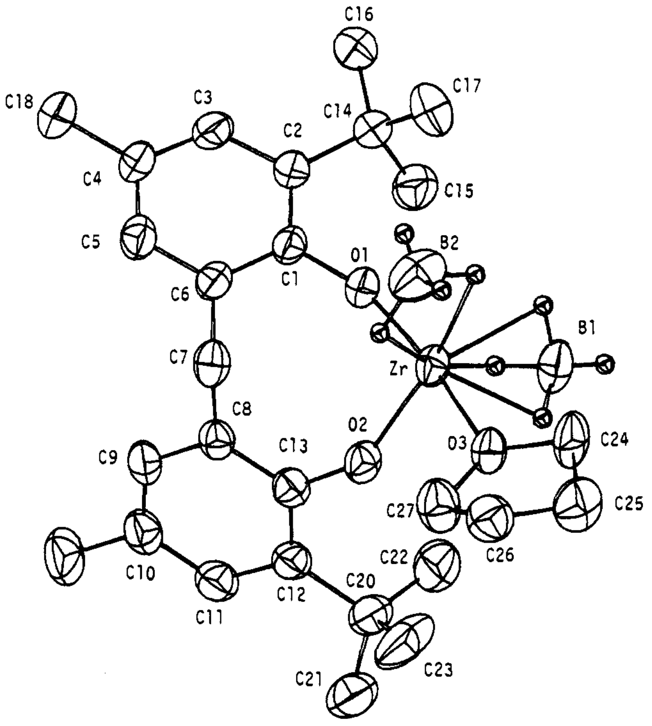

Figure 4. ORTEP drawing of complex **4** (30% probability ellipsoids).

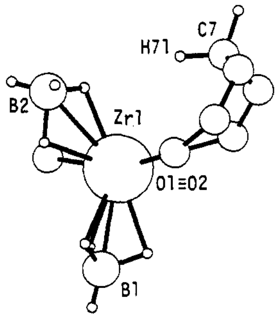

Figure 5. Projection of the chelation ring onto the plane perpendicular to the O1···O2 line.

rings is 68.8 (2)°.

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Supplementary Material Available: Complete listings of crystallographic data, fractional atomic coordinates for hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for complexes **2** and **4** (10 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of (Trifluoroethoxy)boranes[1]

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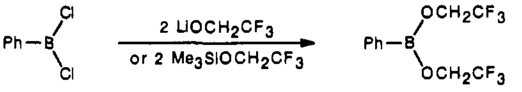
Introduction

The preparative chemistry of several types of boron–nitrogen compounds, especially those containing Si–N–B, B–N–B, and/or P–N–B linkages, is under current investigation in our laboratory.[2] Many of these compounds are of interest either as possible precursors to or structural and stereochemical models[3] for B–N polymer systems. As an aspect of these overall studies, we report here on the synthesis and characterization of several new reagents that should be useful for the introduction of *N*-boryl functional groups into such compounds. In particular, various (*trifluoroethoxy*)boranes were selected as target compounds for synthesis, since the OCH_2CF_3 group is known to be an excellent leaving group in condensation polymerizations [e.g., poly(phosphazenes)].[4]

Results and Discussion

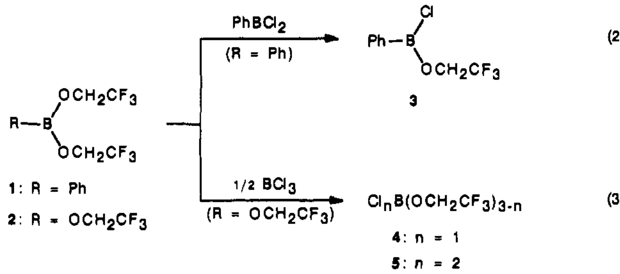
The new bis(trifluoroethoxy)borane **1** was prepared via the reaction of $PhBCl_2$ with 2 equiv of lithium trifluoroethoxide. Compound **1** was obtained in 61% yield as a colorless liquid that was characterized by NMR (^1H, ^{13}C, and ^{11}B) spectroscopy (Table I) and elemental analysis (Table II). Alternatively, **1** could be prepared (in 81% yield) via the Si–O cleavage reaction of $PhBCl_2$ with $Me_3SiOCH_2CF_3$ (eq 1). In a similar manner, treatment



(1)

of BCl_3 with $LiOCH_2CF_3$ in a 1:3 mole ratio afforded tris(trifluoroethoxy)borane, $(CF_3CH_2O)_3B$ (**2**), in 36% isolated yield. A satisfactory elemental analysis of **2** was not obtained, however, due to the presence of a small amount of an unidentified impurity that could not be removed by fractional distillation.

