Molecular Addition Compounds. 10. Borane Adducts with *N,N*-Dialkylanilines for Hydroboration

Herbert C. Brown,* Marek Zaidlewicz,[1a] and Pramod V. Dalvi[1b]

H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received May 26, 1998

Borane adducts with selected *N,N*-dialkylanilines have been prepared and examined as hydroborating agents. The adduct H_3B:NPhPr$^i_2$ is a solid, considered less desirable than liquid adducts as hydroborating agents. Fortunately, the adducts H_3B:NPhBu^{i}Me, H_3B:NPhPr^{i}Me, H_3B:NPhPr^{i}Et, and H_3B:NPhPr^{i}Pr^n are liquids above 0 °C, hydroborating 1-octene in tetrahydrofuran in less than 1 h at room temperature. Convenient procedures are described for generating gaseous diborane quantitatively, either by thermal dissociation of the borane−*N,N*-diisopropylaniline adduct or by the reaction of a 2.00 M solution of sodium borohydride in triglyme with a 5.40 M solution of boron trifluoride in triglyme.

Introduction

Borane adducts with amines are versatile reagents exhibiting many different properties as compared to the metal borohydrides.[3] For example, they are soluble in a variety of solvents, including hydrocarbons or even water, and in some cases can be used in an acidic medium. Many adducts have been synthesized,[4,5] and several are commercially available. They find various uses, e.g., as fuel additives, polymerization catalysts, polymer stabilizers, and stain removers, in metal plating, and in the dye and pharmaceutical industries.[3] Most of these applications are based on their reducing properties. In contrast, the use of borane−amine adducts for hydroboration has been rather limited due to strong complexation in the available derivatives, rendering their reactivity relatively low, as compared to the far weaker borane adducts with ethers and sulfides. A systematic study of the hydroborating and reducing properties of borane adducts with various amines carried out several years ago in this laboratory revealed that in contrast to simple, unhindered alkylamines the less basic aniline derivatives form weaker and hence more reactive adducts with borane.[6] For example, borane−triethylamine does not hydroborate 1-octene in tetrahydrofuran at room temperature, whereas borane−*N,N*-diethylaniline reacts in 2 h under these conditions. Later, the borane−*N,N*-diethylaniline adduct was used for hydroborations and other reactions.[7a] Very recently the adduct was successfully applied for stoichiometric reductions of representative functional groups such as aldehydes, ketones, carboxylic acids, tertiary amides, lactams, and Schiff bases, as well as for the oxazaborolidine-catalyzed enantioselective reduction of prochiral ketones.[7b,c]

Borane adducts with *N*-phenylmorpholine and *N*-phenylaniline are still more reactive,[6,8] hydroborating 1-octene in tetrahydrofuran in less than 1 h at room temperature. However, they are solids, considered to be less convenient to handle than liquids for large-scale applications. Nevertheless, these examples clearly suggest the potential of suitable borane adducts with *N,N*-dialkylanilines for hydroboration.

On the other side, the growing importance of diborane for the synthesis of pharmaceuticals and other compounds[9,10] and certain inconveniences of well-established reagents, e.g., the low concentration and stability of borane−tetrahydrofuran (BH_3·THF) and the high volatility, flammability, and unpleasant odor of dimethyl sulfide from borane−dimethyl sulfide (BMS), create a need for easy-to-handle, stable, and environmentally benign hydroborating agents.

Considering these factors, borane−amine adducts offer the advantages of lower sensitivity to moisture and air, the easy recovery of amines from nonbasic reaction products, and the environmentally important possibility of recycling the borane carrier easily. Consequently, we decided to prepare a series of *N,N*-dialkylanilines and examine their complexing ability toward borane with the objective of developing adducts meeting the following requirements: economic amine synthesis, liquid adduct of high hydride content, relatively stable over long periods, readily soluble in various solvents, and

(1) (a)Visiting Professor from Nicolaus Copernicus University, Torun, supported by the Purdue Borane Research Fund. (b) Postdoctoral research associate supported by the Purdue Borane Research Fund.

(2) In the papers describing our studies in this area, we have found it convenient to represent the groups *n*-propyl, isopropyl, *tert*-butyl, and isobutyl by the symbols *n*-Pr, *i*-Pr, *t*-Bu, and *i*-Bu when they appear before the nitrogen atom of the amine and by the more compact representation Pr^n, Pr^i, Bu^t, Bu^i when they appear after the nitrogen atom of the amine.

