3034 *Inorg. Chem.* **1992**, *31*, 3034–3043

Synthesis, Properties, and Ring–Ring Transformation Reactions of Cyclic Siloxanes Incorporating Skeletal Boron Atoms: X-ray Crystal Structures of the Strained Boracyclotrisiloxane $(PhBO)(Ph_2SiO)_2$ and the Boracyclotetrasiloxane $(PhBO)(Ph_2SiO)_3$

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The cyclic boratrisiloxanes $(PhBO)(RR'SiO)_2$ (**1**, R = R′ = Me; **2**, R = Me, R′ = Ph; **3**, R = R′ = Ph) have been prepared via the reaction of the dichlorodisiloxanes 1,3-ClRR′SiOSiRR′Cl with phenylboric acid in the presence of NEt_3 as an HCl acceptor. Similar procedures using the appropriate α,ω-dichlorosiloxanes $ClMe_2Si(OSiMe_2)_nOSiMe_2Cl$ (n = 1 or 2) afforded the boracyclotetrasiloxane $(PhBO)(Me_2SiO)_3$ (**4**) and the boracyclopentasiloxane $(PhBO)(Me_2SiO)_4$ (**5**). The boracyclotetrasiloxane $(PhBO)(Ph_2SiO)_3$ (**8**) was isolated in low yield from the reaction of 2:1 excess of 1,3-$ClPh_2SiOSiPh_2Cl$ with $PhB(OH)_2$ in the presence of NEt_3. The cyclic borasiloxanes **1** and **3** undergo extensive ring–ring transformation reactions when heated at elevated temperatures in the presence of small quantities of $K[OSiMe_3]$. Similar reactions were detected in solution in the presence of acid or base catalysts. The products of these reactions mainly consist of larger rings containing a single boron atom, together with cyclic and polymeric siloxanes and the boroxin $[PhBO]_3$. Similar, but slower, ring–ring redistribution reactions were detected for the boracyclotetrasiloxane **4**. These results are consistent with the presence of additional strain in borasiloxanes containing a six-membered ring. This analysis was supported by a comparison of X-ray structural data obtained for **3** with that for **8**. Thus, the boracyclotrisiloxane **3** was found to possess a highly strained six-membered ring with considerable bond angle distortion whereas the nonplanar eight-membered ring present in **8** is appreciably less strained. Crystals of **3** are monoclinic, space group $C2/c$, with a = 15.703 (6) Å, b = 10.864 (3) Å, c = 17.733 (4) Å, β = 119.14 (2)°, V = 2641 (14) Å^3, and Z = 4. Crystals of **8** are monoclinic, space group $P2_1/n$, with a = 14.692 (2) Å, b = 13.707 (2) Å, c = 19.932 (3) Å, β = 111.38 (0)°, V = 3737.7 (9) Å^3, and Z = 4.

Introduction

Ring-opening polymerization represents a powerful synthetic route to a variety of organic polymers such as polyamides, polyethers, polycycloolefins, and, most recently, polyacetylenes and polycarbonates.[1] In view of the abundance and the structural diversity of known cyclic inorganic compounds, ring-opening polymerization might be expected to provide access to a similar or even broader range of inorganic macromolecules.[2] However, although the polymerization behavior of cyclic siloxanes and cyclic phosphazenes has been well explored and the ring-opening polymerization of species such as $[Me_2SiO]_n$ (n = 3 or 4) and $[NPCl_2]_3$ provides routes to two of the most important inorganic polymer systems, the polysiloxanes (silicones) and polyphosphazenes, relatively few other inorganic ring systems have been studied in detail.[3–5]

The present state of knowledge indicates that the relationship between inorganic ring structure and observed polymerization behavior is complex. Thus, several inorganic ring systems have been found to preferentially undergo ring–ring interconversions rather than linear polymer formation. For example, the eight-membered boron–nitrogen ring $[t\text{-}BuBNMe]_4$ undergoes a reversible, thermally induced ring-contraction reaction to afford the four-membered heterocycle $[t\text{-}BuBNMe]_2$ at 70 °C.[6] By contrast, the ferrocenylcyclotriphosphazene $N_3P_3(OPh)_4(\eta\text{-}C_5H_4)_2Fe$ undergoes ring expansion to yield a twelve-membered ring at 250 °C, as does the thiophosphazene six-membered ring $(NPPh_2)_2\{NS(NMe_2)\}$ in solution at room temperature.[7,8] Interestingly, the cyclic thionylphosphazene $(NPCl_2)_2(NSOCl)$ undergoes thermally induced ring-opening polymerization without the formation of appreciable amounts of new cyclic species, whereas certain compounds such as the halogenophosphazene $[NPCl_2]_3$ undergo *both* ring–ring transformations and ring-opening polymerization at elevated temperatures.[9,10]

