remaining volatile components were distilled through a U-trap at −45 °C. The contents of the trap were then fractionally distilled to afford **1b** as a colorless liquid (13.17 g, 55% yield, bp 29–30 °C (7 Torr)). The ^1H NMR (δ 0.12, singlet; δ 0.38, doublet, J_{PH} = 0.8 Hz), ^{19}F NMR (+71.7 ppm, doublet, J_{PF} = 965 Hz), and infrared spectral data are in excellent agreement with results reported[4] previously for (bis(trimethylsilyl)amino)difluorophosphine oxide (**1a**). Anal. Calcd for $C_6H_{18}F_2NOPSi_2$: C, 29.37; H, 7.39. Found: C, 29.55; H, 7.69.

***P,P*-Dichloro-*P*-trimethylsiloxy-*N*-trimethylsilylphosphinimine (2).** Using the procedure described by Glemser,[4] the reaction of $P(O)Cl_3$ with $LiN(SiMe_3)_2$ afforded compound **2** as a colorless liquid (50% yield, bp 28–29 °C (0.1 Torr)) identified by its ^1H NMR and infrared spectra.[4]

***P,P*-Diphenyl-*P*-trimethylsiloxy-*N*-trimethylsilylphosphinimine (3).** Diphenylphosphoryl chloride (18.5 mL, 100 mmol) was added slowly to a stirred solution of $LiN(SiMe_3)_2$ (100 mmol) in ether (125 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for ca. 20 min. After filtration and solvent removal, distillation afforded **3** as a low-melting white solid (18.8 g, 52% yield, bp 103–104 °C (0.01 Torr), mp 37–39 °C). Infrared spectrum (KBr disk): 3100 (s), 2950 (m), 2900 (w), 1430 (m), 1290 (s), 1240 (s), 1180 (s), 1120 (m), 1100 (m), 950 (s), 850 (vs), 740 (m), 720 (m), 690 (s) cm^{-1}. The ^1H NMR spectrum (20% CH_2Cl_2 solution) consisted of two Me_3Si singlets (δ −0.02 and 0.21) and a phenyl multiplet centered at δ 7.5. Anal. Calcd for $C_{18}H_{28}NOPSi_2$: C, 59.79; H, 7.81. Found: C, 60.03; H, 7.53.

Attempted Preparation of *P,P*-Dimethyl-*P*-trimethylsiloxy-*N*-trimethylsilylphosphinimine (4). A solution of $Me_2P(O)Cl$ (13.9 g, 124 mmol) in benzene (60 mL) was added to a stirred solution of $LiN(SiMe_3)_2$ (124 mmol) in ether (200 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for ca. 30 min. Solid products (slightly yellow) were removed by filtration and washed with hexane. Distillation of the filtrate gave only solvents and $(Me_3Si)_2NH$ (15 g, 75% yield) which was identified by comparison of its IR and ^1H NMR spectra to those of an authentic sample. Elemental analysis (C, 21.87; H, 5.74; P, 19.08) of the solid indicates that it contains phosphorus product(s), the nature of which is still under investigation.

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Registry No. **1b**, 66416-57-7; **2**, 41309-94-8; **3**, 66416-58-8; Me_3SiNPF_2Ph, 61701-83-5; $LiN(SiMe_3)_2$, 4039-32-1; $ClP(O)F_2$, 13769-75-0; $ClP(O)Ph_2$, 1499-21-4; ^{13}C, 14762-74-4.

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Contribution from the Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Preparation and Thermal Decomposition Reactions of Some *tert*-Butyldimethylsilyl-Substituted Aminoboranes[1]

JAMES R. BOWSER, ROBERT H. NEILSON, and RICHARD L. WELLS*

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A number of (silylamino)boranes containing the bulky *tert*-butyldimethylsilyl group have been prepared by the reaction of the lithiated silylamines *t*-$BuMe_2SiN(R)Li$ (R = H, Me, $SiMe_3$) with various chloroboranes. The products are colorless liquids which in many cases decompose at or above room temperature to form borazines. The thermal stabilities of those compounds where R = Me_3Si is high presumably because of the steric "protection" afforded the boron atom toward nucleophilic attack.

