Molecular Addition Compounds. 12. Borane Adducts of Trialkylamines with Isopropyl and Isobutyl Groups of Intermediate Steric Requirements for Hydroboration

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Borane adducts of selected trialkylamines with isopropyl and isobutyl groups of intermediate steric requirements have been prepared and examined as hydroborating agents. Their reactivity toward 1-octene follows the order *i*-$Pr_2NEt{\cdot}BH_3$ < *i*-$Bu_3N{\cdot}BH_3$ < *i*-$PrNBu^i_2{\cdot}BH_3$ < *i*-$Pr_2NCH_2CH_2OMe{\cdot}BH_3$ < *i*-$Pr_2NBu^i{\cdot}BH_3$ < *i*-$Pr_3N{\cdot}BH_3$ < *i*-$Pr_2NBu^s{\cdot}BH_3$. Borane adducts with *i*-Pr_2NBu^i, *i*-Pr_3N, and *i*-Pr_2NBu^s are highly reactive, hydroborating 1-octene in THF at room temperature in less than 1 h. The adduct *i*-$Pr_2NBu^i{\cdot}BH_3$ is a liquid above 0 °C, 4.6 M in BH_3, stable over long periods, and soluble in diethyl ether, *tert*-butyl methyl ether, tetrahydrofuran, dioxane, dichloromethane, and *n*-pentane. The adduct *i*-$Pr_3N{\cdot}BH_3$ is a solid, while *i*-$Pr_2NBu^s{\cdot}BH_3$ is a liquid, unstable, slowly evolving diborane at room temperature.

Since the first borane−amine adduct with trimethylamine was reported in 1937,[4] almost all structural types of amines have been used for borane complexation. The adducts have a wide range of physical and chemical properties and find a multitude of uses in various areas, e.g., in polymer, dye, metal plating, and pharmaceutical industries.[5] Most of these applications are based on their reducing properties. In contrast, the scope of hydroboration with borane−amine adducts is rather limited due to strong complexation, rendering their reactivity much lower as compared to the adducts with ethers and sulfides. However, the full range of reactivities of borane−amine adducts has not yet been defined.

Amines as borane carriers offer advantages, often forming adducts of low sensitivity to moisture and air, readily soluble in various solvents. Environmentally important is the easy recovery of the amine from the hydroboration products, making possible its ready recycle. The significance of these factors becomes apparent with the growing importance of diborane for the synthesis of pharmaceuticals and other compounds.[6,7] The well-established reagents $BH_3{\cdot}THF$ and $BH_3{\cdot}SMe_2$ (BMS) suffer from certain inconveniences for large-scale applications. Thus, they are highly reactive and must be handled with care. Commercial $BH_3{\cdot}THF$ is a solution of relatively low concentration (1 M), unstable over long periods of time. BMS is highly concentrated (10 M) and stable indefinitely. Unfortunately, the high volatility, flammability, and unpleasant odor of dimethyl sulfide create safety and environmental problems. Clearly, there is a need for reactive, stable, easy to handle, safe to operate, and environmentally benign borane adducts.

Recently, we described new borane adducts with *N*,*N*-dialkylanilines exhibiting excellent reactivity, hydroborating 1-octene in tetrahydrofuran at room temperature in less than 1 h.[8] Prompted by these results, we turned our attention to alkylamines. Despite many adducts known,[4,9,10] almost all amines used are relatively unhindered and hence strongly complexing. On the other hand, it has been reported that the highly hindered 1,2,2,6,6-pentamethylpiperidine does not give a borane adduct.[11] However, the effect of increasing steric requirements of amines on their borane complexing ability is not well delineated. Consequently, we decided to prepare a series of isopropylamines with increasing steric hindrance around the nitrogen atom and then examine these amines for complexation of borane with the hope of finding stable liquid adducts capable of hydroborating 1-octene as a representative alkene in THF at room temperature in less than 1 h. Besides the chemical aspects, we were also concerned with achieving economical syntheses of these amines since the cost of the borane carrier should not contribute significantly to the total cost of its borane adduct.