The desired chlorinated derivatives of these alkoxyboranes were prepared by means of ligand exchange with the appropriate chloroboranes. This type of reaction is well-known in aminoborane chemistry, for example, in the preparation of $ClB(NMe_2)_2$ from $B(NMe_2)_3$ and BCl_3.[5] Thus, treatment of **1** and **2** with $PhBCl_2$ and BCl_3, respectively, in the appropriate proportions afforded the chloro(trifluoroethoxy)boranes **3**–**5** as colorless, moisture-sensitive liquids (eqs 2 and 3). Compound **3** (eq 2) was isolated



(2)

(3)

in 95% yield and was fully characterized by NMR spectroscopy and elemental analysis (Tables I and II). In an alternate attempt to synthesize **3**, a neat sample of $PhBCl_2$ was treated with an equimolar amount of $Me_3SiOCH_2CF_3$. This process resulted in a nearly 1:1 mixture of mono-(**3**) and disubstituted (**1**) products from which **3** could not be isolated in pure form. The ligand-exchange reaction of the tris(trifluoroethoxy) derivative **2** with $^1/_2$ equiv of BCl_3 (eq 3) also resulted in a mixture (of unreacted **2** and the chloroboranes **4** and **5**) instead of only the monosubstituted product **4** as desired. In this case, however, compound **4** was isolated in 36% yield by fractional distillation as a very air-sensitive, colorless liquid.

The reactivity of compound **3** was studied in order to test its usefulness for transferring the $PhB(OCH_2CF_3)-$ moiety to other substrates such as the diazoboracyclohexane ring. Two types of

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[1] Taken in part from: Shaw, S. Y. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1988.

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Table I. NMR Spectroscopic Data^a for (Trifluoroethoxy)boranes

		^{1}H NMR		^{13}C NMR		^{11}B NMR
compd	signal	δ	J_{FH}, Hz	δ	J_{FC}, Hz	δ
$PhB(OCH_2CF_3)_2$ (**1**)	OCH_2	4.42	8.4	62.53	36.4	29.3
	Ph	7.4–7.6^b		129–133^b		
	CF			123.37	277.6	
$B(OCH_2CF_3)_3$ (**2**)	OCH_2	4.17	8.3	62.14	36.8	17.9
	CF_3			123.59	277.4	
$PhB(OCH_2CF_3)Cl$ (**3**)	OCH_2	4.77	8.2	64.84	36.7	38.8
	Ph	7.5–8.0^b		128–135^b		
	CF_3			123.47	277.6	
$ClB(OCH_2CF_3)_2$ (**4**)	OCH_2	4.30	8.3	63.92	37.2	24.4
	CF_3			123.54	277.5	
$Me_2NB(OCH_2CF_3)Ph$ (**6**)	NMe_2	2.54, 2.79^c		35.87, 39.03^c		31.4
	OCH_2	3.90	8.7	64.18	35.0	
	Ph	7.3–7.4^b		128–132^b		
	CF_3			124.45	278.4	
$(Me_3Si)_2NB(OCH_2CF_3)Ph$ (**7**)	Me_3Si	0.88		3.70		37.2
	OCH_2	4.13	8.7	63.56	35.3	
	Ph	7.3–7.4^b		128–133^b		
	CF_3			124.28	277.9	

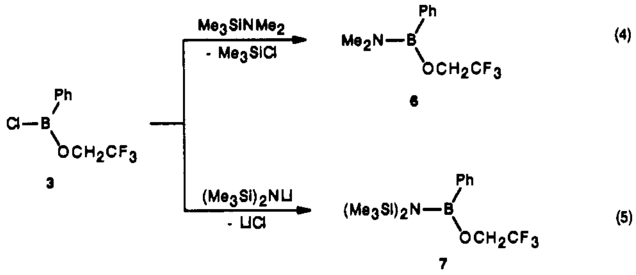
^{a} Proton and ^{13}C chemical shifts downfield from Me_4Si, ^{11}B shifts downfield from Et_2OBF_3; $CDCl_3$ solvent. ^{b} Complex multiplet. ^{c} Hindered B–N bond rotation (see text).

