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Reaction chemistry of tris(trimethylsilyl)amine with monohaloboranes

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Table III. Selected Bond Distances (Å) for $\text{Er}(\text{NO}_3)_3 \cdot (i\text{-PrO})_2\text{P}(\text{O})\text{CH}[\text{C}(\text{O})\text{NEt}_2][\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$

Er-O(1)	2.298 (6)	P(1)-O(3)	1.551 (9)
Er-O(4)	2.326 (7)	P(1)-C(1)	1.819 (11)
Er-O(5)	2.267 (8)	C(1)-C(2)	1.498 (15)
Er-O(6)	2.404 (8)	C(1)-C(2)	1.498 (15)
Er-O(7)	2.399 (9)	C(1)-C(3)	1.552 (16)
Er-O(9)	2.416 (9)	C(2)-O(4)	1.243 (10)
Er-O(10)	2.409 (9)	C(2)-N(1)	1.322 (14)
Er-O(12)	2.404 (9)	C(3)-C(4)	1.511 (15)
Er-O(13)	2.411 (8)	C(4)-O(5)	1.254 (12)
P(1)-O(1)	1.492 (6)	C(4)-N(2)	1.319 (15)
P(1)-O(2)	1.563 (9)		

spectroscopic data do not provide for an unambiguous assignment of the solution-state structure of **2**.

The availability of single crystals of **2** allowed for the determination of the solid-state molecular structure by X-ray diffraction techniques. A view of the molecule is shown in Figure 1, and selected bond distances are listed in Table III. The structure determination confirms the proposed molecular composition, but more importantly, it reveals the interesting ligand coordination transformation from complex **3** to **2**. Addition of TEP results in the loss of a water molecule from the inner Er(III) coordination sphere and tridentate coordination of **1** with $\text{Er}(\text{NO}_3)_3$. The Er ion is nine-coordinate with the three oxygen atoms, O(1), O(4), and O(5), donated by **1** and six oxygen atoms, O(6), O(7), O(9), O(10), O(12) and O(13), provided by bidentate nitrate groups. The Er-O(nitrate) distances are nearly identical: $\text{Er-O(nitrate)}_{\text{av}} = 2.407$ (9) Å; range 2.399 Å–2.416 Å. The Er-O(phosphoryl) distance, $\text{Er-O(1)} = 2.298$ (6) Å, can be compared with the distances in **3**¹, 2.279 (4) and 2.289 (5) Å, and the distances in the CMP complex $\text{Er}(\text{NO}_3)_3 \cdot (i\text{-PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NEt}_2 \cdot \text{H}_2\text{O}$ (**4**),¹² which contains two bifunctional CMP ligands bonded in a monodentate manner: $\text{Er-O(phosphoryl)} = 2.259$ (6) and 2.290 (6) Å. Variations in P=O bond distances between the ligand **1** and the complexes **2** and **3** are dramatic: **1**, 1.459 (3) Å; **2**, 1.492 (6) Å; **3**, 1.469 (4) and 1.476 (5) Å. The bond lengthening going

from **1** to **2** is consistent with the large infrared coordination shift in ν_{PO} .

The Er-O carbonyl distances in **2**, $\text{Er-O(4)} = 2.326$ (7) Å and $\text{Er-O(5)} = 2.267$ (8) Å, are significantly different, and it is interesting to note that the Er-O(5) distance associated with the larger seven-membered chelate ring and the long-leg carbonyl group, $\text{CH}[\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$, provides the shorter Er-O coordination distance. The carbonyl distances, $\text{C(2)-O(4)}(\text{short-leg}) = 1.243$ (10) Å and $\text{C(4)-O(5)}(\text{long-leg}) = 1.254$ (12) Å, are longer than the respective distances in **1**, 1.228 (3) and 1.223 (3) Å. As expected, the carbonyl distances in **2** are longer than the carbonyl distances in **3** and **4**. $\text{CH}[\text{C}(\text{O})\text{NEt}_2]$: **3**, 1.231 (9) and 1.232 (8) Å; **4**, 1.239 (11) and 1.240 (11) Å. $\text{CH}[\text{CH}_2\text{C}(\text{O})\text{NEt}_2]$: **3**, 1.228 (8) and 1.234 (13) Å.

The structure of **2** is unique, and its formation may provide one clue to the mechanism for phase modification chemistry observed in extractions of Nd(III) and Am(III) by carbamoyl-methylphosphonate and phosphine oxide ligands with TBP.² It is known that organophosphates, such as TBP and presumably TEP, act to dehydrate otherwise highly aquated lanthanide and actinide ions.² Whether formation of **2** occurs by dehydration of **3** or by dehydration of $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ followed by ligand coordination is not clear; however, it appears that **3** is a likely intermediate. In the present synthesis, the competing water may be removed in the ether washes, and the coordinatively unsaturated Er(III) ion is able to coordinate with two carbonyl groups. This coordination mode is apparently quite stable, once formed, since water/ethanol mixtures dissolve the complex, but dissolution does not result in water coordination. Clearly, additional studies are required in order to understand the molecular mechanisms of neutral-ligand phase modification and synergism. The observations made here provide a useful guide to those studies.

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Registry No. **2**, 113086-34-3.

Supplementary Material Available: Tables S-I-S-IV, listing hydrogen atom positions, anisotropic thermal parameters, bond angles, and bond distances (7 pages); a table of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

- (11) More detailed NMR studies of the paramagnetic shifts experienced by **1** in the presence of various lanthanide ions will be undertaken in the future.
 (12) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1982**, *61*, 155.

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Reaction Chemistry of Tris(trimethylsilyl)amine with Monohaloboranes

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Received September 4, 1987

Reactions of tris(trimethylsilyl)amine, $\text{N}(\text{SiMe}_3)_3$, with several monochloroboranes, $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{BCl}$, $o\text{-OC}_6\text{H}_4\text{OBCl}$, and $\text{SCH}_2\text{CH}_2\text{SBCl}$, have been examined, and the ((trimethylsilyl)amino)boranes $o\text{-OC}_6\text{H}_4\text{OBN}(\text{SiMe}_3)_2$, $[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{NSiMe}_3$, $\text{SCH}_2\text{CH}_2\text{SBN}(\text{SiMe}_3)_2$, and $[\text{SCH}_2\text{CH}_2\text{SB}]_2\text{NSiMe}_3$ have been prepared and characterized by spectroscopic methods. The molecular structure of $[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{NSiMe}_3$ has been determined by single-crystal X-ray diffraction analysis and found to crystallize in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 7.189$ (1) Å, $b = 19.387$ (4) Å, $c = 24.508$ (4) Å, $Z = 8$, $V = 3416$ (1) Å³, and $\rho_{\text{calcd}} = 1.26$ g cm⁻³. The structure was solved by direct methods, and blocked least-squares refinement converged with $R_F = 10.1\%$ and $R_{wF} = 9.2\%$ on 3012 unique data with $F > 2\sigma(F)$. The structure contains two independent molecules in the unit cell, and the central nitrogen atoms have a trigonal-planar geometry. Important bond distances include $\text{B-N}_{\text{av}} = 1.421$ (13) Å, $\text{Si-N}_{\text{av}} = 1.783$ (7) Å, and $\text{B-O}_{\text{av}} = 1.390$ (13) Å. Attempts to prepare the 1,3,2-diazaborolidine $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{BN}(\text{SiMe}_3)_2$ and triborylamine compounds by this synthetic method were unsuccessful.