Results and Discussion

Diisopropylamine is readily available at low cost. Consequently, we undertook to synthesize tertiary di-

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Table 1. Alkylation of Diisopropylamine with Isobutyl and Methallyl Derivatives in 2:1 Molar Ratio

isobutyl or methallyl derivative[a]	solvent	temp (°C)	time (h)	product yield (%)	remarks
i-BuBr		reflux	24	0	
i-BuBr		150	10	6[b]	autoclave
i-BuBr		175	10	22[b]	autoclave
i-BuBr		125	20	36[c]	NaI in acetone (3 M) added (10 mol %)
i-BuI	glycerol[d]	reflux	98	41[c]	
i-BuO_3SMe		reflux	100	60[b]	
i-BuO_3SPh		reflux	24	55[c]	
i-BuO_3SPh		reflux	72	68[c]	
Meall-Cl		reflux (76 °C)	24	2[b]	
Meall-Br		80→110	18	87[b]	10 h, 85%
Meall-I		86→115	10	93[b]	3 h, 87%; 5 h, 90%; 24 h, 93%
Meall-Cl		150	10	42[c]	autoclave
Meall-Cl		reflux	72	71[b]	NaI in acetone (3 M) added (10 mol %)
Meall-Cl	adiponitrile	reflux	5	81[c]	*n*-Bu_4NI (10 mol %) and adiponitrile (1 molar equiv) added

[a] Methallyl group is abbreviated as Meall. [b] By GC. [c] Isolated. [d] 0.3 molar equiv.

Table 2. Isopropylation of Diisopropylamine with Isopropyl Derivatives

isopropyl derivative	solvent[a]	temp (°C)	time (h)	*i*-Pr_3N yield (%)[b]	remarks
i-PrBr		reflux	12	0	
i-PrI		reflux	12	0	
i-PrI		150	10	~1	autoclave, no unreacted *i*-PrI
i-PrI	DMSO	reflux	12	8	a multicomponent mixture of products
i-PrI	DMF	reflux	12	9	
i-PrI	$AcNMe_2$	reflux	12	9	
i-PrI	HMPA	reflux	12	15	
i-PrOMs		85→97	12	6	
i-PrOTs		85→120	12	19	
i-PrO_3SPh		85→120	12	19	
i-PrO_3SPh		125	12	10	
i-PrO_3SPh		50→90	60	29	24 h, 50 °C; 24 h, 70 °C; 12 h, 90 °C
i-PrO_3SF	*i*-Pr_2NH[c]	0→40	5	37	
$(i\text{-PrO})_2SO_2$		110→160	20	18[d]	2 h, 110 °C; 2 h, 140 °C; 16 h, 160 °C

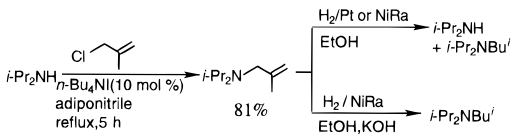
[a] 50% by volume. [b] By GC. [c] 5 molar equivs. [d] Ref 15.

isopropylamines, **1**−**5**, with increasing steric requirements of the alkyl group. The methoxy derivative **2** was included to test the effect of an ether function vicinal to the nitrogen atom on its complexing ability in comparison with the trialkylamines. Since our recent study on *N*,*N*-dialkylanilines revealed a slightly higher steric hindrance exerted by isobutyl groups as compared to isopropyl groups, **6** and **7** were also included.

i-Pr_2NEt **1** *i*-$Pr_2NCH_2CH_2OMe$ **2** *i*-Pr_2NBu^i **3** *i*-Pr_3N **4**

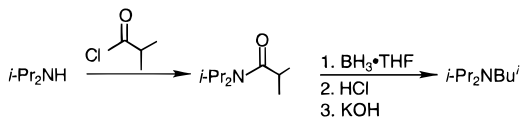
i-Pr_2NBu^s **5** *i*-Bu_3N **6** *i*-$PrNBu^i_2$ **7**

Synthesis of Amines. As mentioned earlier, diisopropylamine is a readily available, low-cost starting material which we hoped could provide simple direct access to **1**−**5**. However, its reactivity in alkylation reactions proved to be extraordinarily low. The yields of alkylation products achieved with various isobutyl and isopropyl derivatives are shown in Tables 1 and 2. The introduction of the isobutyl group requires long reaction times or higher pressure and temperature. The highest yield of **3** at reflux temperature in a reasonable time was achieved using isobutyl benzenesulfonate. Two indirect procedures for the synthesis of **3** have also been developed. Thus, alkylation of diisopropylamine with methallyl chloride in the presence of tetrabutylammonium iodide and adiponitrile proceeds to a good yield in a relatively short time (eq 1), whereas, in their absence, the reaction is sluggish.