(3) Lane, C. F. *Aldrichim. Acta* **1973**, *6*, 51.

(4) Long, L. H. In *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Mellor, W. J., Ed.; Longman: London, 1981; Suppl. Vol. 5, Part B1, p 1.

(5) Meller, A. In Gmelin *Handbook of Inorganic and Organometallic Chemistry*; Springer: Berlin, 1992; 4th Suppl. Vol. 3, p 1.

(6) Brown, H. C.; Murray, L. T. *Inorg. Chem.* **1984**, *23*, 2746.

(7) (a) Narayana, C.; Periasamy, M. *J. Organomet. Chem.* **1987**, *323*, 145. (b) Salunkhe, A. M.; Burkhardt, E. R. *Tetrahedron Lett.* **1997**, *38*, 1519. (c) Salunkhe, A. M.; Burkhardt, E. R. *Tetrahedron Lett.* **1997**, *38*, 1523.

(8) Camacho, C.; Uribe, G.; Contreras, R. *Synthesis* **1982**, 1027.

(9) Follet, M. *Chem. Ind.* **1986**, 123.

(10) Ren, O.; Meatres, C. F. *Bioconjugate Chem.* **1992**, *3*, 563.

S0276-7333(98)00418-X CCC: $15.00
Publication on Web 08/22/1998

Table 1. Borane−*N,N*-Dialkylaniline Adducts Prepared

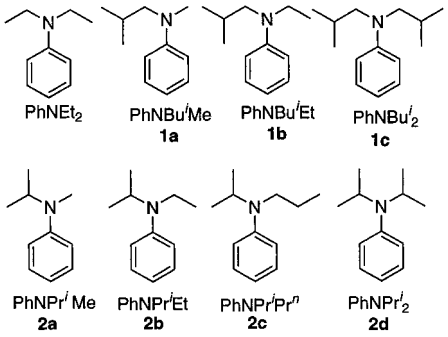
amine	exchange,[a] % BH_3·SMe_2	exchange,[a] % BH_3·THF	amine·BH_3 state[b] (mp, °C)	amine·BH_3 $[BH_3]$[c]	amine·BH_3 ^{11}B NMR[d] d[e]	hydroboration of 1-octene,[f] rt in THF[g]	hydroboration of 1-octene,[f] rt neat
$PhNEt_2$	66	94	liquid	4.8	−11.55	2 h[h]	12 h
$PhNBu^iMe$ (**1a**)	30	80	liquid	4.5	−3.26	30 min	2 h
$PhNBu^iEt$ (**1b**)	19	61	liquid	4.0 ® 3.2[i]	−9.17	15 min	1 h
$PhNBu^i_2$ (**1c**)	0	10	liquid	0.9 ® 0.6[j]	−9.68[k]	15 min	
$PhNPr^iMe$ (**2a**)	50	85	liquid	4.9	−8.77	30 min	12 h
$PhNPr^iEt$ (**2b**)	36	79	liquid	4.7	−14.68	15 min	2 h
$PhNPr^iPr^n$ (**2c**)	25	70	liquid	4.1	−14.21	15 min	2 h
$PhNPr^i_2$ (**2d**)	0	36	solid (36−38)		−16.49[k]	15 min	45 min[l]

[a] Amine mixed with BMS or BH_3·THF in 1:1 molar ratio 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] Recorded on a Varian Gemini 300 multinuclear spectrometer. [e] From the exchange with BMS. [f] 5% excess of 1-octene. [g] 3 M solution in 1-octene. [h] Ref 6. [i] Loss of borane in 4 days at room temperature. [j] Loss of borane in 24 h at room temperature. [k] From the exchange with BH_3·THF. [l] 3 M solution of the adduct in **2d**.

reasonably rapid hydroboration (such as quantitatively hydroborating 1-octene in THF in less than 1 h at room temperature).

Results and Discussion

The reactivity of borane−*N,N*-diethylaniline toward 1-octene is considerably higher than that of borane−*N,N*-dimethylaniline[6] and only slightly too low to meet our requirements. This observation suggested that an increase in the steric requirements of the alkyl groups attached to the nitrogen atom in the *N,N*-dialkylanilines should further lower their complexing ability, providing adducts with the desired properties. Consequently, two series of amines, *N*-alkyl-*N*-isobutylanilines **1a**−**c** and *N*-alkyl-*N*-isopropylanilines **2a**−**d**, have been synthesized and compared for borane complexing ability with the commercially available *N,N*-diethylaniline.



