylamine was isolated by distillation: 8.18 g, (71%), bp 97−99 °C/760 mmHg.

***tert*-Butyldiethylamine 1b.** Diethyl sulfate (33.9 g, 0.22 mol) was slowly added to *tert*-butylamine (14.62 g, 0.2 mol), keeping the reaction mixture at reflux, and it was then stirred for 15 min. Aqueous 8.00 M potassium hydroxide (40 mL, 0.32 mol) was added to the warm mixture. The organic layer was separated, dried over anhydrous magnesium sulfate, and treated with diethyl sulfate (33.9 g, 0.22 mol), followed by heating at 120 °C for 0.5 h. The organic layer, separated after treatment with potassium hydroxide, was heated at 120 °C for 0.5 h. Two layers were formed. The upper layer was separated and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 23.0 g, (88%), bp 126−128 °C (lit.[35] chloroplatinate mp 223−225 °C, dec).

***tert*-Butyldi-*n*-propylamine 1c.** A mixture of *tert*-butylamine (29.3 g, 0.4 mol), 1-iodopropane (51.0 g, 0.3 mol), and glycerol (13.8 g, 0.15 mol) was refluxed for 4 h. Aqueous 8.00 M potassium hydroxide (62.5 mL, 0.5 mol) was added, and the organic layer was separated and dried over anhydrous magnesium sulfate. *tert*-Butylamine was removed, and crude *tert*-butyl-*n*-propylamine, 25.1 g, 72% was obtained. It was treated with 1-iodopropane (25.5 g, 0.15 mol) and glycerol (6.9 g, 75 mmol), and the mixture was refluxed for 6 h. The workup, as described above, followed by distillation gave **1c**: 14.4 g, (61%), bp 62−63 °C/20 mmHg.

***tert*-Butylbis(2-methoxyethyl)amine 1d.** Dimethyl sulfate (50.5 g, 0.4 mol) was added dropwise to a vigorously stirred mixture of *N-tert*-butyldiethanolamine (16.1 g, 0.1 mol), dichloromethane (100 mL), tetrabutylammonium bromide (3.22 g, 10 mmol), and 50% aqueous sodium hydroxide (80 g, 1 mol), at 30−40 °C. The stirring was continued for 1 h after the addition was completed. The organic solution was separated, and the aqueous layer was extracted with dichloromethane. The organic solutions were combined. GC analysis showed a mixture of mono- and diethylated product. The methylation was repeated using the same amounts of reagents as described above. The dichloromethane solution after the second workup was stirred with concentrated aqueous ammonia (50 mL) for 1 h at room temperature, separated, and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 17.0 g, (90%), bp 42−44 °C/0.1 mmHg.

***tert*-Butyldiisobutylamine 1e.** Isobutyryl chloride (10.9 g, 0.1 mol) was added to a solution of *tert*-butylisobutylamine (25.9 g, 0.2 mol) in tetrahydrofuran (150 mL) at room temperature and stirred for 1 h. Solids were filtered off and washed with tetrahydrofuran. *N*,*N-tert*-Butylisobutyl-2-methylpropionamide was isolated by distillation: 18.5 g, 90%, bp 59−60 °C/1.3 mmHg.

A 1.00 M BH_3−THF (150 mL, 0.15 mol) was added dropwise to a solution of the amide (18.0 g, 90 mmol) in tetrahydrofuran (50 mL) at room temperature, and the mixture was refluxed for 1 h. Water was added after cooling, followed by slow addition of 6.00 M hydrochloric acid (60 mL). Tetrahydrofuran was distilled off, and solid sodium hydroxide (20.0 g, 0.5 mol) was added. The organic layer was separated, and the aqueous solution was extracted with *n*-pentane. The organic solutions were combined and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 14.2 g, (85%), bp 34−35 °C/1.5 mmHg.