(1)

Hydrogenation of the intermediate allylic amine on a platinum or Raney nickel catalyst is accompanied with hydrogenolysis. This undesired side reaction was suppressed by the addition of a small amount of potassium hydroxide.[12] Under these conditions, the methallyl derivative was converted to *i*-Pr_2NBu^i quantitatively. An alternative approach was to acylate diisopropylamine with isobutyryl chloride followed by borane reduction of the amide to the desired amine, *i*-Pr_2NBu^i, in an overall yield of 81% (eq 2).



(2)

As might be expected, the direct isopropylation of diisopropylamine is more difficult than the introduction of the primary isobutyl group. Only the highly reactive isopropyl fluorosulfate[13] gave a moderate 37% yield of **4** (Table 2). Although this is the highest yield ever achieved by direct isopropylation of diisopropylamine, the alkylating agent is costly and unstable, making the

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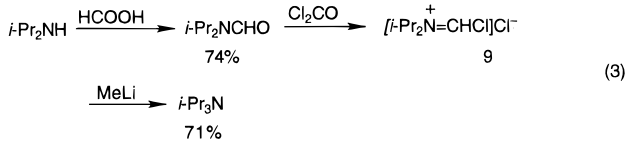
Table 3. Borane Adducts of *i*-Pr_2RN and *i*-Bu_2RN Prepared and Examined

			amine·BH_3				
	exchange,[a] %		state[b]	$[BH_3]$[c]	^{11}B NMR[d]	hydroboration of 1-octene[e]	
amine	BH_3·SMe_2	BH_3·THF	(mp, °C)	(M)	(δ)	in THF[f]	neat
i-Pr_2NEt	100	100			−13.46	24 h (38%)	
i-$Pr_2NCH_2CH_2OMe$	72	86			−13.24	9 h	
i-$PrNBu^i{}_2$	52	87			−12.09	15 h	
i-Bu_3N	50	88	solid (60−61)		−12.05	24 h	
i-Pr_2NBu^i	42	87	liquid	4.6	−13.54	30 min	3 h
i-Pr_3N	18	60	solid (42−43)		−15.66	20 min	
i-Pr_2NBu^s	0	30	liquid	3.3→2.5	−5.82[g]	15 min	1 h

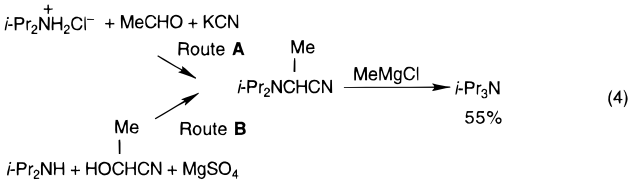
[a] Amine mixed with BMS or 1 M BH_3·THF in 1:1 molar ratio at room temperature and analyzed by ^{11}B NMR. [b] At 0 °C. [c] Estimated by hydrolysis in 2 M HCl−glycerol−water (2:1:1) and measuring hydrogen evolved. [d] From the exchange with BMS. [e] 5% excess of 1-octene, room temperature. [f] 3 M solution in 1-octene. [g] From the exchange with BH_3·THF.

synthesis uneconomical. The best known indirect synthesis of **4** is shown in eq 3.[14]



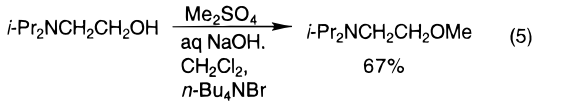
(3)

It is an excellent procedure. Unfortunately, methyllithium is relatively costly. When methylmagnesium chloride is substituted for methyllithium, the overall yield of *i*-Pr_3N from diisopropylamine drops considerably, down to ∼30%. A similarly low yield is reported for an earlier procedure (eq 4, route **A**).[15] However, we found it possible to improve the yield. Using lactonitrile as a starting material, the intermediate aminonitrile was obtained in 75% yield (eq 4, route **B**). By this modification, the overall yield of *i*-Pr_3N is increased to 41% (not optimized), using less costly chemicals than in eq 3.



