(Å) gives excellent agreement with the experimental data.[17] Using the corrected dielectric continuum model, $e = 1$, and calculated[8] values of $d = 7.1$ Å and $a_1 = a_2 = 6.0$ Å for the phosphine-bridged dimer gives a calculated slope of 4080 cm⁻¹ for the plot shown in Figure 3. The calculated value is in good agreement with the experimental value of 4000 cm⁻¹.

The properties of the IT band are also consistent with the kinetic results obtained from outer-sphere rate constant measurements. For the reaction in eq 8 and 9, $k_{obsd} = 4.9 \times 10^7$ M⁻¹ s⁻¹ (in CH₃CN, 25 °C, $I \approx 0$)[4] and $K \approx 0.6$, so that the electron-transfer rate constant within the ion pair is $k_{et} \approx 8 \times 10^7$ M⁻¹ s⁻¹. From the quantum mechanical treatments of Duke,[18] Hopfield,[2b] and others,[19] it is possible to calculate rate constants of intramolecular electron transfer from the properties of IT bands.[20] For the intramolecular electron-transfer process, k_{et} is given by eq 13, where $E_{op} \cong 4\Delta G^* =$

λ and λ is the free-energy term corresponding to χ. In the high-temperature limit, ν_{et} is given by eq 14. For the dimer,

$$k_{et} = \nu_{et} \exp[-(\Delta G^*/RT)] \tag{13}$$

$$\nu_{et} = \frac{2\pi^{3/2}}{\hbar} V_{ab}{}^2 \left(\frac{1}{k_B T \lambda}\right)^{1/2} \tag{14}$$

the calculated value for k_{et} using eq 13 is 8.8×10^8 s⁻¹ which is in reasonable agreement with the value estimated for the outer-sphere reaction especially given the differences in the distances between redox sites for the two reactions ($d = 6.8$ vs. 13.2 Å).[1,20]

Registry No. [(bpy)₂ClRu(dppm)RuCl(bpy)₂](ClO₄)₂, 72378-70-2; [(bpy)₂ClRu(dppm)RuCl(bpy)₂](PF₆)₂, 72378-72-4; *cis*-(bpy)₂RuCl₂, 19542-80-4; [(bpy)₂ClRu(dppm)RuCl(bpy)₂]⁴⁺, 72390-15-9; [(bpy)₂ClRu(dppm)RuCl(bpy)₂]³⁺, 72478-65-0; [(bpy)₂ClRuᴵᴵ-(PPh₃)]⁺, 50576-57-3; [(bpy)₂ClRuᴵᴵᴵ(PPh₃)]²⁺, 72402-36-9.

(17) M. J. Powers, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, N.C., 1977; M. J. Powers and T. J. Meyer, *J. Am. Chem. Soc.*, in press.
(18) C. B. Duke, "Proceedings of the Conference on Tunneling in Biological Systems", in press.
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Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

# Reactions of BCl₃ with Silylamines Containing Si–H Bonds[1]

ROBERT H. NEILSON

The reactions of BCl₃ with a variety of di- and trisilylamines containing at least one Si–H bond have been investigated. In CH₂Cl₂ solution, the chloro-substituted trisilylamines (Me₃Si)₂NSiMe₂Cl and Me₃SiN(SiMe₂Cl)₂ were obtained in high yields from the corresponding Si–H derivatives by chlorination with BCl₃. Depending upon the reaction conditions employed, the *tert*-butylamines *t*-BuN(SiMe₂H)SiMe₃ and *t*-BuN(SiMe₂H)₂ gave either simple H/Cl exchange products or the (silylamino)boranes Me₃Si(Me₂SiCl)NB(Cl)H (**1**) and (Me₂SiCl)₂NBH₂ (**2**) which resulted from an unexpected C–N bond cleavage process. In the case of Me₃Si(Me₂SiH)NMe, the trimethylsilyl–nitrogen bond was selectively cleaved to afford another difunctional (silylamino)borane (Me₂SiCl)(Me)NB(Cl)H (**3**). Spectroscopic data for the aminoboranes (**1–3**) and some new silylamines are reported.