Introduction








Reactions of haloboranes with hexamethyldisilazane (HMDS) have been thoroughly studied,¹⁻¹⁰ and these reactions provide a

generally useful route to the formation of a variety of (silylamino)boranes. In turn, several monomeric (silylamino)boranes,

(1) Becke-Goehring, M.; Krill, H. *Chem. Ber.* **1961**, *94*, 1059.

(2) Nöth, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biol.* **1961**, *16B*, 618.

Table I. Summary of Preparative Conditions for the Synthesis of ((Trimethylsilyl)amino)boranes

borane structure	reactant amt, g (mmol)		ratio	reacn conditions	yield, g (%)	bp, °C/P, torr	product
	borane	N(SiMe ₃) ₃					
	5.55 (41.3)	9.64 (41.3)	1:1	toluene reflux, 48 h			no reacn
	2.88 (18.7)	4.33 (18.6)	1:1	toluene reflux, 48 h	4.42 (85)	70/0.06	2a
	5.54 (35.9)	4.18 (17.9)	2:1	toluene reflux, 48 h	3.17 (63)	70/0.06	2a
	6.19 (40.1)	3.12 (13.4)	3:1	chlorobenzene reflux, 48 h	1.27 (22)	110/0.06	2b
	1.78 (12.8)	3.0 (12.9)	1:1	toluene reflux, 86 h	3.60 (83)	110/0.06	2b
	2.29 (16.5)	2.03 (8.7)	2:1	toluene reflux, 85 h	1.76 (52)	55/0.04	3a
	3.64 (26.3)	2.08 (9.0)	3:1	toluene reflux, 60 h	0.98 (43)	55/0.04	3a
					0.25 (10)	135/0.04	3b
					0.55 (23)	55/0.04	3a
					0.53 (20)	135/0.04	3b

through intermolecular elimination chemistry, act as useful precursors to *N*-silylborazenes.^{2,9,11-13} In this regard, Meller and co-workers¹⁴ have also noted that *B*-organo-*B'*-chloro-*N*-organo-borazenes, in combination with HMDS, produce polyborazenes cross-linked with -N(H)- groups. In addition, we have recently reported that *B*-trichloroborazene (ClBNH)₃ undergoes cross-linking chemistry with HMDS with the formation of an oligomeric gel which, upon pyrolysis, gives good yields of the important ceramic BN.¹⁵

For a variety of reasons, it was of interest to attempt to extend the cross-linking chemistry of borazenes to include bridging groups of the type -N(SiMe₃)-. A reagent that should be useful in this chemistry is tris(trimethylsilyl)amine, N(SiMe₃)₃. Unlike HMDS, relatively few studies of the reactions of N(SiMe₃)₃ with halo-boranes have been reported.^{8,16-19} Consequently, several reactions of monochloroboranes with N(SiMe₃)₃ have been examined, and we report here the results of the chemistry observed for a series of cyclic organoboron chlorides.

Experimental Section

General Information. All experimental manipulations were performed under rigorously anhydrous conditions in a high-vacuum system or in Schlenk equipment. Toluene was successively distilled over LiAlH₄ and sodium benzophenone ketyl under dry nitrogen. Chlorobenzene was stirred over P₂O₅ overnight, decanted, and distilled under dry nitrogen.

Tris(trimethylsilyl)amine,²⁰ 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine,²¹ 2-chloro-1,3,2-benzodioxaborole,²² and 2-chloro-1,3,2-dithiababorolane²³ were prepared as described in the literature. The ¹H, ¹³C, and ¹¹B NMR spectra were reported on Varian FT-80A or GE NT-360 NMR spectrometers and referenced (external) with Me₄Si (¹H, ¹³C) and BF₃·Et₂O (¹¹B). Infrared spectra were obtained on a Nicolet Model 6000 FTIR spectrometer from neat samples or solutions. Mass spectra were obtained on a Finnegan GC/MS system.

Synthesis of CH₃NCH₂CH₂N(CH₃)BN(SiMe₃)₂ (1a). A solution of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (0.97 g, 7.34 mmol) in toluene (10 mL) was added to a solution of sodium bis(trimethylsilyl)amide (1.35 g, 7.38 mmol) in toluene (10 mL) held at -78 °C. The mixture was stirred and warmed to 25 °C, and stirring was continued for 2 days. The resulting mixture was filtered and the filtrate vacuum-evaporated, leaving a colorless oily residue. Distillation: 45 °C (20 Torr); yield 0.56 g (30%). Anal. Calcd for C₁₀H₂₈N₃BSi₂: C, 46.67; H, 10.97; N, 16.33. Found: C, 45.89; H, 10.60; N, 16.82. Mass spectrum (70 eV) [*m/e* (relative intensity)]: [M⁺] 257 (47), 242 (100), 226 (2), 213 (5), 199 (5), 192 (2), 184 (2), 168 (6), 154 (4), 143 (4), 129 (29), 113 (14), 98 (11), 84 (7), 73 (7), 59 (11), 45 (10). Infrared spectrum (thin film, cm⁻¹): 2955 (s), 2885 (s), 2831 (s), 2780 (s), 1498 (s), 1476 (m), 1433 (s), 1397 (s), 1314 (s), 1290 (s), 1260 (s), 1249 (s), 1218 (m), 1157 (m), 1062 (w), 1039 (w), 957 (br, s), 886 (s), 836 (s), 755 (w), 680 (w). NMR spectra (C₆D₆, 25 °C): ¹¹B{¹H} δ 28.4; ¹H δ 2.99 (CH₂, intensity 4), 2.56 (CH₃, intensity 6), 0.2 (SiCH₃, intensity 18).

General Synthetic Procedure for 2a, 2b, 3a, and 3b. An appropriate amount (Table I) of chloroborane was weighed, under nitrogen, into a 100-mL Schlenk vessel and diluted with approximately 20 mL of dry toluene. This solution was then combined with a solution containing a weighed quantity of N(SiMe₃)₃ and about 20 mL of toluene cooled to -78 °C. The mixture was warmed to 25 °C, and a small sample was removed for ¹¹B NMR analysis. In each case, no reaction was detected at 25 °C, as indicated by the observation of a ¹¹B signal for only the chloroborane. Under a nitrogen purge, the reaction flask was fitted with a reflux condenser, and the mixture was heated at reflux for 2-4 days. Progress of the reaction was monitored by using ¹¹B NMR spectrometry. When no further change in the spectrum was detected, the toluene was removed by vacuum evaporation, and the residue was distilled at reduced pressure.