(4)

Amine **5** (*i*-Pr_2NBu^s) was prepared by the same method using ethylmagnesium bromide. Amines **2** and **7** were synthesized according to eqs 5 and 6, respectively.



(5)

(6)

Triisobutylamine is commercially available and was included in the study without examining its synthesis.

Borane−Amine Adducts. The complexing ability of **1**−**7** was tested by the exchange with BMS in 1:1 molar ratio. The amount of borane taken by the amine in the equilibrium was determined by ^{11}B NMR analysis and is shown in Table 3. Values for the exchange with BH_3·THF, a 1 M solution, should be taken qualitatively since THF is in large excess.

As follows from the exchange experiments, the complexing ability of alkyldiisopropylamines decreases in the order **1** > **2** > **3** > **4** > **5**. The strongest complexing, **1**, takes 100% borane from BMS, and the weakest, **5**, does not exchange at all. Triisobutylamine takes almost 3 times more borane than triisopropylamine. Replacing one isobutyl group by an isopropyl group has little effect on the equilibrium, **7** taking even slightly more than **6**. The exchange rate for **6** and **7** is slower as compared to the other amines, the equilibrium being established in 1 h and 15 min, respectively. The amount of borane taken drops by 8% when two isobutyl groups of **6** are replaced by two isopropyl groups, indicating that two isopropyl groups decrease the complexing ability of amines in this series more than isobutyl groups. The effect is opposite that observed for the corresponding *N*,*N*-dialkylanilines.

The exchange picture with BH_3·THF, a weaker adduct than BMS, reveals only major differences in complexing ability of the amines. The strongest, **1**, and the weakest, **4** and **5**, are differentiated, whereas **2**, **3**, **6**, and **7** are not. Hydroboration of 1-octene in THF at room temperature is a sensitive indication of the reactivity of the adducts. Thus, the reaction with **1**·BH_3 is very sluggish and both **6**·BH_3 and **7**·BH_3 also react slowly. It is interesting to note that although **2** takes exothermically 72% of borane from BMS, the second largest value in the series, **2**·BH_3, hydroborates 1-octene in a shorter time than **6**·BH_3 and **7**·BH_3. An increased reactivity of **3**·BH_3 as compared to **6**·BH_3 and **7**·BH_3 might be expected from the lower exchange value of **3** (Table 3). However, a relatively subtle structural difference between **3** and **7** brings about a dramatic increase of the reactivity of **3**·BH_3, hydroborating 1-octene in THF at room temperature in 30 min, whereas **7**·BH_3 requires 15 h. The reaction is still faster with the weaker adducts **4**·BH_3 and **5**·BH_3.

On the basis of the results of hydroboration in THF, amines **3**, **4**, and **5** were selected for the preparation of neat adducts. The adducts were synthesized by passing diborane into a neat amine at 0 °C until no more absorption was observed. The product obtained from **3** is a liquid, 4.6 M in BH_3, stable over long periods at room temperature, and soluble in diethyl ether, tetrahydrofuran, dichloromethane, and *n*-pentane. Triisopropylamine forms a solid adduct, stable at room temperature in a closed container. Diisopropyl-*s*-butylamine gave a liquid product, initially 3.3 M in BH_3,

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losing borane at room temperature, the molarity falling to 2.5 in 24 h. The ^{1}H NMR spectrum indicates 40% of the adduct and 60% of free amine. Clearly, with **5** the limit of borane complexation in the series is reached.

Finally, hydroboration under neat conditions was carried out by the addition of 1-octene to an adduct at 20−25 °C. The reaction with **3**·BH_3 was complete in 3 h and with **4**·BH_3, used as a 3 M solution in **4**, 2 h. In conclusion, this study demonstrates for the first time that hindered trialkylamines can form stable, yet highly reactive adducts with borane, hydroborating 1-octene at room temperature in a short time. The adduct prepared from diisopropylisobutylamine appears to meet best our requirements for a borane carrier. The full synthetic potential of these new reactive borane−amine adducts remains to be explored.