The mixed amines **1a,b** and **2a,b** were prepared from low-cost *N*-methyl- and *N*-ethylaniline, respectively, and isolated by fractional distillation (eq 1).

$$\mathrm{PhNHR} + \mathrm{R'Br} \xrightarrow[\text{2. KOH, } H_2O]{\text{1. reflux, 5-6h}} \mathrm{PhNRR'} \qquad (1)$$

1a: R = Me, R' = *i*-Bu; **2a**: R = Me, R' = *i*-Pr

1b: R = Et, R' = *i*-Bu; **2b**: R = Et, R' = *i*-Pr

An improved synthesis of **2b** based on the alkylation of *N*-ethylaniline by diisopropyl sulfate was developed.

The other amines were prepared from aniline **2c** by reductive alkylation of an intermediate *N*-isopropylaniline, **1c** and **2d**, by stepwise alkylation (eq 2).

$$\mathrm{PhNH_2} \xrightarrow[\text{reflux, 5h}\\ \text{2. KOH, } H_2O]{\text{1. RBr}} \mathrm{PhNHR} \begin{cases} \xrightarrow[\text{EtCOOH}]{\mathrm{NaBH_4}} \mathrm{PhNRPr^n} \\ \xrightarrow[\text{2. KOH, } H_2O]{\text{1. RBr, reflux}} \mathrm{PhNR_2} \end{cases} \qquad (2)$$

2c: R = *i*-Pr

1c: R = *i*-Bu

2d: R = *i*-Pr

The alkylation of *N*-isobutylaniline with isobutyl bromide is very slow.[11] Only 52% of $PhNBu^i_2$ was obtained after 40 h reflux, followed by 5 h heating at 150 °C in an autoclave. Fortunately, the reaction rate is accelerated in the presence of tetrabutylammonium iodide, so that the product can be obtained in a shorter time and higher yield. Similarly, $PhNPr^i_2$ can be prepared by stepwise alkylation of aniline with isopropyl bromide. Other reported procedures for the preparation of **1c** and **2d** are less convenient for scaling up.[12−15]

The complexing ability of the amines prepared was tested by examining the exchange with BMS and BH_3·THF. The amount of borane taken up by the amine in the equilibrium is shown in Table 1. It should be noted that only for BMS, which is a neat adduct, is the molar ratio of borane, amine and dimethyl sulfide precisely 1:1:1, whereas for BH_3·THF, which is a 1.00 M solution the values can be considered only as qualitative, involving the presence of THF in large excess. The exchange experiments reveal an interesting picture. The *N*-alkyl-*N*-isobutylanilines, despite the two alkyl groups being both primary, show lower complexing ability compared to the corresponding isopropyl derivatives. This is observed even for *N,N*-diisobutyl- and *N,N*-diisopropylanilines. Although neither $PhNBu^i_2$ nor $PhNPr^i_2$ takes borane from BMS, $PhNPr^i_2$ takes more than $PhNBu^i_2$ from BH_3·THF. Apparently, the isobutyl group exerts a slightly greater steric influence than that of the isopropyl group in diminishing the donor properties of the alkylated aniline base in these equilibria. The trend revealed by the exchange experiments is reflected in the neat adducts (Table 1). Thus, $PhNBu^iMe$ and $PhNBu^iEt$ form adducts 4.5 and 4.0 M in BH_3, respectively, with $PhNBu^iEt$ complexing more weakly, the molarity dropping to 3.7 in 24 h and to 3.2 in 4 days at room temperature. Both adducts hydroborate 1-octene in

(11) Hickinbottom, W. J.; Lambert, E. W. *J. Chem. Soc.* **1939**, 1383.
(12) Katritzky, A. R.; Rechwal, S.; Wu, J. *Can. J. Chem.* **1990**, *68*, 456.
(13) Caubère, P.; Derozier, N. *Bull. Soc. Chim. Fr.* **1969**, 1737.
(14) Bunnett, J. F.; Brotherton, T. K. *J. Org. Chem.* **1957**, *22*, 832.
(15) Kanth, J. V. B.; Periasamy, M. *J. Org. Chem.* **1993**, *58*, 3156.