Introduction

The cleavage reaction of silicon–nitrogen compounds with boron halides is well documented as an important synthetic method in boron–nitrogen chemistry. With variation of the reaction stoichiometry and the number of Si–N and B–X bonds involved, this process (eq 1) has been used to prepare (silylamino)boranes,[2] diborylamines,[3] borazines,[4] or borazocines.[5]

$$-\!\overset{|}{\underset{|}{Si}}\!-\!N\!< \; + \; X\!-\!B\!< \; \longrightarrow \; -\!\overset{|}{\underset{|}{Si}}\!-\!X \; + \; >\!N\!-\!B\!< \tag{1}$$
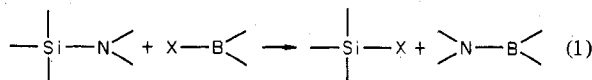
Silicon–hydrogen bonds are also quite reactive toward certain nonmetal halides. For example, treatment of PF₅ with

Me₃SiH is an effective preparative route to HPF₄.[6] Electronegativity and bond energy considerations suggest that similar exchange reactions (eq 2) can occur between silicon hydrides and boron halides, although only a few examples have been reported.[7]

$$-\!\overset{|}{\underset{|}{Si}}\!-\!H \; + \; X\!-\!B\!< \; \longrightarrow \; -\!\overset{|}{\underset{|}{Si}}\!-\!X \; + \; H\!-\!B\!< \tag{2}$$
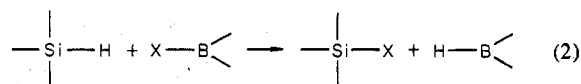
In this context, we report here the results of a study in which trichloroborane was allowed to react with some silicon compounds containing both Si–N and Si–H bonds.

Results and Discussion

In a typical experiment, equimolar quantities of BCl₃ and a silylamine were combined at −78 °C in CH₂Cl₂ solution and the mixture was then allowed to warm slowly to room tem-

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(2) (a) Burg, A. B.; Kulijian, E. S. *J. Am. Chem. Soc.* **1970**, *72*, 3103. (b) Barlos, K.; Nöth, H. *Chem. Ber.* **1977**, *110*, 2790.
(3) Nöth, H.; Storch, W. *Chem. Ber.* **1976**, *109*, 884.
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(5) Neilson, R. H.; Wells, R. L. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 283.
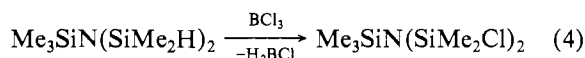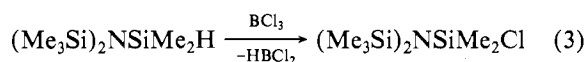
(6) Cowley, A. H.; Braun, R. W. *Inorg. Chem.* **1973**, *12*, 491.
(7) (a) Van Dyke, C. H.; MacDiarmid, A. G. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1503. (b) Vanderwielen, A. J.; Ring, M. A. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 421.

Table I. Proton and ^{13}C NMR Data for Silylamines[a]

		X = H		X = Cl	
compd	signal	δ(^{1}H), J^b	δ(^{13}C)	δ(^{1}H)	δ(^{13}C)
t-Bu(Me$_3$Si)NSiMe$_2$X	Me$_3$Si	0.27	6.26	0.40	7.31
	Me$_2$Si	0.30	3.49	0.70	10.97
	Me_3C	1.35	34.22	1.47	34.56
	SiH	4.62, 3.6			
	Me$_3$C		54.66		56.00
t-BuN(SiMe$_2$X)$_2$	Me$_2$Si	0.25	2.48	0.78	10.72
	Me_3C	1.31	33.34	1.55	34.20
	SiH	4.57, 3.2			
	Me$_3$C		54.09		57.30
(Me$_3$Si)$_2$NSiMe$_2$X	Me$_3$Si	0.27	4.39	0.32	5.57
	Me$_2$Si	0.30	2.28	0.63	8.82
	SiH	4.67, 3.4			
Me$_3$SiN(SiMe$_2$X)$_2$	Me$_3$Si	0.31	3.24	0.32	5.24
	Me$_2$Si	0.37	1.62	0.60	8.49
	SiH	4.70, 3.4			
Me(Me$_3$Si)NSiMe$_2$X	Me$_3$Si	0.21	0.53		
	Me$_2$Si	0.25	−1.10		
	MeN	2.54	30.21		
	SiH	4.48, 3.0			
t-BuN(H)SiMe$_2$X	Me$_2$Si	0.17	0.53		
	Me_3C	1.20	33.51		
	SiH	4.57, 2.8			
	Me$_3$C		49.42		