Experimental Section

All manipulations and reactions with air-sensitive compounds were carried out under a 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.[16]

^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a 300 MHz multinuclear instrument. The ^{11}B NMR chemical shifts are in δ, relative to BF_3·Et_2O. GC analyses were carried out on a chromatograph (catharometer) equipped with a 12 ft × 0.125 in. column packed with 10% SE-30 on Chromosorb W 100−120 mesh. Microanalyses were performed by the Microanalytical Laboratory, Purdue University.

Materials. Tetrahydrofuran was freshly distilled from benzophenone ketyl prior to use. Diisopropylethylamine **1**, triisobutylamine **6**, and lactonitrile, 92% solution in water, were commercial products (Aldrich). The remaining amines **2**, **3**, **4**, **5**, and **7** were synthesized by procedures that are explored and tested.

2-Methoxyethyldiisopropylamine (2). A solution of 2-(diisopropylamino)ethanol (29.05 g, 0.2 mol) in dichloromethane (100.0 mL) was added to 50% aqueous sodium hydroxide solution (64 g, 0.8 mol), followed by tetrabutylammonium bromide (1.00 g). The mixture was vigorously stirred for 15 min, and dimethyl sulfate (50.45 g, 0.4 mol) was added dropwise with vigorous stirring at 30−40 °C in 1 h. The mixture was further stirred at room temperature for 2 h. Water was added, the organic solution was separated, and the aqueous layer was extracted with dichloromethane. The extract was combined with the organic solution and dried with magnesium sulfate, and the product was isolated by distillation, 21.31 g (67%), bp 35−36 °C/0.1 mmHg. It contained 5% of the starting material, which was removed by distillation from lithium aluminum hydride. ^{1}H NMR ($CDCl_3$): δ 1.00 (*d*, J = 6.5, 12H, CH_3), 2.60 (*t*, J = 7.2, 2H, CH_2), 2.98 (*sep*, J = 6.5, 2H, CH), 3.33 (*t*, J = 7.7, 2H, CH_2), 3.34 (*s*, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 20.70 (CH_3), 44.61 (NCH_2), 49.39 (NCH), 58.76 (OCH_2), 74.38 (OCH_3). MS (70 eV), EI, CI: 159 (M^+, 1), 114(100), 72(78), 59(32), 56(55). Anal. Calcd for $C_9H_{21}NO$ (159.28): C, 67.86; H, 13.29; N, 8.80. Found: C, 67.53; H, 13.12; N, 8.85.

Diisopropyl(2-methyl-2-propenyl)amine. A mixture of diisopropylamine (20.24 g, 0.2 mol), methallyl chloride (9.00 g, 0.1 mol), adiponitrile (10.81 g, 0.1 mol), and tetrabutylammonium iodide (3.69 g, 0.01 mol) was refluxed for 5 h with vigorous stirring (two phases). The temperature of the refluxing mixture increased from 88 to 125 °C. After cooling to room temperature, potassium hydroxide solution (5.0 M, 15.0 mL, 0.15 mol) was added. Three layers formed. The mixture was extracted with *n*-pentane. Adiponitrile (the middle layer) was recovered. The pentane solution was dried over anhydrous magnesium sulfate and the product isolated by distillation, 12.58 g (81%), bp 75−77 °C/45 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.98 (*d*, J = 6.5, 12H, CH_3), 1.70 (*s*, 3H, CH_3), 2.97 (*m*, 4H, CH_2, CH), 4.78 (*s*, 1H, CH_2), 4.93 (*m*, 1H, CH_2).

