spondingly, in all the reactions investigated there also has been no spectroscopic evidence of the existence of species such as $[Fe_3Pt_3(CO)_{15}]^{2-}$.[7] This further difference in the carbonyl cluster chemistry of nickel subgroup metals is well in keeping with the tendency to square-planar coordination of both palladium and platinum and with their aversion to high coordination number with CO, contrasted to the preference of nickel for tetrahedral coordination and the stability of $Ni(CO)_4$.

Acknowledgment. The research at Brookhaven National Laboratory was carried out under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. $[N(CH_3)_3CH_2Ph][Fe_3Ni(CO)_{12}H]$, 89322-11-2; $[PPh_3(CH_2Ph)]_2[Fe_3Ni(CO)_{12}]$, 89322-13-4; $[PPh_3(CH_2Ph)]_2[Fe_3(CO)_{11}]$, 89322-14-5; $Ni(CO)_4$, 13463-39-3; $[N(C_4H_9)_4]_2[Fe_3Ni(CO)_{12}]$, 89322-15-6; $[N(CH_3)_3CH_2Ph]_2[Fe_3Ni(CO)_{12}]$, 89322-16-7; $[PPh_3(CH_2Ph)][Fe_3Ni(CO)_{12}H]$, 89322-17-8; $[N(C_4H_9)_4][Fe_3Ni(CO)_{12}H]$, 89322-18-9; $[PPN][Fe_3Ni(CO)_{12}H]$, 89322-19-0; $[N(C_4H_9)_4]_2[Fe_3(CO)_{11}]$, 89322-20-3; $[N(C_4H_9)_4]_2[Fe_2(CO)_8]$, 58341-98-3; $[Fe_3(CO)_{11}H]^-$, 55188-22-2; $[Na(THF)_4]_2[Fe(CO)_4]$, 89322-21-4; Fe, 7439-89-6; Ni, 7440-02-0.

Supplementary Material Available: Thermal parameters (Table I-S), bond distances (Table II-S) and angles (Table III-S) in the $[N(CH_3)_3CH_2Ph]^+$ cation, and a listing of observed and calculated F^2 values (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Stereochemistry of Some Alkyl[bis(trimethylsilyl)amino]boranes

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Several new alkylchloro- and alkyl(dimethylamino)[bis(trimethylsilyl)amino]boranes, $(Me_3Si)_2NB(R)X$ [X = Cl (R = *t*-Bu, *i*-Pr, CH_2SiMe_3); X = *t*-Bu (R = CH_2SiMe_3); X = NMe_2 (R = Me, CH_2SiMe_3, *i*-Pr, *t*-Bu)], have been prepared from $(Me_3Si)_2NBCl_2$ by chloride displacement with organometallic reagents and Me_3SiNMe_2. Rotational barriers ($\Delta G_c^{\ddagger}$ = 17.3–20.9 kcal/mol) about the B–NMe_2 bonds were determined by dynamic ^1H NMR spectroscopy, and the results are discussed in terms of steric interactions between the bulky groups on boron. Analogies between the preparative chemistry of these (silylamino)boranes and that of the comparably substituted phosphines are noted.

Introduction

The chemistry and stereochemistry of compounds containing the silicon–nitrogen–boron linkage have been the subjects of numerous studies during the past two decades. Many of these compounds are, in fact, useful precursors to other B–N systems including diborylamines,[1] borazines,[2] borazocines,[3] monomeric boron imines,[4] and B–H-substituted aminoboranes.[5] Recent interest in our laboratory has focused mainly on the synthetic potential of analogous silicon–nitrogen–phosphorus compounds.[6] Clearly, there exist many parallels between the preparative chemistry of (silylamino)boranes and that of the (silylamino)phosphines [e.g., $(Me_3Si)_2NBCl_2$, $(Me_3Si)_2NPCl_2$]. We are beginning to explore the extent of this analogy in more detail toward the goal of developing new synthetic methods and reactivity patterns in B–N chemistry.