Introduction

Although a large number of acyclic (silylamino)boranes have been synthesized since the initial report by Burg and Kulijian in 1950,[2] the vast majority have contained only methyl groups bonded to silicon. Thus, aside from a few compounds containing silyl,[2,3] triethylsilyl,[4,5] triphenylsilyl,[4] and various halogenated silyl groups,[6,7] relatively little is known about compounds containing the linkage $R_1(R_2)(R_3)Si–N–B$ (R_1, R_2, or $R_3 \neq$ Me).

Since a report by Corey[8] the *tert*-butyldimethylsilyl moiety has come into common use in organic synthesis as a "blocking group" for many alcohols and amines for which the trimethylsilyl group does not provide sufficient protection. The ability of this substituent to lower chemical reactivity is evidenced by the fact that the primary aminosilane *t*-$BuMe_2SiNH_2$ can be isolated at room temperature. This is in contrast to several less hindered primary and secondary aminosilanes (eq 1).[9]

$$2R_3SiN(H)R' \xrightarrow[<25\ ^\circ C]{-NH_2R'} (R_3Si)_2NR' \qquad (1)$$

R = H; R′ = H, Me
R = Me; R′ = H

The presence of large substituents in aminoboranes has occasionally led to the isolation of relatively rare four-[10–14] and eight-membered[15–17] ring systems instead of the more common borazine structure. For example, the thermal decomposition of [*tert*-butyl(trimethylsilyl)amino]dichloroborane resulted in

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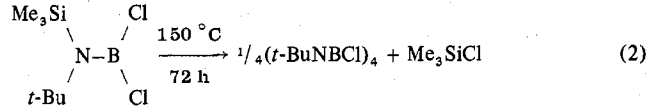
Table I. Boiling Point, Mass Spectral,[a] and ^{1}H NMR Data[b] for (*tert*-Butyldimethylsilyl)amines and Their Boryl Derivatives

No.	Compound	Bp, °C (Torr)	Mass spectrum Calcd	Mass spectrum Found	δ(Me_2Si)	δ(*t*-Bu)	δ(R)	δ(NMe_2)	δ(NH_2)	δ(Ph)
1	*t*-BuMe_2SiNH_2	75 (200)	131.1130	131.1128	0.00	0.80	*c*			
2	*t*-BuMe_2SiN(H)Me	87 (180)	145.1287	145.1284	−0.02	0.85	2.48[d]		(NH)[c]	
3	*t*-BuMe_2SiN(H)SiMe_3	43 (4.0)	203.1526	203.1529	0.00	0.84	0.05		(NH)[c]	
4	*t*-BuMe_2SiN(H)B$(NMe_2)_2$	59 (0.01)	229.2146	229.2148	−0.03	0.83	*c*	2.52		
5	*t*-BuMe_2SiN(H)B(NMe_2)Ph	68 (0.01)	262.2037	262.2033	−0.28	0.92	*c*	2.67		7.30
6	*t*-BuMe_2SiN(H)B(NMe_2)Cl	49 (0.05)	229.2146[e]	229.2144	0.07	0.84	*c*	2.66		
7	*t*-BuMe_2SiN(H)B(Ph)Cl	85 (0.20)[f]		*g*	0.30	0.98	4.34			7.58
8	*t*-BuMe_2SiN(H)BCl_2	35 (0.90)[f]		*g*	0.23	0.93	3.95			
9	*t*-BuMe_2SiN(Me)B$(NMe_2)_2$	56 (0.01)	243.2302	243.2304	−0.02	0.96	2.53	2.61		
10	*t*-BuMe_2SiN(Me)B(NMe_2)Ph	81 (0.01)	276.2193	276.2192	−0.22	0.90	2.71	2.71		7.17
11	*t*-BuMe_2SiN(Me)B(NMe_2)Cl	60 (0.60)	243.2302[e]	243.2306	0.12	0.94	2.65	2.77		
12	*t*-BuMe_2SiN(Me)B(Ph)Cl	79 (0.01)	252.1147[h]	252.1149	0.16	0.99	2.91			7.30
13	*t*-BuMe_2SiN(Me)BCl_2	59 (1.0)		*g*	0.34	0.96	2.89			
14	*t*-BuMe_2SiN(H)B$(NMe_2)NH_2$	*g*		*g*	0.06	0.90	2.30	2.53	1.27	
15	*t*-BuMe_2SiN(H)B(Ph)NH_2	88 (0.01)		*g*	0.15	0.95	2.38		2.77	7.36
16	*t*-BuMe_2SiN(Me)B$(NMe_2)NH_2$	*g*		*g*	0.12	0.98	2.65	2.63	2.28	
17	*t*-BuMe_2SiN(Me)B(Ph)NH_2	84 (0.01)	247.1802[i]	247.1804	0.00	0.89	2.58		1.24	
18	*t*-BuMe_2SiN($SiMe_3$)B$(NMe_2)_2$	72 (0.04)	286.2306[h]	286.2301	0.08	0.90	0.08	2.66		
19	*t*-BuMe_2SiN($SiMe_3$)B(NMe_2)Ph	91 (0.01)	334.2432	334.2433	0.11	0.79	0.22	2.82[d]		7.25
20	*t*-BuMe_2SiN($SiMe_3$)B(NMe_2)Cl	59 (0.10)	277.1494[h]	277.1495	0.02	0.86	0.08	2.84[d]		
21	*t*-BuMe_2SiN($SiMe_3$)B(Ph)Cl	92 (0.01)	325.1620	325.1617	0.29	0.92	0.16			7.62
22	*t*-BuMe_2SiN($SiMe_3$)BCl_2	50 (0.05)	283.0917	283.0918	0.32	0.99	0.36			
23	*t*-BuMe_2SiN($SiMe_3$)B$(NMe_2)NH_2$	62 (0.03)	258.1993[h]	258.1989	0.00	0.87	0.07	2.55	2.04	
24	*t*-BuMe_2SiN($SiMe_3$)B(Ph)NH_2	92 (0.02)	306.2119	306.2120	0.00	0.89	0.09		3.64[d]	7.36
25	[*t*-BuMe_2SiN(H)]$_2$BPh	102 (0.01)	333.2354[h]	333.2357	−0.06	0.90	2.33			7.23
26	[*t*-BuMe_2SiN(H)]$_3$B	133 (0.01)	386.3014[h]	386.3010	0.06	0.88	1.34			
27	[*t*-BuMe_2SiN(H)B–N(H)]$_3$		411.3058[j]	411.3056	0.17	0.94	2.15		2.88 (NH)	
28	[*t*-BuMe_2SiN(Me)B–N(H)]$_3$		510.4232	510.4238	0.21	0.93	2.59		3.36 (NH)	