[a] Chemical shifts in ppm downfield from external Me$_4$Si. Solvents: ^{1}H, CH$_2$Cl$_2$; ^{13}C, CDCl$_3$. [b] Coupling constants (J) in Hz for HSiCH moiety.

perature. In the case of trisilylamines containing one or two Si–H bonds (eq 3 and 4), this procedure afforded excellent

$$(Me_3Si)_2NSiMe_2H \xrightarrow[-HBCl_2]{BCl_3} (Me_3Si)_2NSiMe_2Cl \quad (3)$$

$$Me_3SiN(SiMe_2H)_2 \xrightarrow[-H_2BCl]{BCl_3} Me_3SiN(SiMe_2Cl)_2 \quad (4)$$

yields of the corresponding chloro-substituted silylamines. Under these relatively mild reaction conditions, no Si–N cleavage products were observed.
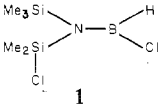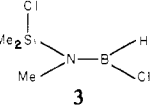
The (chlorosilyl)amines, which have been previously prepared by other methods,[8-10] were characterized by ^{1}H and ^{13}C NMR spectroscopy (Table I). The volatile byproducts, represented simply as HBCl$_2$ and H$_2$BCl, were shown by IR spectral data[11] to consist of mixtures of the disproportionation products B$_2$H$_6$ and BCl$_3$.

Much more surprising results were obtained when a similar reaction (eq 5) was carried out with a disilylamine containing

$$(5)$$
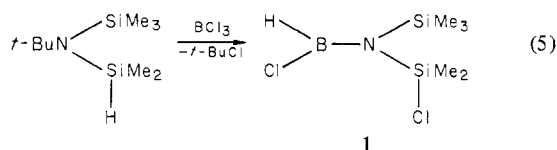
a *tert*-butyl substituent on nitrogen. Under the same conditions as described above, *carbon–nitrogen bond cleavage occurred in addition to hydrogen–chlorine exchange at silicon*. The solvent fraction was shown to contain *tert*-butyl chloride by its ^{1}H NMR spectrum. The boron-containing product, a very air-sensitive liquid, was isolated in 84% yield by distillation and was subsequently identified as chloro[(chlorodimethylsilyl)(trimethylsilyl)amino]borane (**1**). The composition and structure of this novel (silylamino)borane are confirmed by the following evidence: (1) elemental analysis indicates two chlorines per molecule, (2) ^{1}H and ^{13}C NMR spectra (Table

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(9) Breed, L. W.; Elliott, R. L. *J. Organomet. Chem.* **1968**, *11*, 447.
(10) Bush, R. P.; Lloyd, N. C.; Pearce, C. A. *J. Chem. Soc. A* **1969**, 253.
(11) Kerrigan, J. V. *Inorg. Chem.* **1964**, *3*, 908.

Table II. NMR and IR Spectral Data for (Silylamino)boranes

		NMR[a]		
compd	signal	δ-(^{1}H)	δ-(^{13}C)	IR,[b] cm^{-1}
1	Me$_3$Si	0.40	3.66	3140, 3050, 2970, 2805, 2590, 2540, 1400, 1280, 1140, 1060, 1010, 900, 850, 760, 680, 630
	Me$_2$Si	0.70	6.87	
(Me$_2$Si)$_2$NBH$_2$ **2**	Me$_2$Si	0.70	6.82	3140, 3050, 2965, 2595, 2550, 2480, 1400, 1370, 1255, 1190, 1140, 1065, 940, 905, 820, 685, 660
3	Me$_2$Si	0.68	2.44	2980, 2940, 2880, 2590, 2540, 2490, 1350, 1270, 1260, 1140, 1080, 1030, 975, 850, 765, 750, 700
	MeN	2.91	30.98	

[a] See footnote *a*, Table I. [b] Neat liquids for **1** and **2** and gas phase for **3**.

II) both show the presence of Me$_3$Si and Me$_2$SiCl substituents, (3) the ^{11}B NMR consists of a doublet (δ 40.5, J_{B-H} = 169 Hz), and (4) the IR spectrum (Table II) contains B–H stretching bands at 2540 and 2590 cm^{-1}.