From a stereochemical viewpoint, interest in (silylamino)boranes was stimulated by Wells and co-workers,[7] who observed an unexpectedly high barrier to rotation ($\Delta G^{\ddagger}$ = 17.6 kcal/mol) about the Me_2N–B bond in $(Me_3Si)_2NB(Cl)NMe_2$. Subsequent studies[8-10] on related compounds led to the conclusion that the bulky $(Me_3Si)_2N$ group is rotated out of the plane of the B–NMe_2 moiety and thus is not an effective π donor to boron (Figure 1A). The same type of conformation has been recently postulated[11] for the sterically congested (tetramethylpiperidino)boranes (Figure 1B). The previous dynamic NMR studies of (silylamino)boranes $R_3SiN(R)B(X)NR_2$ have probed the effects of varying substituents on silicon[10] as well as on both of the nitrogen atoms.[8,9] For synthetic simplicity, however, the other substituents on boron have been largely restricted to X = phenyl and, in a few cases, to X = Cl or NH_2. The stereochemical influence of groups (e.g., X = alkyl) that may be varied in size and are not π donors to boron has not been investigated.

In the context of these preparative and stereochemical questions, we report here on the synthesis, reactivity, and dynamic NMR study of several new B-alkylated (silylamino)boranes.

Results and Discussion

Synthesis. We have previously reported that bulky organometallic reagents (e.g., *t*-BuLi, Me_3SiCH_2MgCl, *i*-PrMgCl) react with [bis(trimethylsilyl)amino]dichlorophosphine to yield the monosubstituted alkylchlorophosphines $(Me_3Si)_2NP(R)Cl$.[12,13] In the present study, we find that the

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[1] (a) Nöth, H.; Storch, W. *Chem. Ber.* **1976**, *109*, 884. (b) Barlos, K.; Christl, H.; Nöth, H. *Justus Liebigs Ann. Chem.* **1976**, 2272.

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[6] See, for example, the following and references cited therein: (a) Li, B.-L.; Engenito, J. S.; Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1983**, *22*, 575. (b) Neilson, R. H.; Engenito, J. S. *Organometallics* **1982**, 1, 1270. (c) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.

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Table I. Preparative, Analytical, and NMR Spectroscopic Data for the (Silylamino)boranes $(Me_3Si)_2NB(X)R$

			NMR spectra[a]			preparative		anal.[b]	
no.	R	X	signal	^{1}H, δ	^{13}C, δ	bp, °C (*P*, mm)	% yield	% C	% H
1	*t*-Bu	Cl	$(Me_3Si)_2N$	0.30	4.06	50–53 (0.2)	61	45.70 (45.54)	10.48 (10.32)
			t-Bu	1.06	29.04				
2	Me_3SiCH_2	Cl	$(Me_3Si)_2N$	0.32	4.18	57–59 (0.07)	91	40.93 (40.87)	10.10 (9.95)
			Me_3SiC	0.14	0.73				
			CH_2	0.96					
3	*i*-Pr	Cl	$(Me_3Si)_2N$	0.28	3.54	66–69 (3.0)	69[d]	43.19 (43.28)	10.24 (10.09)
			$\mathit{Me}_2\mathrm{CH}$	0.96[c]	18.39				
			$\mathrm{Me}_2\mathit{CH}$	1.50[c]					
4	*t*-Bu	Me_3SiCH_2	$(Me_3Si)_2N$	0.25	5.04	66–67 (0.1)	58	53.16 (53.29)	11.87 (12.14)
			Me_3SiC	0.12	2.31				
			$\mathit{Me}_3\mathrm{C}$	0.95	29.73				
5[e]	NMe_2	Cl	$(Me_3Si)_2N$	0.07	2.40	45–51 (0.5)	94	38.06 (38.32)	9.68 (9.65)
			Me_2N	2.75	39.23				
				2.79	39.35				
6	Me	NMe_2	$(Me_3Si)_2N$	−0.01	2.84	36–37 (0.9)	74	47.14 (46.94)	11.53 (11.82)
			NMe_2	2.69	38.54				
				2.72					
7	Me_3SiCH_2	NMe_2	$(Me_3Si)_2N$	0.14	3.57	58–60 (0.03)	91	47.72 (47.65)	11.68 (11.66)
			Me_3SiC	0.08	1.62				
			CH_2	0.36					
			NMe_2	2.65	39.43				
				2.72					
8	*i*-Pr	NMe_2	$(Me_3Si)_2N$	0.04	3.25	55–60 (0.6)	80[d]		
			$\mathit{Me}_2\mathrm{CH}$	0.94	19.82				
			$\mathrm{Me}_2\mathit{CH}$	1.10[f]					
			Me_2N	2.68	39.55				
9	*t*-Bu	NMe_2	$(Me_3Si)_2N$	0.13	3.77	mp 134–137	100	53.07 (52.91)	12.48 (12.21)
			Me_3C	1.02	30.47				
			NMe_2	2.75	39.70				
				2.80	39.78				