[a] *m/e* values for molecular ions (except where noted) containing the most abundant isotopes of all atoms. [b] Samples run in 20% (v/v) solutions of CCl_4; values in ppm relative to Me_4Si 0.00, negative values upfield from Me_4Si. [c] None observed. [d] Doublet. [e] Rearrangement (see text). [f] Decomposition observed during distillation. [g] None due to low thermal stability. [h] For molecular ion minus Me. [i] For molecular ion minus H. [j] For molecular ion minus *t*-Bu.

the formation of *B*-tetrachloro-*N*-tetra-*tert*-butylborazocine (eq 2).[17]



$$Me_3Si(t\text{-Bu})N{-}BCl \xrightarrow[72\ h]{150\ ^\circ C} {}^1/_4(t\text{-BuNBCl})_4 + Me_3SiCl \qquad (2)$$

As an extension of previous work in these laboratories on the decomposition of (silylamino)boranes[14,17,18] it was of interest to prepare a series of aminoboranes containing the *tert*-butyldimethylsilyl group in the hope of gaining information on the effect of sterically hindered groups on the chemical properties of (silylamino)boranes.

Experimental Section

Dichlorodimethylsilane and chlorotrimethylsilane (Peninsular Chemicals, Gainesville, Fla.) were distilled prior to use. Ammonia, methylamine, dimethylamine, and trichloroborane (Matheson Co, East Rutherford, N.J.), *n*-butyllithium and *tert*-butyllithium (Alfa Inorganics, Beverly, Mass.), and tetraphenylstannane (Eastman Organic Chemicals, Rochester, N.Y.) were used as received.

Dichloro(phenyl)borane was prepared from trichloroborane and tetraphenylstannane by the method of Jolly;[19] chlorobis(dimethylamino)borane, dichloro(dimethylamino)borane, and chloro(dimethylamino)phenylborane were prepared by redistribution reactions.[20] The preparation of *tert*-butylchlorodimethylsilane was adapted from the procedure described by Corey and Venkateswarlu.[8]

Solvents were purified by distillation from calcium hydride immediately prior to use.