***tert*-Butylisobutylmethylamine 2a.** A 37% solution of formaldehyde (6.89 g, 85 mmol) was added dropwise to a mixture of *tert*-butylisobutylamine (10.0 g, 77 mmol) and 88% formic acid (7.85 g, 0.15 mol) at room temperature. The mixture was heated at 50−55 °C for 5 h. Aqueous 8.00 M

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(29) Vogel, A. I. *Practical Organic Chemistry*, 5th ed.; Longman: Essex, 1989.

(30) Reference 8, p 18.

(31) For small-scale generation of diborane, see ref 5a.

(32) Reference 26, p 241.

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(34) Büttner, G.; Hünig, S. *Ber.* **1971**, *104*, 1088.

(35) Reiber, H. G.; Stewart, T. D. *J. Am. Chem. Soc.* **1940**, *62*, 3026.

potassium hydroxide (12.5 mL, 0.1 mol) was added, the organic layer was separated, and the aqueous layer was extracted with *n*-pentane. The extract was combined with the organic layer and dried over anhydrous magnesium sulfate. The product was isolated by distillation: 9.25 g, (84%), bp 44−45 °C/18 mmHg.

***tert*-Butylisopropylmethylamine 2b.** A 37% solution of formaldehyde (5.32 g, 73 mmol) was added to a mixture of *tert*-butylisopropylamine (7.60 g, 66 mmol) and 88% formic acid (5.52 g, 0.12 mol) at 0 °C. The reaction mixture was kept at 50−55 °C for 2 h. Aqueous 8.00 M potassium hydroxide (12 mL, 96 mmol) was added, the organic layer was separated, and the aqueous layer was extracted with *n*-pentane. The organic solutions were combined and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 6.50 g, (80%), bp 126−128 °C/760 mmHg (lit.[36] bp 130 °C).

***tert*-Butylisobutylethylamine 2c.** A mixture of *tert*-butylisobutylamine (25.8 g, 0.2 mol) and diethyl sulfate (46.3 g, 0.3 mol) was warmed to 70 °C with stirring. An exothermic reaction started, and the temperature increased in a few minutes to 150 °C with vigorous boiling of the mixture. When it cooled to ~50 °C, 5.00 M aqueous potassium hydroxide (100 mL, 0.5 mol) was added. The organic layer was separated and dried over anhydrous magnesium sulfate. GC analysis indicated 10% of diethyl sulfate and 17% of unreacted starting amine. Diethyl sulfate (10 mL) was added, and the mixture was stirred at 100 °C for 1 h. Aqueous 5.00 M potassium hydroxide (100 mL) was added, and the mixture was stirred at 80 °C for 1 h. The organic layer was separated and the aqueous layer extracted with diethyl ether. The organic solutions were combined and dried over anhydrous magnesium sulfate, and the product was isolated by distillation. A small amount (1−2%) of *tert*-butylisobutylamine was removed by the addition of 2.5 M *n*-butyllithium in hexanes (5 mL, 10 mmol) and distillation: 22.56 g, (72%), bp 68−70 °C/40 mmHg.

***tert*-Butylisobutyl-*n*-propylamine 2d.** A mixture of *tert*-butylisobutylamine (19.4 g, 0.15 mol), 1-iodopropane (20.4 g, 0.12 mol), and glycerol (5.53 g, 60 mmol) was refluxed for 40 h. Aqueous 8.00 M potassium hydroxide (30 mL, 0.24 mol) was added, the organic layer was separated, and the aqueous layer was extracted with *n*-pentane. The organic solutions were combined and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 12.5 g, (61%), bp 72−73 °C/18 mmHg.

***tert*-Butylisopropylethylamine 2e.** A mixture of *tert*-butylisopropylamine (11.5 g, 0.1 mol) and diethyl sulfate (15.4 g, 0.1 mol) was refluxed for 2 h. Aqueous 8 M potassium hydroxide (20 mL, 0.16 mol) was added and the organic layer separated. The aqueous layer was extracted with pentane. The organic solutions were combined and dried over magnesium sulfate, and the product was isolated by distillation: 7.16 g, (50%), bp 140−142 °C.