Characterization Data. *o*-OC₆H₄OBN(SiMe₃)₂ (**2a**). Anal. Calcd for C₁₂H₂₂Si₂O₂NB: C, 51.60; H, 7.94; N, 5.01. Found: C, 51.38; H, 8.01; N, 5.48. Mass spectrum (70 eV) [*m/e* (relative intensity)]: [M⁺] 279 (14), 264 (35), 248 (3), 234 (1), 206 (1), 191 (8), 176 (6), 166 (14), 161 (7), 146 (6), 130 (14), 98 (100), 84 (3), 73 (38), 59 (8), 45 (27).

- Andrianov, K. A.; Astakhin, V. V.; Kochkin, D. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, 1852.
- Jenne, H.; Niedenzu, K. *Inorg. Chem.* **1964**, *3*, 68.
- Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1966**, *5*, 1327.
- Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1968**, *7*, 419.
- Lappert, M. F.; Srivastava, G. *Proc. Chem. Soc., London* **1964**, 120.
- Srivastava, G. *J. Organomet. Chem.* **1974**, *69*, 179.
- Nöth, H.; Storch, W. *Chem. Ber.* **1976**, *109*, 884.
- Bowser, J. R.; Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1978**, *17*, 1882.
- Geymayer, P.; Rochow, E. G.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 633.
- Geymayer, P.; Rochow, E. G. *Monatsh. Chem.* **1966**, *97*, 28.
- Nutt, W. R.; Wells, R. L. *Inorg. Chem.* **1982**, *21*, 2469.
- Meller, A.; Füllgrabe, H. *J. Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 359; *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 156.
- Narula, C. K.; Schaeffer, R.; Paine, R. T.; Dayte, A.; Hammatter, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 5556.
- Russ, C. R.; MacDiarmid, A. G. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 500.
- Barlos, K.; Christl, H.; Nöth, H. *Liebigs Ann. Chem.* **1976**, 2272.
- Haubold, W.; Kraatz, U. *Z. Anorg. Allg. Chem.* **1976**, *421*, 105.
- Some of the first reactions reported between silylamines and boron halides involved (H₃Si)₃N and related reagents: Burg, A. B.; Kuljian, E. S. *J. Am. Chem. Soc.* **1950**, *72*, 3103.

- Lehn, W. L. *J. Am. Chem. Soc.* **1964**, *86*, 305.
- Wang, T.; Busse, D. J.; Niedenzu, K. *Inorg. Chem.* **1970**, *9*, 2150.
- Gerrand, W.; Lappert, M. F.; Mountfield, B. A. *J. Chem. Soc.* **1959**, 1529.
- Shore, S. G.; Crist, J. L.; Lockman, B.; Long, J. R.; Coon, A. D. *J. Chem. Soc., Dalton Trans.* **1972**, 1123.

Table II. Experimental Data for the X-ray Diffraction Study of $[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{NSiMe}_3$

(A) Crystal Parameters (20 °C)	
chem formula: $\text{Si}_2\text{O}_8\text{N}_2\text{B}_4\text{C}_{30}\text{H}_{34}$	$V = 3416 (1) \text{ \AA}^3$
cryst syst: orthorhombic	$Z = 8$
space group: $P2_12_12_1$ (No. 19)	$D_{\text{calc}} = 1.26 \text{ g cm}^{-3}$
$a = 7.189 (1) \text{ \AA}$	$M_r = 325.04$
$b = 19.387 (4) \text{ \AA}$	$\mu = 1.6 \text{ cm}^{-1}$
$c = 24.508 (4) \text{ \AA}$	$F(000) = 1350$
(B) Data Collection	
diffractometer: Syntex P3/F	
radiation: Mo $K\alpha$ ($\lambda = 0.71069 \text{ \AA}$)	
monochromator: highly oriented graphite crystal	
reflens measd: $h, k, -l$	
2θ range: $2\text{--}45^\circ$	
scan type: ω	
scan speed: $4\text{--}30^\circ$	
scan range: $[w(0) - 0.7] - [w(0) + 0.8]^\circ$	
bkgd measurement: stationary cryst and counter; at beginning and end of ω scan, each for half of the total scan time	
std reflens: $[400, 051, 017]$, 3 measd every 123 reflens	
total no. of reflens collcd: 5340	
no. of unique reflens collcd: 4464	
no. of obsd reflens used in refinement: 3012, $F > 2\sigma(F)$	

Infrared spectrum (thin film, cm^{-1}): 2999 (s), 1480 (s), 1441 (s), 1399 (s), 1349 (s), 1254 (s), 1240 (s), 1173 (s), 960 (s), 912 (s), 848 (s), 769 (s), 740 (s), 687 (s), 671 (s), 639 (s), 626 (s), 554 (s), 429 (s), 389 (s), 369 (s). NMR spectra (C_6D_6): $^1\text{B}^1\text{H}$ δ 26.3 ($h/2 \sim 240 \text{ Hz}$); ^1H δ 6.9 (C_6H_4 , intensity 4), 0.35 (CH_3 , intensity 18); $^{13}\text{C}^1\text{H}$ δ 148.9 (C_6H_4), 122.1 (C_6H_4), 111.7 (C_6H_4), 3.4 (CH_3).

$[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{N}(\text{SiMe}_3)$ (**2b**). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{SiO}_4\text{NB}_2$: C, 55.43; H, 5.27; N, 4.31. Found: C, 55.39; H, 5.43; N, 4.24. Mass spectrum (70 eV) [m/e (relative intensity)]: [M^+] 325 (22), 310 (39), 294 (1), 279 (2), 268 (3), 252 (3), 236 (1), 218 (5), 207 (6), 192 (23), 176 (39), 166 (100), 151 (50), 136 (26), 126 (4), 118 (5), 109 (3), 101 (6), 96 (13), 92 (6), 82 (12), 73 (11), 66 (69), 53 (4), 45 (12). Infrared spectrum (KBr pellet, cm^{-1}): 2957 (s), 1497 (s), 1479 (s), 1443 (s), 1400 (s), 1390 (s), 1334 (s), 1255 (s), 1228 (s), 1131 (s), 1005 (s), 954 (s), 944 (s), 918 (s), 844 (s), 810 (s), 768 (s), 740 (s), 689 (s), 636 (s), 574 (s), 491 (s), 481 (s). NMR spectra (C_6D_6): $^1\text{B}^1\text{H}$ δ 25.8 ($h/2 \sim 375 \text{ Hz}$); ^1H δ 6.9 (C_6H_4 , intensity 8), 0.48 (NSiCH_3 , intensity 9); $^{13}\text{C}^1\text{H}$ δ 148.8 (C_6H_4), 122.6 (C_6H_4), 112.3 (C_6H_4), 1.8 (CH_3).