High-resolution mass spectra were recorded on an MS-902 spectrometer; calculated *m/e* values were obtained from the masses of the most abundant isotopes of the element present. Proton NMR spectra were obtained on a JEOL MH-100 spectrometer. A Perkin-Elmer 137 spectrophotometer was used for IR spectra.

The boiling points, ^{1}H NMR data, and high-resolution mass spectral data obtained for all of the compounds reported here are summarized in Table I.

Amino-*tert*-butyldimethylsilane (1). A 1.0-L flask equipped with a −78 °C condenser and magnetic stirrer was thoroughly flushed with N_2. *tert*-Butylchlorodimethylsilane (54.2 g, 0.359 mol) in pentane (500 mL) was introduced into the flask and cooled to −78 °C. Excess ammonia (17.9 mL, 0.86 mol) was slowly distilled into the stirred solution. Following completion of addition and warming to room temperature, the product was filtered free of solid, stripped of solvent, and distilled at 75–79 °C (200 Torr). The colorless distillate (36.9 g, 78%) crystallized to a white solid upon cooling (mp 59–60 °C).

***tert*-Butyldimethyl(methylamino)silane (2).** In a similar procedure to that given above *tert*-butylchlorodimethylsilane (30.6 g, 0.203 mol) was allowed to react with excess methylamine (24 mL, 0.59 mol) in pentane (300 mL) at −78 °C. After stirring for 2 h at room temperature, filtration, solvent removal, and distillation gave **2** (17.7 g, 60%, bp 87 °C (180 Torr)).

(*tert*-Butyldimethylsilyl)(trimethylsilyl)amine (3). A 1.0-L flask equipped with a reflux condenser, stirring bar, and rubber septum and containing a solution of **1** (52.4 g, 0.40 mol) in hexane (400 mL) was cooled to 0 °C. *n*-Butyllithium (167 mL, 0.40 mol) was added via syringe and the resulting mixture was stirred for 30 min. Chlorotrimethylsilane (51 mL, 0.40 mol) was then added to the system. After stirring for 12 h the mixture was filtered, stripped of solvent, and distilled to yield **3** (60.6 g, 74%, bp 43 °C (4.0 Torr)).

Preparation of (Silylamino)boranes by Lithiation. A representative procedure used for the synthesis of this type of compound is given here for *tert*-butyl(dimethylsilylamino)(dimethylamino)phenylborane (**5**). A 500-mL flask equipped with a reflux condenser, stirring bar, and rubber septum was thoroughly flushed with N_2. Compound **1** (5.37 g, 0.041 mol) in hexane (170 mL) was poured into the flask followed by addition of *n*-butyllithium (0.041 mol) via syringe. After stirring for 30 min the system was cooled to −78 °C and chloro(dimethylamino)phenylborane (6.5 mL, 0.041 mol) added via syringe. Upon warming to room temperature and stirring for 4 h the product was filtered free of solid and the solvent was removed under reduced pressure. Vacuum distillation then yielded **5** (8.50 g, 79%, bp 69–71 °C (0.01 Torr)).

Aminolysis of (Silylamino)chloroboranes. A representative procedure for this type of reaction is given here for amino(*tert*-butyl-

Table II. Pyrolysis Conditions and Products for *tert*-Butyldimethylsilyl-Substituted Aminoboranes

No.	Temp, °C	Time, h	Products
4	185	46	*a*
5	205	27	*a*
6	150	12	**4** + *t*-$BuMe_2SiCl$ + $(HNBCl)_3$
7	85	4	*t*-$BuMe_2SiCl$ + $(HNBPh)_3$
8	25	96	*t*-$BuMe_2SiCl$ + $(HNBCl)_3$
9	190	72	*a*
10	190	25	*a*
11	140	15	**9** + *t*-$BuMe_2SiCl$ + $(MeNBCl)_3$
12	150	7	*t*-$BuMe_2SiCl$ + $(MeNBPh)_3$
13	140	12	*t*-$BuMe_2SiCl$ + $(MeNBCl)_3$
14	25	72	$[t\text{-}BuMe_2SiN(H)B\text{–}N(H)]_3$ + Me_2NH
15	125	11	**1** + $(HNBPh)_3$
16	25	72	$[t\text{-}BuMe_2SiN(Me)B\text{–}N(H)]_3$ + Me_2NH
17	190	10	**2** + $(HNBPh)_3$
18	210	35	*a*
19	205	36	*a*
20	195	22	*a*
21	190	16	*a*
22	200	10	*a*
23	200	30	*a*
24	220	24	*a*
25	250	11	*a*
26	240	18	*a*

[a] No decomposition observed under the conditions stated.

dimethylsilyl(methyl)amino)phenylborane (**17**). A stirred solution of compound **12** (6.22 g, 0.023 mol) in hexane (150 mL) was allowed to react with excess ammonia (2.0 mL, 0.096 mol) at −78 °C. After warming to room temperature, filtration and solvent removal were performed, followed by distillation to give **17** (2.57 g, 45%, bp 84–85 °C (0.01 Torr)).