As part of a broad program to explore the relationship between the structure and polymerization behavior of cyclic inorganic compounds, we are investigating heterocyclosiloxanes. These species are formally derived from conventional cyclosiloxanes

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(1) (a) *Ring Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984. (b) *Ring Opening Polymerization*; McGrath, J. E., Ed.; ACS Symposium Series 286; American Chemical Society: Washington DC, 1985. (c) Grubbs, R. H.; Tomas, W. *Science* **1989**, *243*, 907 and references therein. (d) Brunelle, D. J.; Evans, T. L.; Shannon, T. G.; Boden, E. P.; Stewart, K. R.; Fontana, L. P.; Bonauto, D. K. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1989**, *30* (2), 569.

(2) *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: Toronto, 1987.

(3) For a recent review on siloxanes, see for example Saam, J. C. In *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G. Eds.; Advances in Chemistry 224, American Chemical Society: Washington DC, 1990; see also references therein.

(4) For a recent review on phosphazenes, see for example Allcock, H. R. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, D.C. 1988; see also references therein.

(5) The ring-opening polymerization of cyclic silanes has also been recently reported. See: Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046.

(6) Delpy, K.; Meier, H. U.; Paetzold, P.; von Plotho, C. *Z. Naturforsch.* **1984**, *39b*, 1696.

(7) (a) Manners, I.; Riding, G. H.; Dodge, J. A.; Allcock, H. R. *J. Am. Chem. Soc.* **1989**, *111*, 3067. (b) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596.

(8) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702.

(9) (a) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. (b) Liang, M.; Angelakos, T.; Manners, I. Manuscript in preparation.

(10) Allcock, H. R.; McDonnell, G. S.; Desorcie, J. L. *Inorg. Chem.* **1990**, *29*, 3839.

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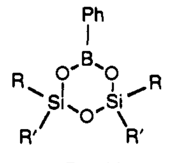
via the replacement of a skeletal silicon atom by an atom of another main group element or a transition metal.[11,12] Compared to cyclic siloxanes, very few attempts to polymerize heterocyclosiloxanes have been reported.[13] Studies of these compounds should provide valuable insight into how the presence of different skeletal atoms influences polymerizability. Furthermore, successful ring-opening polymerization of heterocyclosiloxanes would provide a route to new inorganic polymers which should display interesting and potentially useful properties.[14,15]

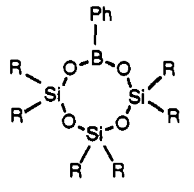
In this paper we discuss in detail our studies on cyclosiloxanes in which a skeletal silicon atom has been replaced by boron. The covalent radius of a boron atom (0.80 Å) is considerably smaller than that of silicon (1.17 Å) and so the replacement of silicon by boron in a siloxane ring might be expected to significantly affect the ring-strain present and hence the polymerization behavior detected.[16,17]

Results and Discussion

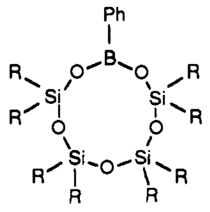
Synthesis and Characterization of Boracyclotrisiloxanes (PhBO)(RR'SiO)$_2$ (1, R = R' = Me; 2, R = Me, R' = Ph; 3, R = R' = Ph). The first aim of the work was to prepare a range of cyclic borasiloxanes of different ring size and therefore of varying ring strain. Access to borasiloxanes containing six-membered rings represented an important target as, by analogy with cyclic siloxanes, these species would be expected to be the most strained. The only example of a well-characterized borasiloxane compound containing a six-membered ring is PhBO(Me$_2$SiO)$_2$ (**1**) which was prepared by Wannagat and Eisele.[18] The synthesis of this species was achieved via the (3+3) cyclocondensation reaction of 1,3-dichlorotetramethyldisiloxane with phenylboric acid in the presence of triethylamine as a hydrogen halide acceptor. Interestingly, compound **1** represents the only well-characterized example of a neutral heterocyclosiloxane containing a discrete, uncomplexed six-membered ring.[19] Synthetic routes which would be expected to yield a six-membered ring product usually result in the isolation of less strained eight-membered ring products.[20]



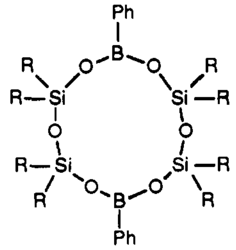
1, R = R' = Me
2, R = Me, R' = Ph
3, R = R' = Ph