Table II. Preparative and Analytical Data for (Trifluoroethoxy)boranes

			analysis^a	
compd	yield, %	bp, °C/mmHg	% C	% H
1	81^b 61^c	46–52/0.6	42.03 (42.00)	3.03 (3.17)
2	36	55–60/50	*d*	
3	95	43–44/0.2	43.32 (43.20)	3.20 (3.12)
4	36	82–100/760	20.01 (19.66)	2.10 (1.65)
6	89	53–55/2.0	51.65 (51.99)	6.09 (5.67)
7	70	53–59/0.01	48.30 (48.41)	7.26 (7.25)

^{a} Calculated values in parentheses. ^{b} Via method A. ^{c} Via method B. ^{d} Elemental analysis not obtained due to impurity (see text).

reactions were investigated. First, when Me_3SiNMe_2 was added to compound **3**, the aminoborane **6** was obtained in 89% yield (eq 4) as a result of facile cleavage of the Si–N bond by the chloroborane. Second, the nucleophilic substitution reaction of **3** with $(Me_3Si)_2NLi$ afforded **7** in 70% yield (eq 5). Compounds **6** and **7** were isolated as colorless liquids and were fully characterized by NMR spectroscopy and elemental analysis (Tables I and II).



Interestingly, both the ^{1}H and ^{13}C NMR spectra of the dimethylamino derivative **6** contained two distinct signals of equal intensity in the NMe_2 region. These spectral features are clearly indicative of hindered rotation about the B–N bond.[6] A variable-temperature ^{1}H NMR study revealed a coalescence temperature of 106 °C, which corresponds to a free energy of activation of 16.5 kcal/mol. This rotational barrier falls at the lower end of the range of values (17–24 kcal/mol) normally found for *mono*aminoboranes, but it is not significantly different from that of the methoxy analogue, $Me_2NB(Ph)OMe$.[7]

In summary, this work has demonstrated that several boranes containing the trifluoroethoxy group, including synthetically useful unsymmetrical compounds (e.g., **3** and **6**) can be readily prepared via nucleophilic substitution and/or ligand-exchange reactions of chloroboranes. Further studies in which the (trifluoroethoxy)boryl groups are attached to 1,3,2-diazaboracyclohexane rings and other potential polymer precursors will be reported in forthcoming papers.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commerical sources and used without further purification: BCl_3, $(Me_3Si)_2NH$, Me_3SiNMe_2, CF_3CH_2OH, and *n*-BuLi (hexane solution). Ether, CH_2Cl_2, and hexane were distilled from CaH_2, and trifluoroethanol was distilled from BaO prior to use. Phenyldichloroborane was prepared from BCl_3 and Ph_4Sn according to the published procedure.[8] The silyl ether $Me_3SiOCH_2CF_3$ was obtained as a byproduct in the condensation polymerization of *N*-silyl-*P*-(trifluoroethoxy)phosphoranimines such as $Me_3SiN{=}PMe_2OCH_2CF_3$.[4] Proton, ^{13}C, ^{11}B, and variable-temperature NMR spectra were recorded on a Varian XL-300 spectrometer. The coalescence temperature method for determining the B–N rotational barrier in **6** has been previously described.[6c] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

Preparation of $PhB(OCH_2CF_3)_2$ (1) and $B(OCH_2CF_3)_3$ (2). Method A (Compound 1 Only). A 50-mL flask, equipped with gas inlet and a magnetic stirrer, was charged with $PhBCl_2$ (7.3 g, 46 mmol) and cooled to 0 °C. The silyl ether $Me_3SiOCH_2CF_3$ (16.5 g, 96 mmol) was added slowly via syringe, and the mixture was allowed to warm to room temperature and was stirred overnight. Distillation afforded **1** as a colorless liquid.