[a] Chemical shifts downfield from Me_4Si. Solvents: ^{1}H, CH_2Cl_2; ^{13}C, $CDCl_3$. [b] Calculated values in parentheses. [c] J_{HH} = 6.5 Hz. [d] Estimated yield (purity ~80%). [e] See also ref 16. [f] Complex multiplet.

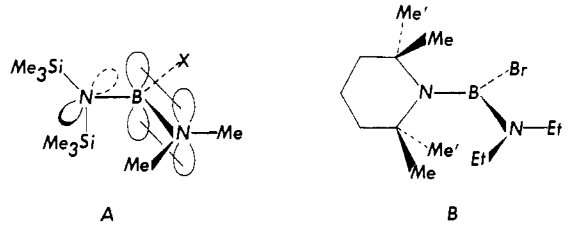
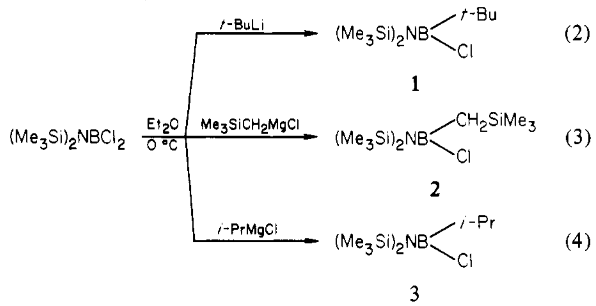


Figure 1. Ground-state conformations: A, (dimethylamino)[bis(trimethylsilyl)amino]boranes (X = Cl,[7] Ph,[8] NH_2[9]); B, bromo(diethylamino)(2,2,6,6-tetramethylpiperidino)borane.[11]

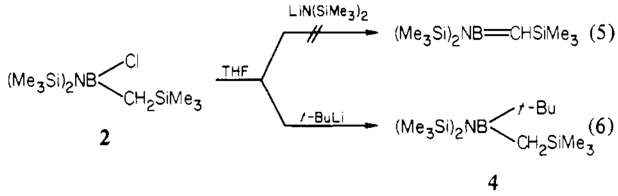
same synthetic approach (eq 1–4) can be used to prepare the alkylchloroboranes **1**–**3** from the readily available precursor $(Me_3Si)_2NBCl_2$.[14]

$$(Me_3Si)_2NLi + BCl_3 \longrightarrow (Me_3Si)_2NBCl_2 + LiCl \quad (1)$$



This method is particularly effective for the synthesis of chloroboranes **1** and **2** (Table I), which were obtained in good yield and high purity after a single vacuum distillation. The results of the reaction with *i*-PrMgCl (eq 4), however, were less satisfactory due to the competing formation of an unidentified byproduct, probably $(Me_3Si)_2NB(i\text{-}Pr)_2$. The best yields of **3** were obtained under conditions (high dilution and deficiency of *i*-PrMgCl) intended to favor the reaction of only one B–Cl bond with the Grignard reagent. Even when prepared in this manner, compound **3** was contaminated with substantial quantities (ca. 20%) of the byproduct. Multiple redistillations did eventually produce an analytically pure sample of **3**, but the quantities obtained were too small to be useful for further reactions. Because of these difficulties encountered with *i*-PrMgCl, no attempts were made to prepare alkylchloroboranes $(Me_3Si)_2NB(R)Cl$ with small alkyl groups (e.g., R = Me, Et) by this procedure.