Hydroboration of Representative Olefins with the Adducts 7−9. General Procedure. An oven-dried, 50 mL hydroboration flask, provided with a septum inlet to introduce and remove compounds, a stirring bar, and a stopper, was cooled to 0 °C under nitrogen. The flask was charged with an amine−borane adduct (5 mmol) and a solvent. A solution of an olefin (15 mmol, 6.00 M, 2.5 mL) was added at 0 °C, and the contents were further stirred at room temperature (19−25 °C). The contents of the reactions were always maintained in the temperature range. Aliquots (1.0 mL) were taken out at intervals and hydrolyzed using 3.00 M HCl−glycerol−THF (2:1:0.2) hydrolysis solvent. The hydrogen evolved was measured using a gasimeter to establish the presence of active hydride. The reactions were simultaneously followed by ^{11}B NMR, observing the relative ratio of an amine−borane signal and the signals due to the hydroboration product.

Regioselectivity Studies. Regioselectivity studies in hydroborations of 1-hexene and styrene using **7**−**9** in THF were carried out. The procedure followed for 1-hexene using **4** in tetrahydrofuran is representative.

(36) Brit. Pat. 876,465, 1961; *Chem. Abstr.* **1963**, *58*, 10077a.

Hydroboration of 1-Hexene with 8 in Tetrahydrofuran. An oven-dried hydroboration flask was cooled to 0 °C under a stream of nitrogen gas. In the flask was placed **8** (0.94 mL, 5.30 M, 5 mmol) in freshly distilled THF (7.6 mL) and undecane (7.5 mmol, GC standard). 1-Hexene (15 mmol, 1.26 g) was added slowly during 5 min at 0 °C. The contents were further stirred for 2 h at room temperature. The reaction was quenched with careful addition of water. The reaction mixture was cooled to 10 °C, and 3.0 mL of 3.00 N NaOH was added, followed by the slow addition of 2.0 mL 30% hydrogen peroxide during 10 min. The contents were further stirred at 50 °C for 2 h to ensure completion of oxidation. The reaction mixture was cooled to room temperature, and the organic layer was separated. The aqueous layer was saturated with potassium carbonate and extracted with ether, and the combined organic extract was washed with brine and dried over anhydrous magnesium sulfate. The combined yield of 1- and 2-hexanols was 98% (by GC using the OV-17 column). The ratio of 1-hexanol−2-hexanol is 96:4.

Hydroboration−Oxidation Studies. Hydroboration and oxidation studies using the adducts **7**−**9** toward olefins, such as 1-hexene, styrene, and cyclohexene, were carried out in THF on a preparative scale. The procedure followed for cyclohexene with **9** in tetrahydrofuran is representative.

Into an oven-dried hydroboration flask was placed **9** (1.11 mL, 4.50 M, 5 mmol) in freshly distilled THF (7.4 mL). Cyclohexene (10 mmol, 0.82 g) was added slowly during 5 min at 0 °C. The contents were further stirred for 1 h at room temperature. The reaction was quenched with careful addition of water. The reaction mixture was cooled to 10 °C, and 3.0 mL of 3.00 N NaOH was added followed by the slow addition of 1.0 mL 30% hydrogen peroxide. The contents were further stirred at 50 °C for 2 h. The reaction mixture was cooled to room temperature, and the organic layer was separated. The aqueous layer was saturated with potassium carbonate and extracted with ether. The combined organic layer was washed with 3.00 N HCl and then with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave essentially pure cyclohexanol, which was further purified by passing through a small silica gel pad, providing a yield of 1.06 g (89%).

The aqueous layer was neutralized with 3.00 N KOH solution and extracted with ether. The combined organic extract was washed with brine and dried over anhydrous magnesium sulfate. GC analysis of the crude showed the presence of cyclohexanol (3%) in addition to **2c** (97%). Amine was recovered in pure form by distillation in 82% (0.65 g) yield.