Thermal Decomposition Experiments. Neat samples (generally 4–8 g) of compounds **4**–**26** were heated in an inert atmosphere, the temperature being slowly increased until evidence of reaction (evolution of gas or formation of solid material) was observed. Generally no effort was made to force decomposition by heating beyond 200 °C. The experimental times and temperatures are summarized in Table II.

Results and Discussion

Synthesis. The reaction of *tert*-butylchlorodimethylsilane with ammonia and methylamine has been used to prepare the aminosilanes **1** and **2** (eq 3).

$$t\text{-}BuMe_2SiCl + 2RNH_2 \xrightarrow[-78\ ^\circ C]{-RNH_3Cl} t\text{-}BuMe_2SiN(H)R \quad (3)$$

1, R = H
2, R = Me

Compound **1**, like its chlorosilane precursor, is a crystalline solid while **2** is colorless liquid at room temperature. Neither aminosilane exhibits any tendency to undergo condensation below 100 °C.

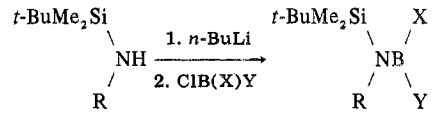
The treatment of **1** with *n*-butyllithium followed by reaction with chlorotrimethylsilane results in the formation of the unsymmetrical disilylamine **3** in ~75% yield (eq 4).

$$t\text{-}BuMe_2SiNH_2 \xrightarrow[2.\ ClSiMe_3]{1.\ n\text{-}BuLi} t\text{-}BuMe_2SiN(H)SiMe_3 \quad (4)$$

3

In a similar procedure the lithiated derivatives of **1** and **2** have been treated with a series of chloroboranes to prepare the new compounds **4**–**13** (eq 5) in good yields (typically >60%).

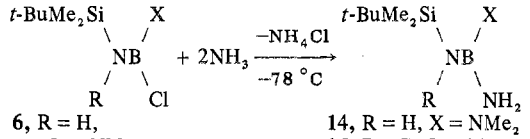
In contrast to certain similar compounds containing the trimethylsilyl group,[18,21] **4**–**13** are stable to distillation at moderate temperatures under reduced pressure (Table I).



(5)

1, R = H
2, R = Me
4, R = H, X = Y = NMe_2
5, R = H, X = NMe_2, Y = Ph
6, R = H, X = NMe_2, Y = Cl
7, R = H, X = Ph, Y = Cl
8, R = H, X = Y = Cl
9, R = Me, X = Y = NMe_2
10, R = Me, X = NMe_2, Y = Ph
11, R = Me, X = NMe_2, Y = Cl
12, R = Me, X = Ph, Y = Cl
13, R = Me, X = Y = Cl

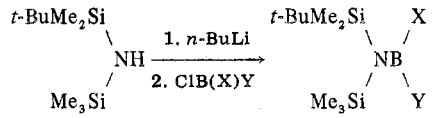
The treatment of **6**, **7**, **11**, and **12** with excess ammonia resulted in the formation of the primary aminoboranes **14**–**17** (eq 6).



(6)

6, R = H, X = NMe_2
7, R = H, X = Ph
11, R = Me, X = NMe_2
12, R = Me, X = Ph
14, R = H, X = NMe_2
15, R = H, X = Ph
16, R = Me, X = NMe_2
17, R = Me, X = Ph

Although it was possible to prepare the lithium salt of **3**, this intermediate was considerably less reactive than its R = H and R = Me analogues. Thus the two (disilylamino)boranes **18** and **19** could not be prepared according to eq 7 and al-



(7)

18, X = Y = NMe_2
19, X = NMe_2, Y = Ph
20, X = NMe_2, Y = Cl
21, X = Ph, Y = Cl
22, X = Y = Cl

though compounds **20**–**22** were formed, the reactions proceeded to completion only after stirring for relatively long periods (5–15 h) at room temperature.