Like those of other (silylamino)boranes including (Me$_3$Si)$_2$NBH$_2$,[12,13] the low-field ^{11}B chemical shift of **1** is indicative of a monomeric rather than dimeric aminoborane. This result is most probably due to the steric bulk of the silyl groups on nitrogen since sterically hindered (dialkylamino)boranes have been shown to be predominantly monomeric.[14] The possibility of restricted B–N bond rotation and cis–trans isomerism in compound **1** was also considered. The ambient temperature NMR data, however, give no indication of a high rotational barrier (ca. 18 kcal/mol) as is usually observed in simple aminoboranes.[15]

The cleavage of the carbon–nitrogen bond according to eq 5 is indeed a most unexpected result. Nonetheless, it is quite reproducible as long as the conditions described above are used. If the conditions are varied, the reaction takes a different course and the results of such experiments shed some light on the possible pathway by which **1** is formed. It appears that the first step of the reaction is simply hydrogen–chlorine exchange at silicon (eq 6). This is, in fact, what was observed

$$(6)$$
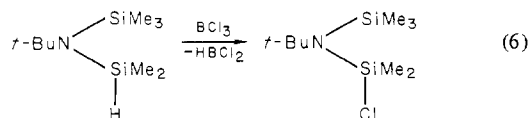
when the reaction was done without a solvent. The chlorosubstituted disilylamine was obtained in 78% yield, and no C–N bond cleavage was observed. The silylamine was characterized by elemental analysis and NMR spectroscopy (Table I). Similar results were obtained in ether solution except that the dichloroborane was trapped as the adduct Et$_2$O·HBCl$_2$. Even in CH$_2$Cl$_2$ solution the reaction occurs mainly according to eq 6 if the mixture is allowed to warm quickly (ca. 5 min) from −78 °C to ambient temperature. A longer warm-up period (ca. 3 h) is required to obtain C–N bond rupture and formation of the aminoborane **1**. These results suggest the key feature in the synthesis of **1** is to keep

(12) Wisian-Neilson, P.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1545.
(13) Nutt, W. R. Ph.D. Dissertation, Duke University, Durham, N.C., 1971.
(14) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1967**, *100*, 3353.
(15) See for example: (a) Dewar, M; Rona, P. *J. Am. Chem. Soc.* **1969**, *91*, 2259. (b) Imbrey, D.; Jaeschke, A.; Friebolin, H. *Org. Magn. Reson.* **1970**, *2*, 271. (c) Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.

the initially formed dichloroborane HBCl₂ in solution so that it may bring about further reaction.

The related disilylamine *t*-BuN(SiHMe₂)₂ reacted similarly, but more slowly, with BCl₃. Under conditions appropriate to the preparation of **1**, only H/Cl exchange (eq 7) was observed.
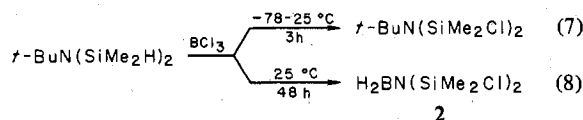
If the reaction mixture was allowed to stir for a longer period at room temperature in a sealed tube to prevent H₂BCl from escaping, then the product isolated in 80% yield was the symmetrical (silylamino)borane **2** (eq 8).

Steric crowding in the starting silylamine appears to be an important factor in determining whether C–N bond cleavage will occur in these systems. Treatment of the *N*-methyl-substituted disilylamine with BCl₃ (eq 9) gave a new (silyl-amino)borane (**3**) which resulted from Si–N rather than C–N bond cleavage.
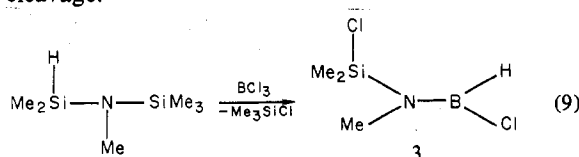
Interestingly, since **3** was obtained in 90% yield, the Si–N cleavage must occur almost exclusively at the Me₃Si–N bond. Reaction at the other Si–N bond (ClMe₂Si–N) might also have been expected since Barlos and Nöth[2] have prepared the related (silylamino)borane Me(ClMe₂Si)NBCl₂ via the reaction of BCl₃ with the symmetrical silylamine (Me₂SiCl)₂NMe. The high selectivity of cleavage reactions such as eq 9 could have synthetic utility in other systems.