$[\text{SCH}_2\text{CH}_2\text{SBN}(\text{SiMe}_3)_2]$ (**3a**). Anal. Calcd for $\text{C}_8\text{H}_{22}\text{S}_2\text{Si}_2\text{NB}$: C, 36.49; H, 8.36; N, 5.32. Found: C, 36.09; H, 8.50; N, 5.29. Mass spectrum (70 eV) [m/e (relative intensity)]: [M^+] 263 (7), 248 (48), 220 (1), 188 (4), 172 (1), 160 (1), 142 (0.5), 135 (5), 130 (13), 116 (4), 98 (100), 86 (4), 73 (32), 68 (6), 59 (7), 54 (2). Infrared spectrum (KBr pellet, cm^{-1}): 1427 (s), 1407 (s), 1334 (s), 1251 (s), 1220 (s), 929 (s), 875 (s), 846 (s), 762 (s), 686 (s), 620 (s), 430 (s). NMR spectra (C_6D_6): $^1\text{B}^1\text{H}$ δ 56.0 ($h/2 = 95 \text{ Hz}$); ^1H δ 2.73 (CH_2 intensity 4), 0.38 (CH_3 intensity 18); $^{13}\text{C}^1\text{H}$ δ 36.2 (CH_2), 3.6 (CH_3).

$[\text{SCH}_2\text{CH}_2\text{SB}]_2\text{N}(\text{SiMe}_3)$ (**3b**). Anal. Calcd for $\text{C}_7\text{H}_{17}\text{S}_4\text{SiNB}_2$: C, 28.68; H, 5.85; N, 4.78. Found: C, 28.19; H, 5.71; N, 4.85. Mass spectrum (70 eV) [m/e (relative intensity)]: [M^+] 293 (55), 278 (74), 265 (15), 250 (40), 218 (11), 190 (6), 184 (3), 176 (5), 167 (2), 158 (12), 142 (4), 135 (35), 122 (47), 116 (29), 107 (11), 98 (66), 91 (23), 84 (18), 73 (100), 66 (51), 59 (57). Infrared spectrum (neat, cm^{-1}): 2954 (s), 2923 (s), 1425 (s), 1410 (s), 1288 (s), 1252 (s), 1172 (s), 1151 (s), 939 (s), 920 (s), 895 (s), 849 (s), 761 (s), 691 (s), 670 (s), 611 (s), 486 (s), 405 (s). NMR spectra (C_6D_6): $^1\text{B}^1\text{H}$ δ 55.1 ($h/2 \sim 130 \text{ Hz}$); ^1H δ 2.75 (CH_2 intensity 8), 0.50 (CH_3 intensity 9); $^{13}\text{C}^1\text{H}$ δ 36.9 (CH_2), 1.9 (CH_3).

Crystallographic Measurements and Structure Solution. A suitable crystal of **2b** ($0.12 \times 0.21 \times 0.68 \text{ mm}$), shaped as an elongated plate (bonding planes 010, 011, 0 $\bar{1}$ 1, 0 $\bar{1}$ 0, 0 $\bar{1}$ 1, 01 $\bar{1}$), was mounted in a glass capillary. The crystal was centered on a Syntex P3/F automated diffractometer, and determinations of crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner. Data were collected at 20 °C in the ω -scan mode with use of Mo $K\alpha$ radiation, a scintillation counter, and pulse height analyzer. The data collection parameters are summarized in Table II. Inspection of the data led to assignment of the orthorhombic space group $P2_12_12_1$ (no. 19).²⁴ A small

Table III. Fractional Coordinates and Their Esd's for $[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{NSiMe}_3$

atom	x/a	y/b	z/c
Si(1)	0.5277 (4)	0.69833 (13)	.12446 (11)
N(1)	0.5355 (11)	0.7478 (3)	0.0633 (3)
B(1)	0.5382 (16)	0.7080 (5)	0.0154 (5)
O(1)	0.5479 (9)	0.6361 (3)	0.0138 (2)
O(2)	0.5294 (10)	0.7319 (3)	-0.0392 (2)
C(1)	0.5387 (14)	0.6164 (5)	-0.0404 (4)
C(2)	0.5409 (15)	0.5511 (5)	-0.0627 (5)
C(3)	0.5288 (19)	0.5470 (8)	-0.1181 (6)
C(4)	0.5110 (20)	0.6048 (8)	-0.1493 (5)
C(5)	0.5151 (15)	0.6710 (5)	-0.1273 (4)
C(6)	0.5276 (14)	0.6744 (5)	-0.0717 (4)
B(2)	0.5334 (17)	0.8216 (5)	0.0593 (4)
O(3)	0.5323 (9)	0.8634 (3)	0.1047 (2)
O(4)	0.5383 (10)	0.8568 (3)	0.0114 (3)
C(7)	0.5349 (12)	0.9287 (5)	0.0842 (4)
C(8)	0.5345 (16)	0.9914 (5)	0.1110 (5)
C(9)	0.5318 (19)	1.0498 (6)	0.0782 (7)
C(10)	0.5346 (18)	1.0459 (5)	0.0222 (6)
C(11)	0.5352 (17)	0.9829 (6)	-0.0056 (5)
C(12)	0.5393 (15)	0.9264 (5)	0.0284 (5)
Si(2)	0.5260 (5)	0.40872 (14)	0.16175 (12)
N(2)	0.5266 (10)	0.3170 (3)	0.1549 (3)
B(3)	0.3859 (17)	0.2716 (5)	0.1740 (4)
O(5)	0.4031 (8)	0.2019 (3)	0.1747 (2)
O(6)	0.2170 (9)	0.2940 (3)	0.1965 (2)
C(13)	0.2389 (15)	0.1787 (5)	0.1953 (4)
C(14)	0.1747 (15)	0.1111 (6)	0.2026 (4)
C(15)	-0.0025 (17)	0.1028 (5)	0.2226 (4)
C(16)	-0.1110 (16)	0.1569 (6)	0.2354 (4)
C(17)	-0.0526 (16)	0.2257 (6)	0.2279 (4)
C(18)	0.1230 (17)	0.2330 (6)	0.2076 (4)
B(4)	0.6811 (17)	0.2891 (6)	0.1260 (5)
O(7)	0.6983 (8)	0.2197 (3)	0.1088 (3)
O(8)	0.8420 (9)	0.3253 (3)	0.1118 (3)
C(19)	0.8696 (13)	0.2145 (5)	0.0845 (4)
C(20)	0.9556 (16)	0.1575 (5)	0.0638 (4)
C(21)	1.1359 (17)	0.1658 (7)	0.0425 (4)
C(22)	1.2187 (16)	0.2295 (8)	0.0427 (5)
C(23)	1.1312 (16)	0.2875 (6)	0.0654 (4)
C(24)	0.9567 (14)	0.2771 (5)	0.0861 (4)
C(25)	0.3139 (15)	0.6426 (5)	0.1219 (4)
C(26)	0.7420 (14)	0.6464 (5)	0.1309 (5)
C(27)	0.5082 (18)	0.7559 (5)	0.1845 (3)
C(28)	0.3090 (18)	0.4391 (6)	0.1962 (6)
C(29)	0.5401 (18)	0.4477 (5)	0.0936 (5)
C(30)	0.7257 (20)	0.4352 (6)	0.2039 (5)

correction for absorption was made empirically on the basis of ψ scans,²⁵ and the agreement factors before and after the absorption correction were 1.80% and 1.73%. The maximum and minimum transmissions were 0.877 and 0.856. Redundant and equivalent data were averaged ($R_{\text{merge}} = 1.17\%$) and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects.