THF at room temperature in less than 1 h and under neat conditions in less than 2 h. The corresponding *N*-alkyl-*N*-isopropylanilines, **2a**−**c**, complex borane slightly more strongly. Although both **1a**·BH_3 and **2a**·BH_3 hydroborate 1-octene in THF in 30 min, under neat conditions the isobutyl derivative, **1a**·BH_3, reacts in 2 h, whereas the isopropyl derivative, **2a**·BH_3, requires 12 h. The borane adducts of **1a** and **2a**−**c** are liquids above 0 °C, stable at room temperature, and readily soluble in typical hydroboration solvents, such as diethyl ether, tetrahydrofuran, and dichloromethane.

The complexing ability of $PhNBu^i_2$ is much lower as compared to the other amines studied. Only a 0.9 M solution of the adduct is formed at 0 °C, losing almost half of its borane content in 24 h at room temperature. Interestingly $PhNPr^i_2$ forms a weak solid highly reactive adduct, hydroborating 1-octene under neat conditions in less than 1 h at room temperature. It loses borane above its melting point (36−38 °C), so that diborane can be quantitatively generated by heating the adduct. The gas is readily reabsorbed upon cooling (eq 3).

$$2\ H_3B{:}NPhPr^i_2 \underset{rt}{\overset{38 \rightarrow 100\ ^\circ C}{\rightleftharpoons}} 2\ PhNPr^i_2 + B_2H_6 \qquad (3)$$

Conclusion

This study has demonstrated that *N*-alkyl-*N*-isobutyl- and *N*-alkyl-*N*-isopropylanilines **1a** and **2a**−**c** are new promising borane carriers, forming liquid borane adducts, stable at room temperature, soluble in various solvents, hydroborating 1-octene in THF in less than 1 h at room temperature. Borane−*N*,*N*-diisopropylaniline is a convenient source of diborane, liberating the gas quantitatively by heating the adduct above its melting point, 36−38 °C.

Experimental Section

General Methods. Techniques for handling air-sensitive compounds described elsewhere were followed.[19] Glassware was oven dried for several hours, assembled while hot, and cooled in a stream of dry nitrogen gas. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded at 300, 75, and 96 MHz, respectively. The ^{11}B NMR shifts are in δ relative to $BF_3{\cdot}Et_2O$. GC analyses were performed on a chromatograph (katharometer) equipped with a 12 ft x 0.125 in column packed with 10% SE-30 on Chromosorb W 100−120 mesh. Microanalyses were performed at the Microanalytical Laboratory, Purdue University.

Materials. Tetrahydrofuran was freshly distilled from benzophenone ketyl prior to use. Borane trifluoride−diethyl etherate was distilled under vacuum from calcium hydride. Diglyme and triglyme were distilled under vacuum from a small amount of lithium aluminum hydride. Diisopropyl sulfate was prepared by absorbing propene in concentrated sulfuric acid at −10 to 0 °C according to the literature procedure.[20] Borane−methyl sulfide (BMS), borane−THF, aniline, *N*-methylaniline, and *N*-ethylaniline were commercial products (Aldrich).

(16) van Hoek, T. C.; Verkade, P. E.; Wepster, B. M. *Rec. Trav. Chim. Pays-Bas* **1958**, *77*, 559.
(17) Fröchlich, E. *Ber.* **1909**, *42*, 1561.
(18) Rosser, M.; Ritter, J. J. *J. Am. Chem. Soc.* **1937**, *59*, 2179.
(19) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975; p 18. A reprinted edition, *Organic Syntheses via Boranes*, Vol 1; Aldrich Chemical Co., Inc.: Milwaukee, 1997, is currently available.
(20) Kranzfelder, A. L.; Sowa, F. J. *J. Am. Chem. Soc.* **1937**, *59*, 1491.

***N*-Ethyl-*N*-isopropylaniline (2b). Procedure A, Typical for 1a,b and 2a,b.** A mixture of *N*-ethylaniline (12.12 g, 0.10 mol) and 2-bromopropane (13.53 g, 0.11 mol) was refluxed with stirring until the temperature of the reaction mixture rose to 120 °C. The mixture was cooled to 80 °C, and 5.0 M aqueous potassium hydroxide (30.0 mL) was added. The organic layer was separated and dried with magnesium sulfate. Excess 2-bromopropane was removed by distillation, and the crude product containing *N*-ethyl-*N*-isopropylaniline (83.5%), *N*-ethylaniline (16%), and *N*,*N*-diethylaniline (0.5%) was obtained. *N*-Ethyl-*N*-isopropylaniline was isolated by fractional distillation under vacuum, treated with 2.5 M *n*-butyllithium solution in hexanes (2.0 mL) and distilled, 10.03 g (61%), bp 50−51 °C/1 mmHg, $n_D^{20} = 1.5310$, 98.5% pure by GC (30 m SPB-5 capillary column).