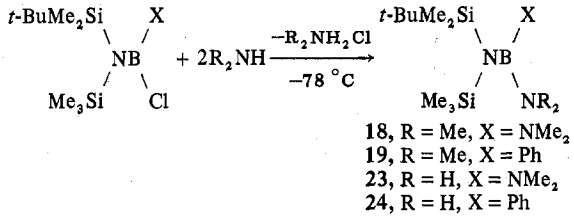
Even after refluxing hexane solutions overnight in attempts to prepare **18** and **19**, only a small quantity of lithium chloride was precipitated. Moreover, distillation of the product mixture gave, surprisingly, the unreacted lithium salt, which crystallized to a moisture-sensitive white solid. The observed boiling point (110 °C (0.01 Torr)) of this silylamide is somewhat higher than the literature value for the structurally similar lithium bis(trimethylsilyl)amide (80–84 °C (0.01 Torr)).[22]

The relatively low reactivity of this intermediate can be attributed to a combination of steric and electronic factors. The presence of two large substituents would be expected to reduce the likelihood of electrophilic attack at the central nitrogen on steric grounds. In addition, Sujishi and Witz[3,23] have demonstrated that the basicity of amines decreases upon successive addition of silicon-containing groups, presumably because of an electron-withdrawing effect.

Nevertheless the synthesis of compounds **18** and **19** was accomplished by aminolysis reactions similar to those used to prepare the primary aminoboranes **23** and **24** (eq 8).

These reactions, like those described by eq 6, proceeded rapidly at −78 °C to give quantitative amounts of amine hydrochloride and good yields (66–77%) of silylaminoboranes, which were isolated by distillation as colorless liquids.

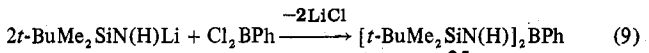
It was also of interest to determine whether two or three bulky *tert*-butyldimethylsilyl groups could be incorporated into



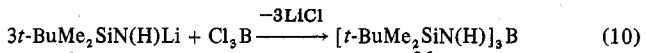
(8)

18, R = Me, X = NMe_2
19, R = Me, X = Ph
23, R = H, X = NMe_2
24, R = H, X = Ph

one molecule by use of the proper mole ratios of reagents. It was found that compounds **25** and **26** could be prepared from lithiation reactions (eq 9 and 10).



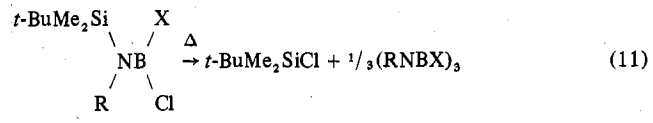
(9)



(10)

Boiling points and mass spectral and ^1H NMR data for these and the other previously unreported compounds are compiled in Table I.

Thermal Decomposition Reactions. It was found that those (silylamino)boranes which underwent thermal degradation below 200 °C gave borazines as decomposition products. Several chlorine-containing compounds eliminated *tert*-butylchlorodimethylsilane as shown in eq 11.

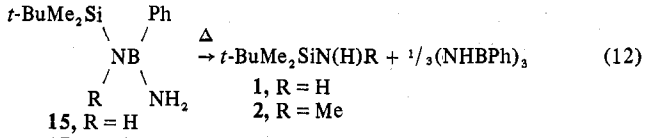


(11)

7, R = H, X = Ph
8, R = H, X = Cl
12, R = Me, X = Ph
13, R = Me, X = Cl

This result parallels observations that have been made on analogous systems containing the trimethylsilyl group.[13,18,21,24-28]

A somewhat similar reaction was observed upon heating compounds **15** and **17** (eq 12), with the elimination products now being the silylamines **1** and **2**.

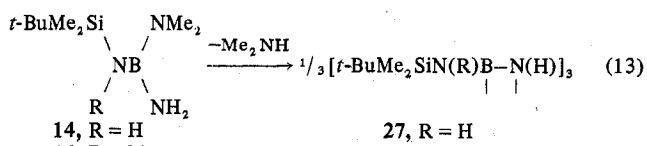


(12)

15, R = H
17, R = Me
1, R = H
2, R = Me

This decomposition can only occur through the cleavage of a boron–nitrogen bond. Interestingly, the isolation of **2** and *B*-triphenylborazine from the degradation of **17** indicates that the central B–N bond is ruptured in preference to the terminal B–NH_2 moiety. Relief of steric strain can be suggested as a possible explanation for this observation.