All calculations were performed with the R3/SHELXTL structure determination package.²⁶ Least-squares refinements in the package use a blocked-cascade algorithm with full-matrix blocks of 103 parameters.²⁷

(25) The empirical absorption correction uses an ellipsoidal model fitted to azimuthal scan data which is then applied to the intensity data: *SHELXTL Manual, Revision 4*; Nicolet XRD Corp.: Madison, WI, 1983.

(26) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and scattering data compiled in: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 55–60, 99–101, 149–150. Anomalous dispersion terms were included for all atoms with atomic numbers greater than 2.

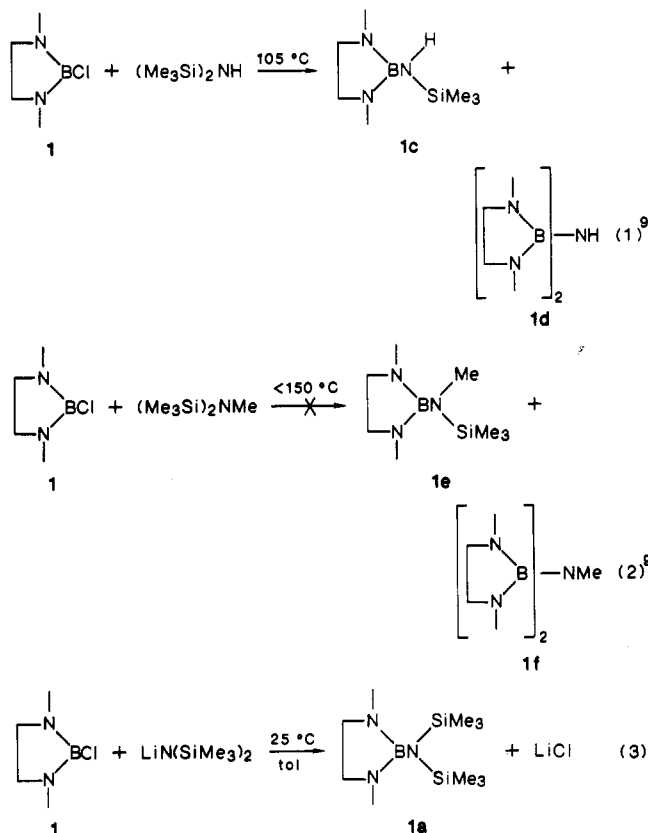
(27) A general description of the least-squares algebra is found in: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$ and $g = 0.00261$. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum (|F_o| - |F_c|)^2 / \sum wF_o^2]$, and $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$, where NO = number of observations and NV = number of variables (415).

(24) Space group notation as given in: *International Tables for X-ray Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. I, pp 73–346.

The structure was solved by direct methods. The best E map gave trial positions for 27 heavy atoms. The remaining non-hydrogen atoms were located in a subsequent Fourier map. Isotropic refinement on all heavy atoms gave $R_F = 13.6\%$, and anisotropic refinements on these atoms converged with $R_F = 11.8\%$. Hydrogen atoms were included in idealized positions with a fixed C-H distance, 0.95 Å, with their positions riding on the positions of their parent atom. The hydrogen atom U_{iso} 's were fixed at 1.2 times the last U_{equiv} of their parent atom. Final refinements²⁷ converged at $R_F = 10.1\%$ and $R_{wF} = 9.2\%$ on 415 variables and 3012 unique data with $F > 2\sigma(F)$. A final difference map showed no peak greater than the peak-trough amplitude, 0.63 e Å⁻³. The observed and calculated structure factor amplitudes (Table S-1), hydrogen atom positions (Table S-2), anisotropic thermal parameters (Table S-3), and full listings of bond angles and distances (Table S-4) are provided in supplementary material. The non-hydrogen positional parameters are listed in Table III.

Results and Discussion

Nöth and Storch⁹ have previously reported the reactions of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (**1**) with hexamethyldisilazane, (Me₃Si)₂NH, and heptamethyldisilazane, (Me₃Si)₂NCH₃. In the former case, no solvent was employed, and a reaction temperature of 105 °C was required to initiate Me₃Si-N bond cleavage. Both the diazaborolidinyl(trimethylsilyl)amine (**1c**), MeNCH₂CH₂N(Me)BN(H)(SiMe₃), and bis-(diazaborolidinyl)amine (**1d**), [MeNCH₂CH₂N(Me)B]₂NH, were isolated from this reaction (eq 1). In the case of hepta-

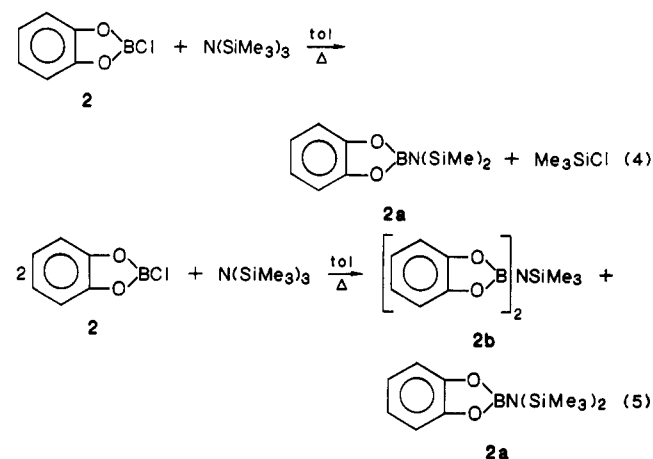


methylidisilazane and **1**, no reaction was observed in the absence of solvent up to a temperature of 150 °C. The respective substituted amines MeNCH₂CH₂N(Me)BN(Me)(SiMe₃) (**1e**) and [MeNCH₂CH₂N(Me)B]₂N(Me) (**1f**) were obtained only when the first substitution was accomplished with the lithium salt LiN(Me)(SiMe₃) (eq 2).