Method B. Trifluoroethanol (14.6 mL, 200 mmol) was combined with Et_2O (ca. 200 mL) in a 500-mL, 3-necked flask. After the mixture was cooled to 0 °C, *n*-BuLi (80 mL, 200 mmol, 2.5 M) was added from an addition funnel to the solution which was then allowed to warm to room temperature and was stirred for 1 h. After the mixture was recooled to 0 °C, $PhBCl_2$ (15.9 g, 100 mmol) was slowly added via syringe and the resulting mixture was stirred overnight. Distillation through a short path column afforded **1** as a colorless liquid. Compound **2** was prepared in the same manner except that the BCl_3 was first condensed into a precalibrated round-bottomed flask and was then allowed to condense into the stirred suspension of $LiOCH_2CF_3$ at -78 °C.

Preparation of Chloro(trifluoroethoxy)boranes 3–5. In a 50-mL, one-necked flask, $PhB(OCH_2CF_3)_2$ (**1**) (12.4 g, 43 mmol) was combined at 0 °C with an equimolar amount of $PhBCl_2$ (6.9 g, 43 mmol). The mixture, which turned slightly yellow, was stirred overnight. Distillation

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[6] See, for example, the following and references cited therein: (a) Li, B.-L.; Goodman, M. A.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 1368. (b) Beswick, Y. V.; Wisian-Neilson, P.; Neilson, R. H. *Inorg. Nucl. Chem. Lett.* **1981**, *43*, 2639. (c) Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.

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afforded $PhB(OCH_2CF_3)Cl$ (**3**) as a colorless liquid in 95% yield. The mixture of compounds (**2**, **4**, and **5**) was prepared in the same manner except that the BCl_3 ($^1/_2$ equiv) was condensed into a solution of $(CF_3CH_2O)_3B$ (**2**) in pentane at −78 °C. Distillation through a 10-cm column afforded a center fraction (bp 82–100 °C/760 mm) that was identified as the monochloroborane **4**.

Preparation of $Me_2NB(Ph)OCH_2CF_3$ (6). The phenylchloroborane **3** (6.5 g, 29 mmol) was combined with dry CH_2Cl_2 (ca. 30 mL) and cooled to 0 °C. Then Me_3SiNMe_2 (4.6 mL, 29 mmol) was slowly added via syringe, and the solution was allowed to warm to room temperature and was stirred overnight. Fractional distillation afforded **6** as a colorless liquid. In a few attempts of this reaction, an unidentified impurity (^1H NMR: δ 2.44) developed during distillation, which could not be removed by repeated distillations.

Preparation of $(Me_3Si)_2NB(Ph)OCH_2CF_3$ (7). A 250-mL, one-necked flask, was charged with $(Me_3Si)_2NH$ (6.3 mL, 30 mmol, 4.8 g) and dry Et_2O (30 mL). After cooling to 0 °C, *n*-BuLi (12 mL, 30 mmol, 2.5 M) was slowly added. The solution was allowed to warm to room temperature, stirred for 30 min, and then recooled to 0 °C. Compound **3** (6.7 g, 30 mmol) was added dropwise to the cold anion slurry. The mixture was stirred overnight, then filtered under nitrogen to remove LiCl. The solvents were removed under reduced pressure. Distillation afforded **7** as a colorless liquid.

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Contribution from the Dipartimento di Chimica Industriale e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Pz. L. da Vinci 32, 20133 Milano, Italy, Dipartimento di Chimica Organica Industriale, Università di Milano, Via Venezian 21, 20131 Milano, Italy, and Istituto di Fotochimica e Radiazioni di Alta Frequenza del CNR, Sezione di Legnaro, Via Romea 4, 35020 Legnaro, Padova, Italy

Complexes of Hexaphenoxycyclotriphosphazene and Sulfur Trioxide

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and Maria C. Gallazzi[†]