Initially, we were interested in the possibility of preparing the novel 2-coordinate, π-bonded borane $(Me_3Si)_2NB{=}CHSiMe_3$ using a method (eq 5) that had been successful for the analogous phosphine.[12] No reaction occurred at room temperature, however, when a THF solution of the chloroborane **2** was treated with lithium bis(trimethylsilyl)amide. Also, a complex mixture, from which no identified products were obtained, resulted when the reaction mixture was refluxed overnight. On the other hand, just as was observed in the chlorophosphine system,[12] the reaction of **2** with *t*-BuLi (eq 6) proceeded via nucleophilic substitution rather than dehydrohalogenation. Thus, the sterically crowded dialkyl(silylamino)borane **4** was obtained as a fully characterized, distillable liquid (Table I).



The dichloroborane $(Me_3Si)_2NBCl_2$ is also a useful substrate for preparing various bis- and tris(amino)boranes.[15] In this

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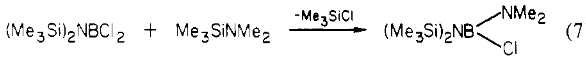
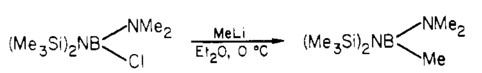
[14] Geymayer, P.; Rochow, E. G.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 633.

study, we found that it underwent a smooth Si–N cleavage reaction with 1 equiv of Me_3SiNMe_2 (eq 7) to give the known[16]


(7)

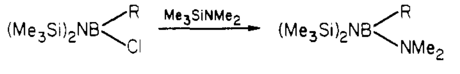
5

bis(amino)borane **5** in 94% yield. In addition to the improved yield, this synthesis of **5** offers the advantage of convenience, since it avoids the preparation and storage of Me_2NBCl_2. The remaining B–Cl bond of **5** was found to be moderately reactive toward organometallic reagents. For example, treatment of **5** with MeLi readily gave the *B*-methyl derivative **6** (eq 8).


(8)

5 6

In spite of the steric hindrance provided by the bulky alkyl groups, the chloroboranes **1–3** reacted smoothly and exothermically with the (dimethylamino)silane (eq 9) to afford


(9)

7, R = CH_2SiMe_3
8, R = *i*-Pr
9, R = *t*-Bu

high yields (~90%) of the B–NMe_2 derivatives **7–9**. Both the (trimethylsilyl)methyl compound **7**, a colorless liquid, and the *tert*-butyl derivative **9**, a white solid (mp 134–137 °C), were easily obtained in high purity (Table I). The isopropyl analogue **8**, however, could not be purified completely due to the presence of impurities in the starting chloroborane **3** as described above. Thus, a satisfactory elemental analysis of **8** was not obtained. Nevertheless, the ^1H and ^{13}C NMR data for **8** were consistent with the proposed structure, and the samples were of sufficient purity to provide reliable variable-temperature ^1H NMR spectra (see below).

When the chemistry of the (silylamino)boranes described herein is compared with that of the related phosphorus compounds, the following points are noteworthy: (1) The preparation of monosubstituted derivatives $(Me_3Si)_2NE(R)Cl$ (E = B, P) is more difficult in the boron series as evidenced by the problems encountered with the isopropyl compound **3**. In contrast, the phosphine analogue $(Me_3Si)_2NP(i\text{-}Pr)Cl$ is easily prepared[13] without high-dilution procedures. (2) The dehydrohalogenation to form E=C bonds (eq 5) is more easily achieved for the phosphorus compounds.[12] (3) The alkylchloroboranes are apparently not as prone to the reduction (E–H) and/or coupling (E–E) side reactions that we have sometimes observed in the reactions of chlorophosphines with bulky organometallic reagents.[13,17] (4) The Si–N cleavage reaction (eq 9) occurs more readily for the chloroboranes; for example, $(Me_3Si)_2NP(t\text{-}Bu)Cl$ does not react with Me_3SiNMe_2 even under forcing conditions.[17] All of these observations are consistent with the fact that, despite the small size of boron relative to phosphorus, the B–Cl compounds are more susceptible to nucleophilic displacement reactions than are comparably substituted P–Cl systems. Additional derivative chemistry of the alkylchloroboranes **1–3** and related compounds is presently under investigation in our laboratory.