Procedure B. Diisopropyl sulfate (21.88 g, 0.12 mol) was added dropwise with stirring to *N*-ethylaniline (12.12 g 0.10 mol) at 60−80 °C. After 2 h at 100 °C, 5.0 M aqueous potassium hydroxide (60.0 mL, 0.30 mol) was added. The organic layer was separated, washed with 5.0 M potassium hydroxide (10.0 mL, 50.0 mmol), and dried with magnesium sulfate. Distillation gave 14.69 g of *N*-ethyl-*N*-isopropylaniline, **2b** (90%), bp 50−51 °C/1 mmHg.

***N*,*N*-Diisobutylaniline (1c).** A mixture of aniline (14.90 g, 0.16 mol), 1-bromo-2-methylpropane (21.92 g, 0.16 mol), and tetrabutylammonium iodide (2.95 g, 8.0 mmol) was refluxed for 2.5 h. Aqueous 5.0 M potassium hydroxide solution (60.0 mL, 0.30 mol) was added, and the organic layer was separated and dried over magnesium sulfate. The crude product was further treated with 1-bromo-2-methylpropane (21.92 g) and tetrabutylammonium iodide (2.95 g) and refluxed for 5.5 h. The mixture was worked up as described above. GC analysis showed *N*-isobutylaniline (63%) and *N*,*N*-diisobutylaniline (37%). The mixture was treated with the same amounts of 1-bromo-2-methylpropane and tetrabutylammonium iodide as above and refluxed for 8 h. The basic workup as described above and fractional distillation gave **1c**, 20.90 g (64%), bp 86−87 °C/1.5 mmHg (lit.[11] bp 142−144 °C/21 mmHg).

***N*-Propyl-*N*-isopropylaniline (2c).** Sodium borohydride (12.86 g, 0.34 mol) was added in portions to a mixture of propionic acid (16.23 g, 0.22 mol) and *N*-isopropylaniline (10.00 g, 74.0 mmol) at room temperature under nitrogen, and the mixture was kept at 55 °C for 1 h. Aqueous 5.0 M potassium hydroxide solution (50.0 mL, 0.25 mol) was added, the organic layer was separated, and the aqueous layer was extracted with diethyl ether. The extracts were combined with the organic layer and dried over magnesium sulfate. The product was isolated by distillation, 9.73 g (74%), bp 88−89 °C/5 mmHg.

***N*,*N*-Diisopropylaniline (2d).** A mixture of aniline (18.63 g, 0.20 mol) and 2-bromopropane (24.60 g, 0.20 mol) was refluxed until the temperature increased to 130 °C (5 h). After cooling to room temperature, aqueous 5.0 M potassium hydroxide solution (50.0 mL, 0.25 mol) was added, the organic layer was separated, and the aqueous layer was extracted with diethyl ether. The extracts were combined with the organic layer and dried over magnesium sulfate. Ether was removed to give 25.15 g of a crude product. GC analysis on a 12 ft × 0.125 in. column packed with 10% SE-30 on Chromosorb W 100−120 mesh showed aniline (7%), *N*-isopropylaniline (89%) and *N*,*N*-diisopropylaniline (4%). 2-Bromopropane (24.60 g, 0.20 mol) was added, and the mixture was refluxed until the temperature increased to 130 °C (∼40 h). The same workup as described above and fractional distillation gave 31.15 g (88%) of product containing ∼2% of *N*-isopropylaniline, which was removed by the addition of 2.5 M *n*-butyllithium in hexane (5.0 mL) and distillation. There was obtained 28.67 g of **2d** (81%), bp 50−52 °C/1 mmHg, >99% GC pure (lit.[18] bp 98−100 °C/13 mmHg).