Similar observations are made in the present study employing N(SiMe₃)₃. Combinations of **1** with N(SiMe₃)₃ in refluxing toluene (48 h) or in the absence of solvent at 150 °C result in no reaction. However, an equimolar mixture of **1** and NaN-(SiMe₃)₂ in toluene at 25 °C for 2 days produces 2-(bis(trimethylsilyl)amino)-1,3-dimethyl-1,3,2-diazaborolidine (**1a**), MeNCH₂CH₂N(Me)BN(SiMe₃)₂, in small yield (eq 3).²⁴ It, therefore, appears that the first step in the reactions of **1** with N(R)R' (R = H, Me, SiMe₃; R' = SiMe₃) is hindered in the cases R = CH₃ and SiMe₃ even in the absence of solvent and elevated reaction temperatures. Whether this is a steric or electronic effect is not certain; however, steric hindrance would be expected to dominate at least in the case of N(SiMe₃)₃. It is noteworthy that replacement of the chloride substituent in **1** with a better leaving group, OSO₂CF₃⁻, results in no reaction with N(SiMe₃)₃.

Product **1a** has been characterized by spectroscopic techniques. The compound displays a parent ion and predictable fragmentation pattern in its mass spectrum. The ¹¹B{¹H} NMR spectrum shows a single resonance centered at δ 28.4 that is comparable to the ¹¹B NMR shifts^{9,29} for **1** (δ 27.6), **1c** (δ 26.0), **1d** (δ 26.3), **1e** (δ 28.7), and **1f** (δ 27.4). The ¹H and ¹³C NMR data show distinct resonances for the CH₃ and CH₂ groups in the diazaborolidine ring and the trimethylsilyl methyl group.

Although the silylamino substitution derivatives of $\overline{\text{OCH}_2\text{C-H}_2\text{OBCl}}$ have been reported,⁸ related derivatives of $\text{o-OC}_6\text{H}_4\text{OBCl}$ (**2**) apparently have not been prepared. Combinations of **2** and N(SiMe₃)₃ in 1:1, 2:1, and 3:1 ratios in refluxing toluene lead to the formation of borylamines as shown in eq 4 and 5. The 1:1 reactant combination gives exclusively the mono-



substitution product **2a** in good yield. The 2:1 reactant combination under the conditions employed (Table I) gives primarily **2a** with a small amount of disubstitution product **2b**. The 3:1 reactant combination gives good yields of **2b**, and traces of **2a** may be removed by vacuum distillation. No evidence was found for the triborylamine [$\text{o-OC}_6\text{H}_4\text{OB}$]₃N.

Both **2a** and **2b** have been fully characterized. The mass spectra of the pure compounds show a parent ion and anticipated fragmentation patterns. The ¹¹B NMR spectra show a single broad resonance: **2a**, δ 26.3 ($h/2 \sim 240$ Hz); **2b**, δ 25.8 ($h/2 = 375$ Hz). Both resonances are shifted slightly upfield from the chloroborane precursor **2** (δ 29).^{29,30} The ¹³C{¹H} NMR spectra show distinct resonances for the three inequivalent phenyl ring carbon atom environments and the trimethylsilyl methyl groups. The ratios of integrated ¹H NMR peak areas for the phenyl and silyl methyl protons also provide confirmation of the structural assignments.

(28) Bis(1,3-dimethyl-1,3,2-diazaborolidinyl)(trimethylsilyl)amine, [MeNCH₂CH₂N(Me)B]₂N(SiMe₃) (**1b**), and tris(1,3-dimethyl-1,3,2-diazaborolidinyl)amine, [MeNCH₂CH₂N(Me)B]₃N, were also detected in the residue by GC/mass spectrometry; however, no attempt was made to isolate these compounds.

(29) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer: Berlin, 1978.

(30) This sample was found in our laboratory to give a ¹¹B resonance at δ 28.8 (C₆D₆).

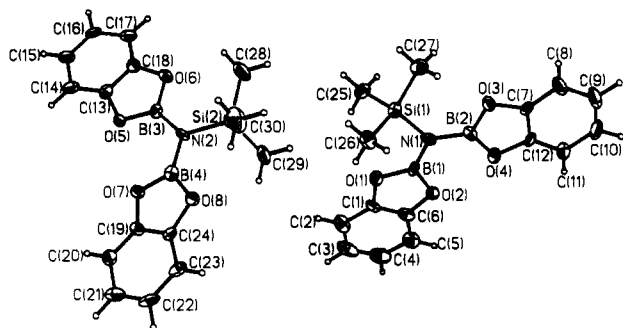


Figure 1. Molecular geometry and atom-labeling scheme for $[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{NSiMe}_3$ (20% thermal ellipsoids).

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[o\text{-OC}_6\text{H}_4\text{OB}]_2\text{NSiMe}_3$

(A) Distances			
Si(1)–N(1)	1.780 (7)	Si(2)–N(2)	1.787 (7)
B(1)–N(1)	1.406 (13)	B(3)–N(2)	1.420 (13)
B(2)–N(1)	1.435 (12)	B(4)–N(2)	1.423 (14)
B(1)–O(1)	1.397 (12)	B(3)–O(5)	1.357 (12)
B(1)–O(2)	1.417 (13)	B(3)–O(6)	1.402 (14)
B(2)–O(3)	1.377 (12)	B(4)–O(7)	1.414 (13)
B(2)–O(4)	1.358 (12)	B(4)–O(8)	1.397 (14)
C(1)–O(1)	1.383 (11)	C(13)–O(5)	1.361 (12)
C(6)–O(2)	1.369 (11)	C(18)–O(6)	1.389 (13)
C(13)–C(6)	1.363 (11)	C(13)–C(18)	1.376 (16)
C(7)–O(3)	1.362 (11)	C(19)–O(7)	1.371 (11)
C(12)–O(4)	1.411 (11)	C(24)–O(8)	1.396 (12)
C(7)–C(12)	1.369 (15)	C(19)–C(24)	1.367 (14)
C(ring)–C(ring) _{av}	1.377 (17)	C(ring)–C(ring) _{av}	1.379 (17)
Si–C _{av}	1.860 (10)	Si–C _{av}	1.849 (13)
(B) Angles			
Si(1)–N(1)–B(1)	114.1 (6)	Si(2)–N(2)–B(3)	125.7 (6)
Si(1)–N(1)–B(2)	126.5 (6)	Si(2)–N(2)–B(4)	115.3 (7)
B(1)–N(1)–B(2)	119.3 (8)	B(3)–N(2)–B(4)	119.0 (8)
N(1)–B(1)–O(1)	124.9 (9)	N(2)–B(3)–O(5)	123.7 (9)
N(1)–B(1)–O(2)	127.5 (8)	N(2)–B(3)–O(6)	123.7 (8)
O(1)–B(1)–O(2)	107.5 (8)	O(5)–B(3)–O(6)	112.5 (9)
N(1)–B(2)–O(3)	122.1 (8)	N(2)–B(4)–O(7)	125.3 (9)
N(1)–B(2)–O(4)	124.1 (9)	N(2)–B(4)–O(8)	125.4 (9)
O(3)–B(2)–O(4)	113.8 (8)	O(7)–B(4)–O(8)	109.3 (9)