***N,N*-Diisopropyl-2-methylpropionamide.** Isobutyryl chloride (10.65 g, 0.1 mol) was added dropwise with stirring to diisopropylamine (20.24 g, 0.2 mol), and the mixture was stirred for 1 h at room temperature. The solid product was filtered off and crystallized from diethyl ether, 15.59 g, 91%, mp 34−35 °C, lit.[17]

Diisopropylisobutylamine (3). By the Reduction of Diisopropyl(2-methyl-2-propenyl)amine. Diisopropyl(2-methyl-2-propenyl)amine (15.53 g, 0.1 mol) and Raney nickel catalyst (5.00 g, slurry in ethanol) was added to a solution of potassium hydroxide (1.00 g) in anhydrous ethanol (30.0 mL). The mixture was hydrogenated at 40−50 °C with stirring under normal pressure until absorption of hydrogen ceased (~20 h). The solution was decanted from the catalyst, water was added, and the product was extracted with *n*-pentane, dried with magnesium sulfate, and isolated by distillation: 16.49 g, 94%, bp 75−77 °C/45 mmHg, lit.[14] bp 65 °C/25 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.83 (*d*, J = 6.5, 6H, CH_3), 0.95 (*d*, J = 6.5, 12H, CH_3), 1.59 (*n*, J = 6.5, 1H, CH), 2.10 (*d*, J = 6.5, 2H, CH_2), 2.95 (*sep*, J = 6.5, 2H, CH).

By the Reduction of *N,N*-Diisopropyl-2-methylpropionamide. A solution of *N,N*-diisopropyl-2-methylpropionamide (8.57 g, 50 mmol) in tetrahydrofuran−dichloromethane (4:1) was added to borane−tetrahydrofuran (50.0 mL, 50.0 mmol), and the mixture was refluxed for 1.5 h. Water (5.0 mL) was slowly added, followed by 3.0 M hydrochloric acid (40.0 mL). Organic solvents were distilled off and solid sodium hydroxide (12.00 g, 0.3 mol) was added. The product was extracted with diethyl ether, dried with magnesium sulfate, and isolated by distillation, 6.90 g (89%), bp 58−59 °C/19 mmHg.

2-(Diisopropylamino)propionitrile. Anhydrous magnesium sulfate (12.04 g, 0.1 mol) was added to diisopropylamine (12.14 g, 0.12 mol), followed by lactonitrile (7.73 g of 92% aqueous solution, 0.1 mol) added all at once with stirring. The reaction mixture spontaneously warmed to 51 °C. It was left overnight at room temperature. Diethyl ether was added, and magnesium sulfate was filtered off and washed with ether. The product was isolated by distillation: 11.57 g, 75%, bp 49−50 °C/0.1 mmHg, lit.[15] bp 70−79 °C/13 Torr; ^{1}H NMR ($CDCl_3$) δ 1.02 (*d*, J = 6.5, 6H, CH_3), 1.17 (*d*, J = 6.5, 6H, CH_3), 1.41 (*d*, J = 6.5, 3H, CH_3), 3.21 (*sep*, J = 6.5, 2H, CH), 3.89 (*q*, J = 6.5, 1H, CH).

Triisopropylamine (4). A solution of 2-(diisopropylamino)-propionitrile (15.43 g, 0.1 mol) in diethyl ether (25.0 mL) was added dropwise with stirring to a suspension of methylmagnesium chloride (22.44 g, 0.3 mol) in diethyl ether (250 mL) at reflux. The mixture was refluxed for 30 min after completing the addition and left overnight at room temperature. Water was slowly added and the organic solution was decanted from the solids, which were treated with potassium hydroxide (100 mL, 1.0 mol) and steam distilled. The distillate was extracted with diethyl ether, and the extract was combined with the decanted solution and dried over magnesium sulfate. The product was isolated by distillation: 7.88 g, 55%, bp 139−140 °C/760 mmHg, lit.[18] 139 °C/760; ^{1}H NMR ($CDCl_3$) δ 0.99 (*d*, J = 6.5, 18H, CH_3), 3.11 (*sep*, J = 6.5, 3H, CH).