Reduction of Organic Functional Groups with 8 at Room Temperature in THF. General Procedure. All reductions were carried out under a dry nitrogen atmosphere. In a 50 mL flask, fitted with a sidearm capped by a rubber septum (to permit introduction and removal of material with a hypodermic syringe), was placed amine−borane **8** (5.30 M, 8.3 mmol) in freshly distilled THF (20 mL). To this solution was added the compound to be reduced in THF (5.00 mL, 6.25 mmol) slowly during 5 min. The final solution is 0.25 M in reducible compound and 1.00 M in hydride. At appropriate time intervals, samples were withdrawn and hydrolyzed using glycerol−2.00 N HCl−THF (1:3:1), and hydrogen evolved was measured using the gasimeter to determine the amount of residual hydride. Progress of the reaction was also checked by ^{11}B NMR and GC analysis. In a separate run using the same quantities and conditions, the reaction flask was attached to a gasimeter to measure the hydrogen evolved.

In a number of cases, the reduction was carried out as described above to establish yield and stoichiometry. However, the reaction mixtures were then worked up to isolate and characterize the reduction products. A few representative examples are described below for isolation of the reduced product and recovery of borane carrier amine.

Reduction of Benzaldehyde (2 Equiv) with 8 (1 Equiv) in THF at Room Temperature. An oven-dried two-necked round bottom flask provided with a condenser, septum inlet, and stirring bar was cooled to 0 °C under nitrogen. Into the flask were placed freshly distilled THF (21.90 mL) and **8** (1.56 mL, 5.30 M, 8.3 mmol). Benzaldehyde (1.68 mL, 16.6 mmol)

was added slowly during 5 min, and the contents were further stirred at room temperature for 2 h. The reaction was quenched with water, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic extract was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the crude product was subjected to distillation under reduced pressure: the yield of benzyl alcohol was 1.47 g (82%) and amine was 0.93 g (87%).

Reduction of Acetophenone (2 Equiv) with 8 (1 Equiv) in THF at Room Temperature. An oven-dried two-necked round bottom flask, provided with a condenser, septum inlet, and stirring bar, was cooled to 0 °C under nitrogen. Into the flask were placed freshly distilled THF (21.4 mL) and **8** (1.56 mL, 5.30 M, 8.3 mmol). Acetophenone (1.99 g, 16.6 mmol) was added slowly during 5 min, and the contents were further stirred at room temperature for 18 h. The reaction was quenched with water, and diethyl ether was added. The organic layer was separated, washed with 3.00 N HCl, and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave essentially pure 1-phenylethanol, which was further purified by passing through a small silica gel pad. The yield of 1-phenylethanol was 1.72 g (86%).

The combined aqueous layer was neutralized using aqueous KOH and extracted with ether. The combined organic extract was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator, and the GC analysis of crude product on the OV-17 column revealed the presence of **2b** in a purity of 97%. The yield of recovered amine after distillation was 0.91 g (85%).

Reduction of Representative Esters with 8 in THF and Dioxane at Reflux. Amine−borane adduct **8** in THF or dioxane was treated with representative esters such as ethyl undecanoate, methyl caproate, and methyl benzoate. The procedure followed for methyl benzoate in THF is representative.

An oven-dried, round bottom flask (50 mL), provided with a condenser, septum inlet, and a stirring bar, was cooled under a flow of nitrogen. Into the flask were placed freshly distilled THF (21.7 mL) and **8** (1.69 mL, 5.30 M, 9 mmol) at room temperature. Methyl benzoate (1.55 mL, 12.5 mmol) was added, and the reaction mixture was stirred under reflux. Aliquots of the reaction mixture were removed at appropriate intervals, hydrolyzed, and tested for the remaining unreacted ester on GC using the OV-17 column. Thus, the progress of reaction was monitored. After 12 h no residual ester was detected and the exclusive formation of benzyl alcohol noted in addition to **2b**.

In a separate run, the contents were refluxed for 12 h and cooled, the reaction was then quenched with water, and aqueous NaOH was added (3.00 N). The organic layer was separated, and the aqueous layer was saturated with K_2CO_3 and extracted with ether. The combined organic extract was dried over anhydrous magnesium sulfate, the solvent was evaporated, and benzyl alcohol and carrier amine were separated by distillation.