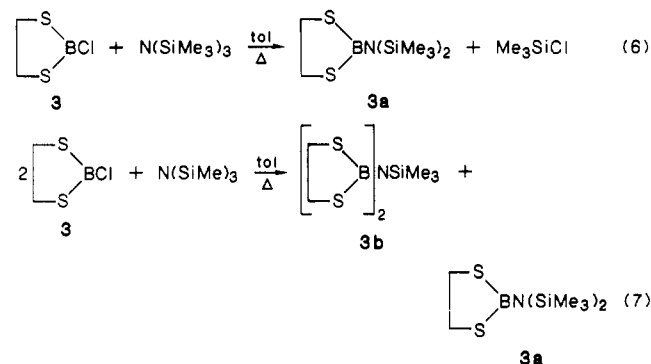
The molecular structure of **2b** has been determined by single-crystal X-ray diffraction techniques. A view of the molecule is shown in Figure 1, and selected bond distances and angles are listed in Table IV. There are two crystallographically independent molecules in the unit cell, and both are shown in the figure. Molecule I is designated to contain N(1), and molecule II contains N(2). Both molecules contain a central, trigonal-planar nitrogen atom [sum of the bond angles: N(1), 359.9°; N(2), 360.0°] and two planar boron atoms [sum of the bond angles: B(1), 359.9°; B(2), 360.0°; B(3), 359.9°; B(4), 360°]. The benzodioxaborole rings, however, are not perfectly coplanar with the NSiB₂ planes. In I, the N(1)–B(1)–O(1)–O(2) plane is twisted by 3.9° from the N(1)–B(2)–O(3)–O(4) plane, and in II, the N(2)–B(3)–O(5)–O(6) plane is twisted by 16.2° with respect to the N(2)–B(4)–O(7)–O(8) plane. The smaller twist angle is similar to the largest twist angle in the related molecule $[o\text{-OC}_6\text{H}_4\text{OB}]_3\text{N}$, 4.3°, which was assigned an idealized D_{3h} geometry.³¹

The average B–N bond distance 1.421 Å (range 1.406 (13)–1.435 (12) Å) falls in the range 1.40–1.43 Å, which is normally identified with contributions of π -bonding between boron and nitrogen atoms.³² The average distance in **2b** can be compared with the average B–N distances in $[o\text{-OC}_6\text{H}_4\text{OB}]_3\text{N}$, 1.438 (11) Å, $\text{Ph}_2\text{BN}(\text{SiMe}_3)(t\text{-Bu})$, 1.433 (6) Å,³³ $(\text{Ph}_2\text{B})_2\text{NH}$ 1.435

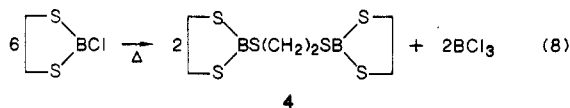
(3) Å (average),³³ and $(\text{Ph}_2\text{B})_2\text{NCH}_3$, 1.446 (3) Å (average).³³ The average Si–N bond distance, 1.788 (7) Å, is slightly longer than the usual range of Si–N bond distances, 1.47–1.76 Å, found in aminosilanes^{33,34} and in $\text{Ph}_2\text{BN}(\text{SiMe}_3)(t\text{-Bu})$, 1.767 (6) Å.

The B–O bond distances span a large range, 1.357 (12)–1.417 (13) Å, and the average distance is 1.390 Å. These values may be compared with the average B–O distance, 1.381 Å, and range, 1.366 (10)–1.394 (10) Å, in $[o\text{-OC}_6\text{H}_4\text{OB}]_3\text{N}$. The average C–O bond length, 1.380 Å, and range, 1.361 (12)–1.411 Å, are very similar to the values for $[o\text{-OC}_6\text{H}_4\text{OB}]_3\text{N}$, 1.381 Å and range 1.375 (10)–1.410 (10) Å, although the range is again greater for **2b**. The average C–C bond distance, 1.378 Å, is comparable within experimental error with the average distance, 1.388 Å, in $[o\text{-OC}_6\text{H}_4\text{OB}]_3\text{N}$.

In a fashion similar to the reactions of **2**, 2-chloro-1,3,2-dithiaboralane (**3**) was allowed to react with $\text{N}(\text{SiMe}_3)_3$ in 1:1, 2:1, and 3:1 mole ratios in refluxing toluene. The resulting chemistry is summarized in eq 6 and 7. The 1:1 reactant combination leads



to 2-(bis(trimethylsilyl)amino)-1,3,2-dithiaboralane (**3a**) in good yield. The reactant combinations 2:1 and 3:1 result in mixtures of **3a** and **3b**, but the latter is obtained only in relatively low yield. Widely separated boiling points allow for ready separation of the two species, and the compounds have been characterized by spectroscopic methods. Mass spectra of **3a** and **3b** show a parent ion and anticipated fragmentation patterns. The ¹¹B NMR spectra of **3a** and **3b** each show a single resonance centered at δ 56 ($h/2 \sim 95$ Hz) and δ 55.1 ($h/2 \sim 130$ Hz), respectively. These resonances are slightly upfield from the δ 62.7 resonance in the chloroborane precursor, $\text{SCH}_2\text{CH}_2\text{SBCl}$.²⁹ The ¹³C{¹H} and ¹H NMR spectra display resonances for the methyl and methylene environments, and the integrated ¹H NMR peak areas support the proposed structures for the compounds. Attempts to force the elimination chemistry to form the trisborylamine by increasing amounts of **3** employed or by increasing the reaction temperature or time were unsuccessful. Yields of **3a** and **3b** were also typically reduced, and a parasitic side reaction, described in eq 8, took place.



Compound **4** has been previously reported to form from thermal decomposition of 1,3,2-dithiaboralanes.³⁵

On the basis of the results of this study and previous reports regarding the reactivity of $\text{N}(\text{SiMe}_3)_3$ with chloroboranes, it appears that these reactions are sluggish and less complete than elimination reactions employing hexamethyldisilazane. These observations are also consistent with unpublished work from our

(31) Bullen, G. J.; Mallinson, P. R. *J. Chem. Soc. A* **1970**, 2213.

(32) Buckingham, A. D. *Proc. Chem. Soc., London* **1962**, 351.

(33) Männig, D.; Nöth, H.; Prigge, H.; Rotsch, A.-R.; Gopinathan, S.; Wilson, J. W. *J. Organomet. Chem.* **1986**, 310, 1.

(34) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Horwood: Chichester, England, 1980.

(35) Abel, E. A.; Armitage, D. A.; Bush, R. P. *J. Chem. Soc.* **1965**, 7098. Biffar, W.; Nöth, H.; Schwerthöffer, R. *Liebigs Ann. Chem.* **1981**, 2067.

laboratory that demonstrates that $N(\text{SiMe}_3)_3$ undergoes limited elimination chemistry with *B*-chloroborazenes.