Unlike compound **1** which was routinely prepared and purified without difficulty, the (silylamino)boranes **2** and **3** could not be completely freed of small amounts of unidentified impurities. Satisfactory elemental analyses could not be obtained for these compounds, but the spectroscopic data (Table II) leave little doubt concerning their structural assignments. Their purity is most probably high enough for further synthetic studies.

In summary, therefore, we have observed three types of reactivity between trichloroborane and hydride-containing silylamines: (1) facile chlorination of the Si–H bonds in all cases, (2) silicon–nitrogen bond cleavage in only one instance (eq 9), and (3) quite unexpectedly, carbon–nitrogen bond cleavage in the systems where a *tert*-butyl group was present on nitrogen. This latter process is viewed as being a new synthetic route to difunctional (silylamino)boranes such as **1** which should have a rich derivative chemistry.

Experimental Section

Materials and General Procedures. Trichloroborane and the organosilicon reagents (Me₃SiCl, Me₂SiHCl, and (Me₃Si)₂NH) were obtained commercially and used without further purification. The *tert*-butylsilylamines *t*-BuN(H)SiMe₂R (R = Me, H) were prepared by the addition of the appropriate chlorosilane ClSiMe₂R to an excess of *tert*-butylamine in pentane. A similar procedure was used to prepare Me(Me₃Si)NH from Me₃SiCl and MeNH₂. Dichloromethane was distilled from P₂O₅ and stored over molecular sieves. Proton, ¹³C, and ¹¹B NMR spectra were recorded on JEOL MH-100, JEOL FX-60, and Varian HA-100 spectrometers, respectively. Infrared spectra were obtained on Perkin-Elmer 297 or Beckman 4250 spectrophotometers. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are typical of those used for the preparation of the silylamine reagents and for their reactions with BCl₃.

Preparation of *t*-Bu(Me₃Si)NSiMe₂H. A solution of *t*-Bu-(Me₃Si)NLi was first prepared by addition of *n*-BuLi (110 mmol, 50 mL of 2.2 M hexane solution) to a stirred solution of *t*-Bu-(Me₃Si)NH (100 mmol, 19.2 mL) in Et₂O (200 mL) at 0 °C. The mixture was then allowed to warm to room temperature and was stirred for ca. 30 min. After the *t*-Bu(Me₃Si)NLi solution was recooled to 0 °C, Me₂SiHCl (110 mmol, 12.2 mL) was added from a syringe. A white precipitate formed as the mixture was warmed to room temperature. After the solution was stirred for 2 h, the mixture was filtered and solvents were removed under vacuum. Distillation afforded *t*-Bu(Me₃Si)NSiMe₂H as a colorless liquid (16.5 g, 81% yield, bp 71–73 °C (12 torr)). Anal. Calcd: C, 53.10; H, 12.38. Found: C, 52.93; H, 12.31.

Preparation of Me(Me₃Si)NSiMe₂H. In a similar manner, Me-(Me₃Si)NLi was treated with Me₂SiHCl to afford Me(Me₃Si)-NSiMe₂H as a colorless liquid (93% yield, bp 128–129 °C). Anal. Calcd: C, 44.65; H, 11.87. Found: C, 44.50; H, 11.71.

Preparation of *t*-BuN(SiMe₂H)₂. In a similar manner, *t*-Bu-(Me₂SiH)NLi was treated with Me₂SiHCl to afford *t*-BuN(SiMe₂H)₂ as a colorless liquid (63% yield, bp 48–50 °C (8 torr)). Anal. Calcd: C, 50.70; H, 12.23. Found: C, 50.42; H, 12.28.

Preparation of *t*-Bu(Me₃Si)NSiMe₂Cl. With a standard vacuum system, BCl₃ (21 mmol) was condensed into a flask containing *t*-Bu(Me₃Si)NSiMe₂H (4.023 g, 20.6 mmol) at –78 °C. The flask was then allowed to warm slowly, and, as the contents melted and began to stir, a rapid reaction occurred and a gas was evolved. The volatile material was transferred to a trap at –196 °C and identified as a mixture of B₂H₆ and BCl₃ by an IR spectrum.[11] The remaining liquid was distilled to afford *t*-Bu(Me₃Si)NSiMe₂Cl as a colorless liquid (3.385 g, 78% yield; bp 66–67 °C (2.5 torr)) which solidified on standing. Anal. Calcd: C, 45.55; H, 10.17; Cl, 14.90. Found: C, 45.79; H, 10.33; Cl, 14.69.