In the case of water-insoluble alcohol products, such as 1-undecanol (reduction of ethyl undecanoate), the workup procedure can be simplified as follows. After completion of the reduction, the reaction mixture was quenched with water, ether was added, and amine was extracted in to the aqueous layer using HCl (3.00 N). The organic layer was dried over anhydrous $MgSO_4$, and evaporation of the solvent provided essentially pure 1-undecanol (99% by GC). The aqueous layer was neutralized with NaOH to liberate amine (97% pure by GC).

Reduction of Representative Nitriles with 8 in THF and Dioxane at Reflux. Reduction studies of heptanenitrile and benzonitrile using amine−borane adduct **8** in THF and dioxane under reflux conditions were carried out. The procedure followed for benzonitrile in THF is representative.

An oven-dried round bottom flask (50 mL), provided with a reflux condenser, a septum inlet, and a stirring bar, was cooled under a flow of nitrogen. Into the flask were placed freshly distilled THF (22.4 mL) and **8** (1.69 mL, 5.30 M, 9 mmol). Benzonitrile (0.85 mL, 8.3 mmol) was added, and the reaction mixture was stirred under reflux. Aliquots were removed at appropriate intervals and after hydrolysis tested for the presence of residual benzonitrile using GC analysis on the OV-17 column. After refluxing for 6 h, no residual nitrile was found. In a separate experiment, after refluxing for 6 h, the reaction mixture was cooled and quenched with water, and HCl (6.00 N) was added. The contents were refluxed further for 1 h, cooled, and neutralized by the addition of solid NaOH. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extract was dried over anhydrous $MgSO_4$. Analysis (by GC) of the reaction mixture revealed a quantitative yield of benzylamine.

Reduction of Representative Amides with 8 in THF and Dioxane under Reflux. Reduction studies of caproamide, benzamide, *N*-methylbenzamide, *N*,*N*-dimethylcaproamide, and *N*,*N*-dimethylbenzamide using **8** in dioxane and THF were carried out under reflux conditions. The course of the reaction was followed by GC analysis of the reaction mixture after hydrolysis. The reactions were quenched as soon as the starting amide is fully consumed. The reduction of *N*,*N*-dimethylbenzamide with **8** in dioxane is representative.

Reduction of *N*,*N*-Dimethylbenzamide with 8. An oven-dried 50 mL round bottom flask, provided with reflux condenser, septum inlet, and a stirring bar, was cooled under a flow of nitrogen. The outlet of the condenser was connected to a mercury bubbler. Into the flask was placed *N*,*N*-dimethylbenzamide (1.76 g, 12.5 mmol) in dry dioxane (21.0 mL), and **8** (4.15 mL, 22 mmol) was added. The contents were heated under reflux for 15 min, by which time no starting amide was present (by GC analysis). The reaction was quenched with water, 6.00 N HCl (18 mL) was added, and the contents were heated to reflux for 1 h. The reaction mixture was cooled to 0 °C, and solid NaOH was added until the mixture became basic. The organic compounds were extracted with ether, and the combined organic extracts were dried over $MgSO_4$. GC analysis of the mixture revealed the quantitative conversion. Distillation under reduced pressure gave **2b** (2.32 g, 82% yield (isolated), 95% (pure by GC) and *N*,*N*-dimethylbenzylamine (1.31 g, 78%, 98% pure by GC).

An alternate procedure can also be used to isolate the amines. In a similar experiment as outlined above, after the reduction was complete the excess active hydride was destroyed by the addition of water. The reaction mixture was taken in ether and washed with dilute HCl (3.00 N), and the organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent provided essentially pure *N*,*N*-dimethylbenzylamine−borane (^{11}B NMR δ −8.3, quartet, in THF) adduct from which the amine was liberated by the addition of $BF_3{\cdot}OEt_2$. The combined aqueous layer was neutralized with base to obtain *tert*-butyl-*N*-methyl-*N*-isopropylamine in 90% pure form (by GC).

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, mass spectral, elemental analysis data for the amines reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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