Upon standing under N_2 at 25 °C, compounds **14** and **16** slowly eliminated dimethylamine and crystallized to the novel borazines **27** and **28** (eq 13).

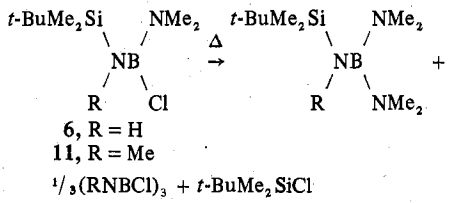


(13)

14, R = H
16, R = Me
27, R = H
28, R = Me

This condensation is analogous to that reported for amino(dimethylamino)phenylborane[29] as well as to those recently observed for certain primary amino-substituted diborylamines.[30]

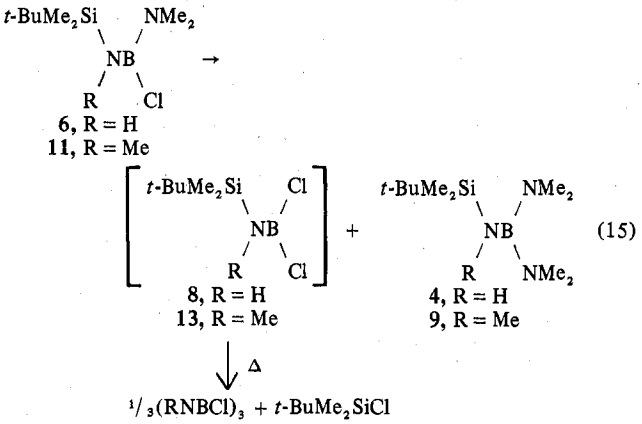
The thermal decompositions of compounds **6** and **11** resulted in the isolation of redistribution products as well as borazines and *tert*-butylchlorodimethylsilane (eq 14).



6, R = H
11, R = Me

$^1/_3(RNBCl)_3 + t\text{-}BuMe_2SiCl$ (14)

This result can be rationalized if one assumes that the initial step of the reaction involves an exchange of substituents between two molecules (eq 15), followed by the decomposition of **8** or **13** as in eq 11.

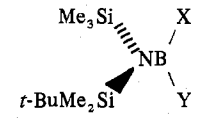


(15)

High-resolution mass spectral data obtained for **6** and **11** offered supporting evidence for this decomposition pathway. Neither gave the predicted molecular ion peaks; rather, the parent ion clusters were centered at *m/e* 229 and 243, respectively, which correspond to the more stable rearrangement products **4** and **9**.

Similar redistribution reactions involving the exchange of chloro and dimethylamino substituents at boron are well documented and are often synthetically useful.[20] In this specific instance the reaction may be driven toward the formation of the dichloroborane since its subsequent decomposition effectively removes that species from the system.

It was found that a number of (silylamino)boranes did not undergo decomposition when heated to ~200 °C for prolonged periods and thus for purposes of this study are considered to be "stable". These included compounds **4**, **5**, **9**, **10**, and **18–26**. It is worth noting that all of the compounds studied for which R = $SiMe_3$ were unaffected by heating. Electron diffraction[31] and NMR[32] data on similar compounds have supported the suggestion that such bulky silyl groups can cause nonplanarity in aminoboranes. Molecular models of compounds **18–24** indicate that the least hindered configuration available to these systems is that in which the Si_2N moiety is rotated ~90° from the plane defined by the three bonds to boron.



In this geometry the boron atom is protected from nucleophilic attack in, above, and below the molecular plane. Thus steric "protection" afforded by such a configuration can be advanced as a reasonable explanation for the high thermal stabilities observed for **18–24** relative to other (silylamino)boranes.

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by the National Institutes of Health. Financial assistance from the Duke University Research Council is gratefully acknowledged.