4, R = Me
8, R = Ph



5, R = Me
9, R = Ph



6, R = Me
7, R = Ph

In our work we also prepared compound **1** by the (3+3) cyclocondensation route reported by Wannagat. The pure product was isolated in moderate yield as a low-melting-point, colorless solid after repeated vacuum distillation. We also used an analogous cyclocondensation procedure to prepare the two boracyclotrisiloxanes PhBO(MePhSiO)$_2$ (**2**) and PhBO(Ph$_2$SiO)$_2$ (**3**). In comparison to **1**, the borasiloxanes **2** and **3** were formed in higher yield and were markedly easier to isolate and purify. Product **2**, which was isolated as an inseparable mixture of cis and trans isomers, was only partially solid at room temperature. Compound **3**, on the other hand, was isolated as a colorless crystalline material.

The new compounds **2** and **3** were characterized by ^{11}B, ^{29}Si, ^{1}H, and ^{13}C NMR, mass spectrometry, elemental analysis, and, in the case of **3**, X-ray crystallography. The ^{11}B, ^{29}Si, and ^{13}C NMR spectra of **1** were also determined, as these were not previously reported. The ^{11}B NMR spectra of **1**–**3** consisted of extremely broad, singlet resonances ($\nu_{1/2}$ = 400 Hz) with chemical shifts at ca. 28 ppm which are typical for boron centers bonded to two oxygen atoms. However, these spectra were otherwise rather uninformative as virtually no significant chemical shift differences were detected between the individual species **1**–**3**. By contrast, ^{29}Si NMR spectroscopy provided an extremely useful tool for characterizing and monitoring the chemistry of these species. Thus, the ^{29}Si NMR spectrum of **1** (in CDCl$_3$) consisted of a singlet resonance at −3.3 ppm, which is at slightly lower field than that of [Me$_2$SiO]$_3$ (δ = −9.0 ppm). The ^{29}Si NMR resonances of **2** (δ = −16.5 ppm) and **3** (δ = −30.8 ppm) were also similarly shifted to slightly lower field compared to those of their cyclosiloxane counterparts ([MePhSiO]$_3$, δ = −20.6 ppm; [Ph$_2$SiO]$_3$, δ = −33.0 ppm). The high-field ^{1}H and ^{13}C NMR spectra of **2** and **3** also provided useful characterization. For example, ^{1}H NMR assignments in the phenyl region and assignments of the ^{13}C resonances to the carbon atoms of the phenyl groups bonded to boron and silicon were possible by comparison with the ^{1}H and ^{13}C spectra of [PhBO]$_3$ and [Ph$_2$SiO]$_3$. This is illustrated by the ^{13}C NMR spectrum of compound **3** shown in Figure 1 where the expected 1:4 ratio for the intensities of the ^{13}C resonances arising from the carbon atoms of the phenyl groups attached to boron compared to those bonded to silicon is detected. Interestingly, the ^{29}Si NMR signal for

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[11] For recent work on heterocyclosiloxanes, see for example (a) Haoudi-Mazzah, A.; Mazzah, A.; Schmid, H.; Noltemeyer, M.; Roesky, H. W. *Z. Naturforsch.* **1991**, *46b*, 587. (b) Hossain, M. A.; Hursthouse, M. B.; Mazid, M. A.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1305. (c) Hursthouse, M. B.; Hossain, M. A. *Polyhedron* **1984**, *3*, 95. (d) Hursthouse, M. B.; Mazid, M. A.; Motevalli, M.; Sanganee, M.; Sullivan, A. C. *J. Organomet. Chem.* **1990**, *381*, C43. (e) Graalman, O.; Meyer, M.; Klingebiel, U. *Z. Anorg. Allg. Chem.* **1986**, *534*, 109. (f) Hossain, M. A.; Hursthouse, M. B.; Ibrahim, A.; Mazid, M. A.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1989**, 2347 and references therein. (g) Mazzah, A.; Haoudi-Mazzah, A.; Noltemeyer, M; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 93.

[12] A number of remarkable three-dimensional heterosiloxane species have also been recently reported. See for example (a) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850. (b) Levitsky, M. M.; Schegolikhina, O. I.; Zhdanov, A. A.; Igonin, V. A.; Ovchinnikov, Y. E.; Shklover, V. E.; Struchkov, Y. T. *J. Organomet. Chem.* **1991**, *401*, 210.

[13] See: Borisov, S. N.; Voronkov, M. G.; Lukevits, E. Y. *Organosilicon Heteropolymers and Heterocompounds*; Plenum: New York, 1970; see also references therein.

[14] Polymers referred to as "polyborasiloxanes" have attracted widespread interest as "bouncing putty". However, the structure of these intriguing materials is not well understood. See ref 13 for details on these and other reported heterosiloxane polymers.