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***N,N*-Diisopropyl-*sec*-butylamine (5).** A solution of 2-(diisopropylamino)propionitrile (25.00 g, 0.162 mol) in diethyl ether (20.0 mL) was added dropwise to a 1.0 M solution of ethylmagnesium bromide in diethyl ether (32.4 mL, 0.324 mol), and the mixture was refluxed for 30 min. Water was added, and white precipitate was filtered off and washed with diethyl ether. The ether solutions were combined and dried over anhydrous magnesium sulfate, and the product was isolated by distillation: 13.80 g, 51%, bp 60−62 °C/20 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.85 (*t*, J = 6.5, 3H, CH_3), 0.98 (*d*, J = 6.5, 6H, CH_3), 0.99 (*d*, J = 6.5, 3H, CH_3), 1.05 (*d*, J = 6.5, 6H, CH_3), 1.17−1.44 (*m*, 2H, CH_2), 2.70 (*m*, 1H, CH), 3.08 (*sep*, J = 6.5, 2H, CH); ^{13}C NMR ($CDCl_3$) δ 12.32 (CH_3), 20.75 (CH_3), 22.52 (CH_3), 23.78 (CH_3), 29.35 (CH_2), 43.99 (CH) 50.56 (CH); MS EI CI 70 eV 157 (M^+, 2H), 142(34), 128(100), 58(24). Anal. Calcd for $C_{10}H_{23}N$: C, 76.35; H, 14.73; N, 8.90. Found: C, 75.99; H, 14.57; N, 8.98.

Diisobutylisopropylamine (7). A mixture of diisobutylamine (30.00 g, 0.23 mol), glycerol (8.20 g, 0.089 mmol), and 2-iodopropane (30.30 g, 0.18 mol) was refluxed for 28 h. Aqueous potassium hydroxide (30.0 mL, 0.34 moL) was added, and the organic layer was separated. The aqueous layer was extracted with *n*-pentane. The extract was combined with the organic layer and dried over magnesium sulfate, and the product was isolated by distillation, 15.00 g, 49%, bp 68−69 °C/17 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.84 (*d*, J = 6.6, 12H, CH_3), 0.90 (*d*, J = 6.6, 6H, CH_3), 1.59 (*nonet*, J = 6.6, 2H, CH), 2.03 (*d*, J = 7.2, 4H, CH_2), 2.83 (*sep*, J = 6.6, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 17.57 (CH_3), 20.80 (CH_3), 27.05 (CH), 49.73 (CH), 58.94 (CH_2); MS EI CI 70 eV 171 (M^+, 2), 128(100), 86(21), 72(13), 57(19). Anal. Calcd for $C_{11}H_{25}N$: C, 77.12; H, 14.70; N, 8.17. Found: C, 76.82; H, 14.79; N, 8.55.

Borane−Amine Adducts. General Procedure. Diborane generated as described elsewhere[19,20] was passed into a neat amine (50.0 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 (10.0 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 THF reached ∼1 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[21] using a 2 M hydrochloric acid−glycerol−water (2:1:1) hydrolysis solution.

Exchange Reaction of BMS and H_3B:THF with Tertiary Isopropyl/Isobutylamines (1−7). General Procedure. An oven-dried 25 mL round-bottomed flask, provided with septum inlet and a stirring bar, was cooled to room temperature under nitrogen. The flask was charged with tertiary isopropyl/isobutylamine (4.0 mmol), and BMS or H_3B:THF (4.0 mmol) was added. The contents were further stirred at room temperature. The progress of equilibration was followed by ^{11}B NMR (see Table 3).

Hydroboration of 1-Octene with Borane Adducts of Tertiary Isopropyl/Isobutylamines (1−7). General Procedure. An oven-dried 25 mL round-bottomed flask, provided with septum inlet and a stirring bar, was cooled to room temperature under nitrogen. The flask was charged with tertiary isopropyl/isobutylamine−borane in THF (3.0 mmol), and 1-octene in THF (9.0 mmol) was added. The solvent THF is taken in such a way that the final solution is 1.0 M in borane and 3.0 M in 1-octene. The contents were further stirred at room temperature. The progress of hydroboration was followed by ^{11}B NMR (see Table 3).

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(19) Ref 16, p 18.

(20) For small-scale diborane generation, this procedure was improved (ref 8) by adding a 2.00 M solution of sodium borohydride in triglyme (Aldrich) to boron trifluoride in diglyme. Under these conditions diborane is smoothly evolved without precipitation of a product.

(21) Ref 16, p 241.