When the same reaction was carried out in Et₂O solution, the products were shown by ¹H NMR spectroscopy to be an equimolar mixture of *t*-Bu(Me₃Si)NSiMe₂Cl and HBCl₂·OEt₂. These products could not be separated by fractional distillation.

Preparation of *t*-BuN(SiMe₂Cl)₂. Trichloroborane (18.1 mmol) was condensed slowly (over ca. 15 min) into a stirred solution of *t*-BuN(SiMe₂H)₂ (3.397 g, 17.9 mmol) in CH₂Cl₂ (10 mL) at –78 °C. A white solid was observed at –78 °C, but this disappeared as the mixture was warmed slowly to room temperature (over ca. 1.5 h). The solvent and other volatile components were removed under vacuum, leaving a liquid residue from which *t*-BuN(SiMe₂Cl)₂ was distilled as a colorless liquid (3.44 g, 74% yield, bp 65–66 °C (0.7 torr)). Anal. Calcd: C, 37.18; H, 8.19; Cl, 27.44. Found: C, 36.98; H, 8.21; Cl, 27.36.

Preparation of (Me₃Si)(Me₂SiCl)NB(Cl)H (1). Trichloroborane (15.0 mmol) was condensed slowly (over ca. 15 min) into a stirred solution of *t*-Bu(Me₃Si)NSiMe₂H (2.95 g, 14.5 mmol) in CH₂Cl₂ (10 mL) at –78 °C. A white solid, which formed initially, disappeared as the mixture was warmed slowly to room temperature (over ca. 3 h). The volatile components were removed under vacuum and shown by ¹H NMR to consist of CH₂Cl₂ and *t*-BuCl. Distillation of the residual liquid gave the (silylamino)borane **1** as a colorless liquid (2.77 g, 84% yield, bp 54–55 °C (5 torr)). Anal. Calcd: C, 26.33; H, 7.07; Cl, 31.09. Found: C, 26.51; H, 7.03; Cl, 30.99. The ¹¹B NMR spectrum (CH₂Cl₂ solution) consisted of a doublet (J_{BH} = 169 Hz) at 40.5 ppm downfield from external BF₃·OEt₂.

Preparation of (Me₂SiCl)₂NBH₂ (2). In a 175-mL glass tube equipped with a Teflon stopcock, BCl₃ (22 mmol) was condensed slowly into a stirred solution of *t*-BuN(SiMe₂H)₂ (4.07 g, 21.5 mmol) in CH₂Cl₂ (15 mL) at –78 °C. The stopcock was closed, and the mixture was warmed slowly to room temperature (over ca. 3h) and was then stirred for 45 h. The volatile components were removed under vacuum and identified as CH₂Cl₂ and *t*-BuCl by ¹H NMR. Distillation then afforded the (silylamino)borane **2** as a colorless liquid (3.67 g, 80% yield, bp 47–52 °C (2.4 torr)). A redistillation did not remove small amounts (ca. 5% by ¹H NMR) of impurities, and a satisfactory elemental analysis was not obtained.

Preparation of Me(Me₂SiCl)NB(Cl)H (3). In a procedure similar to that described for the preparation of **1**, BCl₃ (28 mmol) was allowed to react with Me(Me₃Si)NSiMe₂H (4.50 g, 27.9 mmol). Trimethylchlorosilane was identified in the solvent fraction by ¹H NMR. The less volatile components were distilled through U-traps cooled to –45 °C and –196 °C. The –45 °C trap retained the (silyl-amino)borane **3** as a colorless liquid (4.28 g, 90% yield). Repeated

fractional condensation did not completely separate **3** from small amounts (ca. 10% by ^{1}H NMR) of unidentified impurities.

Acknowledgment. The author thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for generous financial support. The ^{11}B NMR spectrum was recorded by Dr. Christopher Foret of the University of Texas at Arlington.