Stereochemistry. The ^1H NMR spectra of the new alkyl[bis(trimethylsilyl)amino](dimethylamino)boranes **6–9** revealed a temperature dependence similar to that observed previously for the related compounds $(Me_3Si)_2NB(X)NMe_2$ (X = Cl,[7] Ph,[8] NH_2[9]). At room temperature, the *N*-methyl groups are nonequivalent as a result of restricted rotation about the B–NMe_2 bonds. The free energies of activation ($\Delta G_c^{\ddagger}$, Table II) were determined[18] by measurement of the coalescence temperature (T_c) and the chemical shift difference ($\Delta\nu$) at the slow-exchange limit. The rotational barrier for chloroborane **5** was also redetermined and was found to agree (within experimental error of ca. ±0.3 kcal/mol) very well with the value reported earlier.[7] The literature data for the *B*-phenyl derivative[8] is also included in Table II for comparison purposes.

Table II. Variable-Temperature ^1H NMR Data[a] for the (Silylamino)boranes $(Me_3Si)_2NB(R)NMe_2$

no.	R	T_c, °C	$\Delta\nu$, Hz	$\Delta G_c^{\ddagger}$, kcal/mol
5[b]	Cl	60 (67)	14.4 (13.0)	17.3 (17.6)
6	Me	80	8.4	18.7
7	Me_3SiCH_2	106	12.0	19.9
8	*i*-Pr	103	6.0	20.2
9	*t*-Bu	104	2.7	20.9
c	Ph	102	9.1	19.8

[a] Spectra recorded at 90 MHz on 20% (v/v) solutions in benzene. Values of $\Delta\nu$ were measured at ca. 30 °C (i.e., at least 30 °C below T_c). Experimental uncertainties: T_c, ±2 °C; $\Delta\nu$, ±0.2 Hz; $\Delta G_c^{\ddagger}$, ±0.3 kcal/mol. [b] Data in parentheses taken from ref 7. [c] Data taken from ref 8 (solvent: *n*-butyl ether).

All of the $\Delta G_c^{\ddagger}$ values for the alkylboranes **6–9** are high enough to indicate a substantial degree of (p–p)π interaction in the Me_2N–B bond. The results are completely consistent with the previous suggestion of a "twisted" ground-state configuration (Figure 1A) in which only the Me_2N group is properly oriented for π bonding with boron. Moreover, examination of molecular models indicates that this is the least congested arrangement of the substituents even when R = *t*-Bu (**9**).

Interestingly, the rotation barriers measured for compounds **6–9** show a slight, but definitely significant, upward trend with increasing size of the alkyl group. This is most likely a result of increasing steric interference of the *N*-methyl and *C*-methyl substituents that would tend to further restrict the B–N rotation process. A similar steric inhibition of rotation about P–N bonds has been observed for some closely related (silylamino)phosphines,[19] once again pointing to a rather close analogy between these types of boron and phosphorus compounds.