Registry No. **1**, 41879-37-2; **2**, 61012-64-4; **3**, 66417-55-8; **4**, 66417-56-9; **5**, 66417-57-0; **6**, 66417-58-1; **7**, 66417-59-2; **8**, 66417-60-5; **9**, 66417-61-6; **10**, 66417-62-7; **11**, 66417-63-8; **12**, 66417-64-9; **13**, 66417-65-0; **14**, 66417-66-1; **15**, 66417-67-2; **16**, 66417-68-3; **17**, 66417-69-4; **18**, 66417-70-7; **19**, 66417-71-8; **20**, 66417-72-9; **21**, 66417-32-1; **22**, 66417-33-2; **23**, 66417-34-3; **24**, 66417-35-4; **25**, 66417-36-5; **26**, 66417-37-6; **27**, 66417-38-7; **28**, 66417-39-8.

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Contribution from the Department of Chemistry, University of California at San Diego, La Jolla, California 92093

Coordination Isomers of Antibiotic Thiohydroxamate–Metal Complexes. Geometrical Isomers of Tris(*N*-methylthioformohydroxamato)rhodium(III) and Bis(*N*-methylthioformohydroxamato)platinum(II)

JOHN LEONG* and STUART J. BELL

Received January 17, 1978

The low molecular weight bacterial products bis(*N*-methylthioformohydroxamato)copper(II) (fluopsin C) and tris(*N*-methylthioformohydroxamato)iron(III) (fluopsin F) display broad-spectrum antibiotic activity against both gram-positive and -negative bacteria and fungi. The kinetic lability of these complexes precludes the isolation of cis and trans geometrical coordination isomers in each case. Replacement of these metal ions with ions possessing large crystal field stabilization energies induces kinetic inertness and thereby allows the possibility of isomer separation. In the series of octahedral tris(*N*-methylthioformohydroxamate)–metal ion substituted complexes, $M(th)_3$ (M = Fe, Co, Cr, Rh), the latter two complexes were sufficiently substitution inert to permit the isolation and characterization of cis and trans geometrical isomers. Geometric isomerism occurs with a half-life of several hours for the chromium(III) complex and several days for the rhodium(III) complex. *cis*-$Rh(th)_3$ has NMR signals for the coordinated ligand at 3.70 ppm (CH_3N) and 7.17 ppm (HC(S)), whereas *trans*-$Rh(th)_3$ has corresponding signals at 3.51, 3.52, and 3.76 and 7.09, 7.46, and 7.53 ppm, respectively. The cis isomer has a visible absorption maximum at 437 nm (ϵ 490), whereas the trans isomer has the same band at 452 nm (ϵ 725). In the series of square-planar bis(*N*-methylthioformohydroxamate)–metal ion substituted complexes, $M(th)_2$ (M = Cu, Ni, Pd, Pt), cis and trans isomers were isolated and characterized in the last case. The infrared spectra of the two platinum(II) isomers are virtually superimposable except in the vicinity of 675 and 875 cm^{-1}. In these regions the trans isomer has absorption bands at 686 and 878 cm^{-1}, whereas the cis isomer has absorptions at 649 and 681 cm^{-1} and 874 and 893 cm^{-1}. The cis isomer has a visible absorption maximum at 429 nm (ϵ 126), whereas the trans isomer has the same absorption at 439 nm (ϵ 116). Geometric isomerism occurs with a half-life of several days.

Introduction

Certain low molecular weight bacterial products which contain cupric or ferric ion display broad-spectrum antibiotic activity against both gram-positive and -negative bacteria and fungi.[1] Bis(*N*-methylthioformohydroxamato)copper(II) (also known as fluopsin C, antibiotic YC 73, or antibiotic B_1) and tris(*N*-methylthioformohydroxamato)iron(III) (fluopsin F) have been isolated from the culture supernatant fluids of *Pseudomonas fluorescens* KY 4032[2] and MCRL 10107,[3] *Pseudomonas reptilivora* N-51968,[4-6] and *Streptomyces* ATCC 21775.[7] In *P. reptilivora* N-51968 the production of the cupric complex is dependent on the amount of cupric ion in the culture medium.[6] Unless the ferric to cupric ion ratio is significantly increased in the culture medium of *P. fluorescens* KY 4032, the cupric complex is the dominant product, suggesting that it has the higher formation constant.[1]

Ferric complexes of chemically synthesized N-substituted thioformohydroxamic acids, which are analogues of thioformin (*N*-methylthioformohydroxamic acid), and the native ferric and cupric complexes exhibit comparable antibiotic activity against *Bacillus subtilis* PCI 219, *Staphylococcus aureus* 209P, *Escherichia coli* NIHJ, and *Klebsiella pneumoniae*

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