Contribution from the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, and the Department of Chemistry, Depauw University, Greencastle, Indiana 46135

Fluorosilicate Equilibria in Sodium Chloride Solutions from 0 to 60 °C[†]

R. H. BUSEY,[1a] EUGENE SCHWARTZ,[1b] and R. E. MESMER*[1a]

A potentiometric method employing quinhydrone and solid-state fluoride electrodes was used to observe the free hydrogen ion and the free fluoride ion concentrations in equilibrium experiments in aqueous solutions at 0–60 °C. In dilute silicic acid solutions the predominant reaction can be expressed as Si(OH)$_4$(aq) + 4H$^+$ + 6F$^-$ $\rightleftharpoons$ SiF$_6^{2-}$ + 4H$_2$O. The logarithm of the equilibrium quotient has values of 31.610, 29.980, and 28.23 at 0, 25, and 60 °C in 1 *m* NaCl (molal units). There is evidence for the existence of small amounts of additional species with fewer fluorides under certain conditions. The absence of a regular sequence of species from the array Si(OH)$_{4-x}$F$_y^{x-y}$ is proven by an analysis of the results. The average number of fluoride ions complexed by millimolal silicic acid approaches 6.0 in 0.01 *m* fluoride as the pH is reduced to 3 or lower in titration experiments. Simultaneously the average number of hydrogen ions consumed approaches 4.0.

Introduction

There is considerable interest in the detailed chemistry of dilute solutions that occur naturally and in practical processes. The fluoride concentrations in geothermal brines are commonly found in the range 10^{-3}–10^{-4} *m*.[2a] The interactions that occur between fluoride ion and silicic acid in dilute solutions are poorly understood. The only species in aqueous solution whose identity is well-known[2b] from Raman and NMR spectroscopy is SiF$_6^{2-}$, an octahedral ion. Also, a common means for preparation of salts of hexafluorosilicic acid is by precipitation from aqueous solution. However, there are no definitive equilibrium data involving this species with other dissolved species of silica.

There are indeed a large number of conceivable species of the type Si(OH)$_{4-x}$F$_y^{x-y}$ which might occur and must be considered if a complete description of even dilute solutions is to be made. For the analogous system[3-5] B–F, a sequence of species has been observed including BF$_4^-$, BF$_3$OH$^-$, BF$_2$-(OH)$_2^-$, and probably BF(OH)$_3^-$ in dilute solutions, all of which involve replacement of a hydroxide ion from tetrahedral B(OH)$_4^-$. There have been several reports[6-11] describing equilibria of SiF$_6^{2-}$ with other fluorosilicates or with Si(OH)$_4$, but none of these studies present conclusive data. Silica can be dissolved in relatively concentrated H$_2$SiF$_6$ solutions to attain SiO$_2$ concentrations well beyond the solubility of amorphous silica, indicating the formation of additional species. Several authors[11,12] have suggested the presence of species such as SiF$_5^-$ and SiF$_4$(aq) to account for such observations. In this paper we have employed precision potentiometric methods for the examination of the complexing behavior in dilute (0.001 *m*) silicic acid solutions in 1 *m* NaCl.

Experimental Section

Materials. A stock solution of about 5.2 *m* NaCl prepared from Fisher Scientific Co. analyzed reagent was purified by acidifying with hydrochloric acid to pH 3.5 and sparging with H$_2$ to remove CO$_2$.

After sparging, the solution was again neutralized with a small amount of carbonate-free NaOH solution.

A stock solution of 0.25 *m* NaF and 0.75 *m* NaCl was prepared from recrystallized NaF (J. T. Baker Chemical Co.) and the above NaCl stock solution. The recrystallized NaF was dried at 150 °C.

Stock solutions of 1 *m* NaOH, 1 *m* HCl, and approximately 0.5 *m* Si(IV), the same solutions employed and described in our silicic acid equilibrium studies,[13] were employed together with the two above stock solutions to prepare the required cell solutions, reference solutions, and titrant solution. Quinhydrone (Eastman Kodak Co.) was added as a solid to the cell-solution aliquot and reference-solution aliquot when these solutions were introduced into the electrode compartments of the cell, giving a concentration of approximately 0.003 *m*. The silicic acid concentration used in these experiments was about 0.001 *m*, which is believed to be below the saturation level for amorphous silica in these experiments. Should the solubility be exceeded by a small amount in the pH range of these experiments, it is well-known[14] that polymerization of the Si(OH)$_4$ is very slow under these conditions.

Potentiometric Cells. The potentiometric-cell assembly was similar to that described previously for the study of fluoride complexes of beryllium.[15] However, for most of this work quinhydrone electrodes were used in place of hydrogen electrodes. The cell consisted of an

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