Experimental Section

The following reagents were obtained from commercial sources and used without further purification: BCl_3, $(Me_3Si)_2NH$, Me_3SiNMe_2, *n*-BuLi (hexane solution), *t*-BuLi (pentane solution), *i*-PrMgCl (ether solution), and MeLi (ether solution). The Grignard reagent Me_3SiCH_2MgCl was prepared in Et_2O according to the published procedure.[20] Solvents were distilled from CaH_2 and stored over molecular sieves. Proton and ^{13}C NMR spectra were recorded on Varian EM-390 and JEOL FX-60 spectrometers, respectively. High-temperature ^1H NMR spectra were obtained on the EM-390 instrument equipped with a standard Varian temperature controller. Probe temperatures were reproducible to within ±2 °C and were calibrated by using an ethylene glycol reference sample. The $\Delta G_c^{\ddagger}$ values (Table II) were calculated[18] by the so-called "approximate method", which has been shown to give accurate results when applied to such two-site exchange processes.[21] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described below are typical of those used for the preparation of the new

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(15) Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1968**, *7*, 419.
(16) Wells, R. L.; Paige, H. L. *Inorg. Chem.* **1971**, *10*, 1526.
(17) Neilson, R. H.; Roy, A. K.; Engenito, J. S., unpublished results.
(18) The equation $\Delta G_c^{\ddagger} = T_c[45.67 + 4.58 \log (T_c/\Delta\nu)]$ gives $\Delta G_c^{\ddagger}$ in cal/mol with T_c in K (see ref 8).
(19) Goldwhite, H.; Power, P. P. *Org. Magn. Reson.* **1978**, *11*, 499.
(20) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262.
(21) Kost, D.; Carlson, E. H.; Raban, M. *Chem. Commun.* **1971**, 656.

(silylamino)boranes in this study.

Preparation of [Bis(trimethylsilyl)amino]dichloroborane. This procedure is adapted from that described in the literature;[14] it affords high yield and can be done safely and conveniently on large scales (ca. 0.5–1.0 mol). A 2-L, 3-necked flask, equipped with a mechanical stirrer, a gas inlet tube, and an addition funnel, was charged with $(Me_3Si)_2NH$ (0.50 mol, 104 mL) and hexane (700 mL). After the mixture was cooled to 0 °C, *n*-BuLi (0.51 mol, 319 mL, 1.6 M) was added with stirring. The mixture was warmed to room temperature, stirred for 30 min, and then cooled to −78 °C. With use of a standard vacuum system, BCl_3 (0.5 mol, 43 mL) was measured as a liquid at −78 °C in a precalibrated flask equipped with a magnetic stirrer and a stopcock to permit its isolation from the vacuum line. The flask containing the BCl_3 was then connected to the gas inlet tube of the reaction flask via Tygon tubing. While being stirred magnetically, the BCl_3 was allowed to evaporate and condense slowly into the slurry of $LiN(SiMe_3)_2$, which was mechanically stirred at −78 °C. After complete addition of BCl_3, the mixture was allowed to warm to room temperature and was stirred for 1 h. Solids were removed by suction filtration under N_2, and solvent was removed under reduced pressure. Distillation afforded $(Me_3Si)_2NBCl_2$ as a colorless liquid (91.6 g, 76% yield, bp 51–62 °C (3.0 mm)), which is extremely sensitive to atmospheric moisture but can be stored indefinitely in tightly sealed containers: ^1H NMR (CH_2Cl_2) δ 0.36; ^{13}C NMR δ 3.65.

Preparation of Alkyl[bis(trimethylsilyl)amino]chloroboranes, $(Me_3Si)_2NB(R)Cl$. 1, R = *t*-Bu. *tert*-Butyllithium (0.059 mol, 28.1 mL, 2.1 M) was added slowly from an addition funnel to a magnetically stirred solution of $(Me_3Si)_2NBCl_2$ (14.3 g, 0.059 mol) in Et_2O (100 mL) at 0 °C. The mixture was allowed to warm to room temperature while stirring. Following filtration and solvent removal, distillation gave **1** as a colorless liquid (Table I).

2, R = CH_2SiMe_3. Similarly, $(Me_3Si)_2NBCl_2$ (34.9 g, 0.144 mol) in Et_2O (50 mL) was treated with freshly prepared[20] Me_3SiCH_2MgCl (ca. 0.15 mol in 90 mL of Et_2O) at 0 °C. After the solution was warmed to room temperature and stirred overnight, hexane (ca. 150 mL) was added prior to filtration. Following filtration and solvent removal, distillation gave **2** as a colorless liquid (Table I).