Procedure B. Diisopropyl sulfate (21.88 g, 0.12 mol) was added dropwise with stirring to aniline (9.31 g, 0.10 mol) at 60−80 °C. After 2 h at 100 °C, 5.0 M aqueous potassium

hydroxide (60.0 mL, 0.30 mol) was added. The organic layer was separated, washed with 5.0 M potassium hydroxide (10.0 mL, 50.0 mmol), and dried with magnesium sulfate. GC analysis showed the presence of aniline (5%) and *N,N*-diisopropylaniline (10%) in addition to *N*-isopropylaniline (85%). To this mixture was added diisopropyl sulfate (21.88 g, 0.12 mol) at 60−80 °C, and the mixture was maintained at 100 °C for 2 h. After the same workup as described above and fractional distillation *N,N*-diisopropylaniline was obtained in 92% yield.

General Procedure for Borane−Amine Adducts. Diborane, generated as described below, 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 diborane not absorbed by the amine was absorbed in the next bubbler containing tetrahydrofuran (10.0 mL) over mercury, 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 was ~1 M. The borane−amine adduct was stirred overnight at room temperature prior to disconnecting the bubblers and then analyzed for active hydrogen by a standard procedure, using a 2.0 M hydrochloric acid−glycerol−water (2:1:1) hydrolysis solution.[21]

Borane Trifluoride Adducts with Diglyme or Triglyme. **Typical Procedure.** Boron trifluoride−diethyl etherate (14.19 g, 0.10 mol) was added to diglyme (13.42 g, 0.10 mol), and the mixture was stirred under 100 mmHg and finally under 12 mmHg at room temperature to constant weight. Diethyl ether (7.31 g, 98.6% yield) was collected in a cold trap (liquid nitrogen). A pale yellow liquid adduct, 20.3 g, ^{11}B NMR, δ 0.00 ppm, was obtained. It darkened slowly when kept at 0 °C and was used within two weeks. The triglyme additive was prepared similarly. The adducts with diglyme and triglyme are 5.4 and 4.5 M in BF_3, respectively. For preparation on a large scale, the use of boron trifluoride−triglymate facilitates recovery and recycle of triglyme.

Generation of Diborane. Procedure A. A 50 mL one-neck, round-bottom flask provided with a septum inlet, magnetic stirring bar, and an adapter with a stopcock, connected to a bubbler containing tetrahydrofuran (30.0 mL), was charged with boron trifluoride−diglyme or −triglyme adduct (75.0 mmol). A 2.0 M solution of sodium borohydride in triglyme (28.5 mL, 57.0 mmol) was added dropwise by means of a hypodermic syringe. Generation of diborane is smooth, and the reaction is not exothermic. After the addition was completed, the flask was heated to 100 °C and kept at this temperature for 15 min. Diborane was absorbed in tetrahydrofuran (30.0 mL) at 0 °C. Analysis for active hydride of the BH_3·THF solution obtained according to the standard procedure, revealed a 2.41 M concentration of borane (95%); ^{11}B NMR, δ +1.00 ppm.

Procedure B. Crystalline H_3B:NPhPr$^i_2$ (1.15 g, 6.0 mmol) was placed in a flask (10 mL volume) flushed with nitrogen and attached to a buret filled with mercury. The flask was slowly heated from 24 °C to 100 °C. Liberation of diborane started at 40 °C, and the total amount of diborane evolved was 2.94 mol (98%). Diborane was reabsorbed upon cooling the flask to room temperature.

Exchange Reaction of BMS and H_3B:THF with *N,N*-Dialkylanilines. General Procedure. An oven-dried 25 mL RB flask, provided with septum inlet and a stirring bar was cooled to room temperature under nitrogen. The flask was charged with *N,N*-dialkylaniline (4 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 1).

Hydroboration of 1-Octene with *N,N*-Dialkylaniline−Borane Adducts in THF. General Procedure. An oven-dried 25 mL RB flask, provided with septum inlet and a stirring bar, was cooled to room temperature under nitrogen. The flask was charged with *N,N*-dialkylaniline−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 1).

Acknowledgment. Financial support of this study by the Purdue Borane Research Fund is acknowledged. The assistance provided by Dr. J. V. B. Kanth with some of the experiments is appreciated.

Supporting Information Available: ^{1}H, ^{13}C NMR, and mass spectral data for amines **1a**−**c** and **2a**−**d** (2 pages). Ordering information is given on any current masthead page.

OM980418U

(21) Reference 19, p 241.