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Introduction

Most of the known addition compounds[1-3] of cyclotriphosphazene, $(NPX_2)_3$, involve halogen (X = F, Cl, Br) and alkylamino (X = NHR, NR_2) substituted derivatives, as ligands, and the acceptor coordinated to the ring nitrogen. The aryloxy derivatives (X = OAr) have not been studied as much. On the basis of ^{31}P NMR spectroscopic data and relative basicity arguments, Horn and Kolkmann[4] concluded that hexaphenoxycyclotriphosphazene, $[P(OAr)_2{=}N]_3$ (II), yields an addition compound with BCl_3 and that the metal halide coordinates to the endocyclic nitrogen of the phosphazene rather than to the exocyclic oxygen. On the other hand, alkylation studies of substituted cyclotriphosphazenes[5] suggest that the phenoxy substituents reduce (or mask), by steric effects, the basicity of the endocyclic nitrogen and, thus, favor the reaction at the pendent substituent. Finally, in the sulfonation of the linear polymer[6] $[-NP(OAr)_2-]_{15000}$ (I), the electrophilic attack of N by SO_3 is probably the first reaction step:

$$-P(OAr)_2{=}N- + SO_3 \rightarrow -P(OAr)_2{=}N{\cdot}(SO_3)- \qquad (1)$$

Using II to mimic[7] the reactivity of the high polymer I, we expected in this spectroscopic study to find direct evidence of the favored coordination site in the $-NP(OAr)_2-$ moiety.

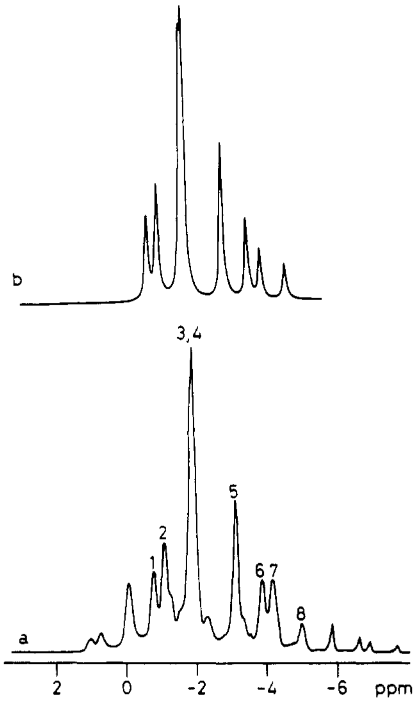

Figure 1. Simulated (b) and experimental (a) ^1H-decoupled ^{31}P NMR spectra of complex V (SO_3/II mole ratio = 3.0) recorded in CH_2Cl_2 at 80.961 MHz and at −90 °C. Signals 1–8 identify the resonance pattern coincident with the simulated spectra. Other signals are discussed in text.

Experimental Section

Sulfur trioxide[8] and II[9] were obtained as previously reported. All other reagents are C. Erba RPE products.

II (1 g) was dissolved in 5 mL of a chlorinated solvent (*sym*-dichloroethane, $CDCl_3$, $CHCl_3$, CH_2Cl_2 or CD_2Cl_2) at $-30 \geq T$ (°C) ≤ 0, and SO_3 was added [$0.5 \leq SO_3$/II (mol/mol) ≤ 3.0] under N_2 and stirring. The system was then kept at room temperature for 3 h and filtered to separate some deposited solid material (≤5 wt % initial II). The solid, washed with fresh solvent and dried under vacuum, was found to be soluble in water and to contain organic sulfur by total sulfur-inorganic sulfur analysis.[8a] The filtrate was analyzed by IR and NMR spectroscopy, as such and after addition of 1,4-dioxane. Duplicate mixtures were made at each mole ratio as above, and 30 mL of water was added at the end of the reaction time. The aqueous phase was separated from the organic layer and then extracted twice with equal volumes of the fresh organic solvent. Evaporation of the combined organic extracts to dryness left a residue (95–98 wt % initial II). This residue was identified as II by its IR and NMR spectra, which were identical with those of an authentic sample.

The IR spectra (AgCl plates; liquid films) were recorded under nitrogen by using a Perkin-Elmer 782 spectrometer. ^1H NMR spectra were recorded on a WP-80 Bruker spectrometer operating in the Fourier transform mode at 80 MHz. The ^{13}C and ^{31}P NMR spectra were recorded by using a Varian XL-200 spectrometer at 50.288 and 80.961 MHz, respectively. ^1H and ^{13}C chemical shifts [$\delta(^1H)$ and $\delta(^{13}C)$, ppm] are referred to internal TMS. ^{31}P chemical shifts [$\delta(^{31}P)$, ppm] are

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