3, R = *i*-Pr. A dilute solution of *i*-PrMgCl (0.090 mol, 40.9 mL, 2.2 M) in Et_2O (200 mL) was added slowly over a period of 5 h to a stirred solution of $(Me_3Si)_2NBCl_2$ (24.3 g, 0.100 mol) in Et_2O (200 mL). After warming to room temperature and stirring overnight, the mixture was filtered and solvent was removed. Distillation gave a colorless liquid (15.6 g, ca. 69% yield, bp 45–48 °C (0.5 mm)), which as shown by ^1H NMR, consisted of a mixture of **3** (~80%) and an impurity (~20%), probably $(Me_3Si)_2NB(i\text{-}Pr)_2$. Three redistillations through a 10-cm column afforded a purified center fraction of **3** (5.21 g, 23% yield, bp 66–69 °C (3.0 mm)).

Preparation of [Bis(trimethylsilyl)amino](*tert*-butyl)((trimethylsilyl)methyl)borane (4). Chloroborane **2** (8.5 g, 0.029 mol) in THF (25 mL) was treated at 0 °C with *t*-BuLi (0.029 mol, 16.1 mL, 1.8 M). After warming to room temperature and stirring 3 h, the mixture was filtered and solvents were removed. Hexane (20 mL) was added to the residue, and it was filtered again to remove additional LiCl. Distillation gave **4** as a colorless liquid (Table I).

Preparation of Chloro[bis(trimethylsilyl)amino](dimethylamino)borane (5). The silylamine Me_3SiNMe_2 (0.15 mol, 23.9 mL) was added slowly from an addition funnel to $(Me_3Si)_2NBCl_2$ (0.15 mol, 36.3 g), which was stirring at 0 °C. After the mixture was warmed to room temperature and stirred overnight, Me_3SiCl was removed under vacuum. Distillation gave **5** as a colorless liquid (Table I), which was in all respects identical with that reported earlier.[16]

Preparation of Alkyl[bis(trimethylsilyl)amino](dimethylamino)boranes, $(Me_3Si)_2NB(R)NMe_2$. 6, R = Me. Methyllithium (0.112 mol, 80 mL, 1.4 M) was added dropwise to a stirred solution of **5** (28.0 g, 0.112 mol) in Et_2O (200 mL) at 0 °C. After warming to room temperature and stirring overnight, the mixture was filtered and freed of solvent. Hexane (100 mL) was added, and the mixture was refiltered. After solvent removal, distillation gave **6** as a colorless liquid (Table I).

7, R = CH_2SiMe_3; 8, R = *i*-Pr; 9, R = *t*-Bu. These were all prepared by adding Me_3SiNMe_2 (ca. 50 mmol) to an equimolar quantity of the chloroborane $(Me_3Si)_2NB(R)Cl$, which was stirred at 0 °C. After the mixture was warmed to room temperature and stirred overnight, Me_3SiCl was removed under vacuum. Compound **7** distilled as a colorless liquid, **8** also distilled but it could not be separated from unidentified impurities (see text), and **9** was obtained directly as a white solid that required no further purification, although it readily sublimed at ca. 90 °C (0.1 mm). Relevant characterization data for **7**–**9** are listed in Table I.

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Registry No. **1**, 89487-06-9; **2**, 89487-07-0; **3**, 89487-08-1; **4**, 89487-09-2; **5**, 32882-72-7; **6**, 72895-75-1; **7**, 89487-10-5; **8**, 89487-11-6; **9**, 89487-12-7; $(Me_3Si)_2NLi$, 4039-32-1; BCl_3, 10294-34-5; $(Me_3Si)_2NBCl_2$, 6591-26-0; *t*-BuLi, 594-19-4; Me_3SiCH_2Cl, 2344-80-1; *i*-PrCl, 75-29-6; Me_3SiNMe_2, 2083-91-2; MeLi, 917-54-4; $(Me_3Si)_2NB(i\text{-}Pr)_2$, 89487-13-8.