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Supplementary Material Available: Tables S-2-S-4, listing hydrogen atom positional parameters, thermal parameters, and bond distances and angles (7 pages); Table S-1, listing observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Copper(II) and Nickel(II) Chelates of the Dihydrogen Nitrilotriacetate(1-) Ion: Crystal and Molecular Structure of Bis(*N,N*-bis(carboxymethyl)glycinato)copper(II) Dihydrate

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Bis(dihydrogen nitrilotriacetato) chelates of copper(II) and nickel(II) have been obtained as dihydrates, $[\text{M}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cu}, \text{Ni}$; $\text{H}_2\text{NTA} =$ nitrilotriacetic acid or *N,N*-bis(carboxymethyl)glycine). The potentiometric and conductometric titration curves, TG-DTA analysis, spectral properties (IR, reflectance, ESR), and magnetic susceptibility data of these sparingly soluble in water compounds are discussed, taking in view the crystal structure of the copper complex $[\text{Cu}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$, which crystallizes in the monoclinic system, space group $P2_1/c$ ($a = 6.845$ (1) Å, $b = 14.095$ (4) Å, $c = 9.427$ (3) Å, $\beta = 91.95$ (2)°, $Z = 2$, $V = 909.1$ Å³, $d_{\text{meas}} = 1.73$ (2) g·cm⁻³, $d_{\text{exptl}} = 1.75$ g·cm⁻³, $\mu = 1.631$ mm⁻¹ (Mo Kα)). Final $R = 0.032$ and $R_w = 0.033$ for 1416 independent observed reflections. The copper atom lies in the center of symmetry. Two dihydrogen nitrilotriacetate(1-) or *N,N*-bis(carboxymethyl)glycinate(1-) ions, H_2NTA^- , act as tridentate chelating agents, making up an "all-trans" elongated octahedral coordination around the same copper atom ($\text{Cu}-\text{N} = 2.062$ (3) Å, $\text{Cu}-\text{O}(3) = 1.954$ (2) Å, $\text{Cu}-\text{O}(13) = 2.321$ (2) Å) where each ligand remains with a free carboxylic group of one of the two acetic or *N*-carboxymethyl arms. Two interesting structural features of this solid are (1) the very short trans-apical $\text{Cu}-\text{O}(13)$ and $\text{Cu}-\text{O}(13')$ bonds (symmetry code $i: 1-x, 1-y, 1-z$), as compared with the un-ionized carboxyl-to-copper(II) coordination bonds in related compounds (2.467–2.518 Å), and (2) the formation of hydrogen bonds $\text{O}(14)-\text{H} \cdots \text{OW}$ (2.598 (4) Å; 164°) involving one water oxygen atom and the carboxylic group of each ligand bonded to copper.

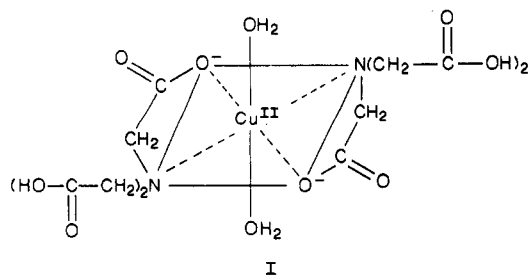
Introduction

During the last few years, the sodium salts of nitrilotriacetic acid (H_3NTA , H_3X) have been used as alternatives to polyphosphate in detergents, with a serious impact on heavy-metal remobilization in the environment.²⁻⁵ In this regard, crystal structure determination of H_3NTA , Na_3NTA , $\text{CaHNTA} \cdot 2\text{H}_2\text{O}$, and several metal chelates such as $\text{Na}[\text{Cu}(\text{NTA})] \cdot \text{H}_2\text{O}$ ⁵ have been carried out. Divalent metal ions of Co, Ni, Cu, Zn, Pb, and Hg give water-soluble $\text{M}(\text{HNTA}) \cdot n\text{H}_2\text{O}$ acid chelates.⁶ In addition, only copper⁵⁻⁷ and nickel^{6,7} form sparingly soluble $\text{M}(\text{H}_2\text{NTA})_2 \cdot 2\text{H}_2\text{O}$ solids. The two $\nu(\text{C}=\text{O})$ absorption bands in the IR spectrum of $[\text{Cu}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$ ^{5,6} and $[\text{Ni}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$ ⁶ were assigned by Whitlow⁵ and Rajabalee⁶ to two uncoordinated carboxylic groups in the H_2NTA^- ligand. They then assumed that the dihydrogen nitrilotriacetate(1-) ion or *N,N*-bis(carboxymethyl)glycinate(1-) ion acts as a glycinate bidentate chelating agent, where the two water molecules probably complete an octahedral coordination around copper or nickel atoms (I). Our results also confirm the isolation of two acid forms of

nitrilotriacetate complexes for Cu(II) and Ni(II), but the intensity ratio 2:1 of $\nu(\text{C}=\text{O})$ IR absorption and the titration behavior against KOH in aqueous solution of the acid bis chelates are not in accord with this previous hypothesis. This paper deals with the properties of these complexes and the crystal structure of the copper chelate. The structure agrees well with the formula $[\text{Cu}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$ but does not confirm a bidentate role for the H_2NTA^- ion.⁸

Experimental Section

Synthesis of the Complexes. (a) (*N,N*-Bis(carboxymethyl)glycinato)copper(II) Dihydrate or Bis(dihydrogen nitrilotriacetato)copper(II) Dihydrate, $[\text{Cu}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$. This compound was obtained in aqueous medium by reaction of nitrilotriacetic acid ($\text{H}_3\text{NTA} = \text{H}_3\text{X}$, Sigma) and $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (Merck) in a 4:1 molar ratio. Thus, for



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- (1) (a) Université de Paris-Luxembourg. (b) Université de Poitiers. (c) Université de Caen. (d) University of Granada.
- (2) Jorgensen, S. E.; Jensen, A. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1984; Vol. 18, Chapter 3, and ref 13-16 therein.
- (3) Schindler, P. W. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1984; Vol. 18, Chapter 4.
- (4) Eichenberger, E. In *Metal Ions in Biological Systems*; Sigel, H., ed.; Marcel Dekker: New York, 1986; Vol. 20, Chapter 3.
- (5) Whitlow, S. H. *Inorg. Chem.* 1973, 12, 2286.
- (6) Rajabalee, F. J. M. *J. Inorg. Nucl. Chem.* 1974, 36, 557.
- (7) Niclós Gutiérrez, J.; González García, S.; Niclós Gutiérrez, E.; González Pérez, J. M.; Nguyen-Huy Dung; Viossat, B. Paper presented at the XXI Reunión Biental Real Sociedad Española Química, Symposium de Química de la Coordinación, Santiago de Compostela, Spain, 1986; Report No. 18-039.
- (8) Nguyen-Huy Dung; Viossat, B.; Busnot, A.; González Pérez, J. M.; Niclós Gutiérrez, E.; Niclós Gutiérrez, J. Paper presented at the 3rd International Conference on Bioinorganic Chemistry, Noordwijkerhout, The Netherlands, 1987.