[15] The ring-opening polymerization of cyclic phosphazenes which incorporate other elements has recently provided access to a variety of new polymer systems. See for example ref 9 and (a) Roesky, H. W.; Lucke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (b) Manners, I.; Renner, G.; Allcock, H. R.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (c) Allcock, H. R.; Coley, S. M.; Manners, I.; Renner, G.; Nuyken, O. *Macromolecules* **1991**, *24*, 2024. (d) Dodge, J. A.; Manners, I.; Renner, G.; Allcock, H. R.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268.

[16] (a) A preliminary report of the X-ray structure of 3 has appeared. See: Foucher, D. A.; Lough, A. J.; Manners, I. *J. Organomet. Chem.* **1991**, *414*, C1. (b) Presented, in part, at the 6th International Symposium on Inorganic Ring Systems held at Berlin, August 1991.

[17] Stark, J. G.; Wallace, H. G. *Chemistry Data Book*; John Murray: London, 1975.

[18] Wannagat, U.; Eisele, G. *Z. Naturforsch.* **1978**, *33b*, 475.

[19] An anionic species containing zirconatrisiloxane six-membered rings has been characterized crystallographically; see: Hossain, M. A.; Hursthouse, M. B. *Inorg. Chim. Acta* **1980**, *44*, L259. Other uncomplexed six-membered rings have been reported, but pure compounds are seldom isolated and little structural characterization data is given. For work on borasiloxanes, see for example Bhardwaj, P. N.; Srivastava, G. *J. Indian Chem. Soc.* **1982**, *59*, 300.

[20] See for example ref 11b,f.

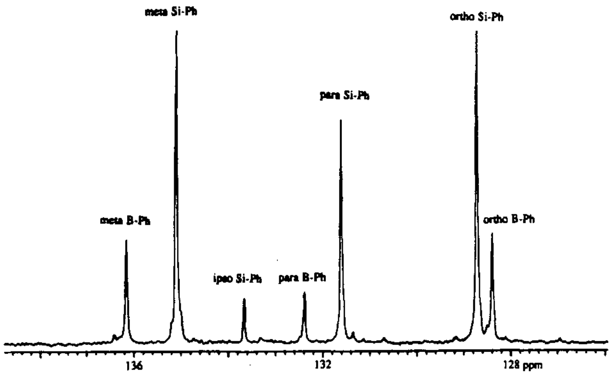

Figure 1. ^{13}C NMR spectrum (100.5 MHz) of 3 in $CDCl_3$.

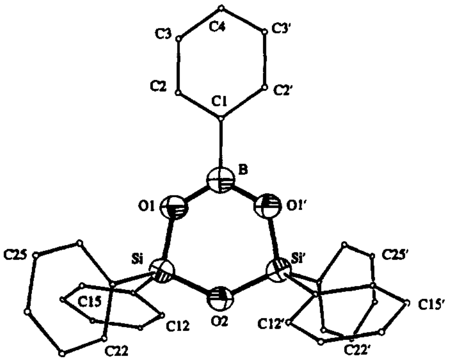

Figure 2. Molecular structure of 3.

compound 2 appears as a singlet, while both the ^{13}C and the ^{1}H NMR spectra indicate the presence of both the cis and trans isomers, with an approximate 45% cis:55% trans ratio based on ^{1}H NMR integration.[21] High-resolution 2D $^{29}Si/^{1}H$ NMR HETCOR experiments revealed a very small ^{29}Si chemical shift difference between the two isomers of approximately 0.05 ppm. This suggests that the environments of the phenyl and methyl groups differ more in the two isomers than the environments of the silicon atoms, as would be expected from geometrical considerations. The mass spectra of 2 and 3 showed the presence of molecular ions and intense peaks arising from loss of a methyl group or phenyl group. Elemental analysis data for 2 and 3 were consistent with the assigned structures. The six-membered ring borasiloxanes 1–3 are indefinitely stable in the pure state and appear unaffected by atmospheric moisture. However, the compounds slowly hydrolyze when dissolved in moist solvents.

In order to examine the structural changes arising from the replacement of a skeletal silicon atom in a cyclotrisiloxane by boron and in view of the lack of any crystallographic data on neutral uncomplexed heterosiloxane six-membered rings, an X-ray diffraction study of a single crystal of 3 was undertaken.[22]

X-ray Structure of $(PhBO)(Ph_2SiO)_2$ (3). Single crystals of 3 suitable for an X-ray diffraction study were grown by cooling a solution of the compound in a 1:1 mixture of dichloromethane and hexanes to –6 °C for 24 h.

The molecular structure of 3 is shown in Figure 2. Molecules of 3 were found to lie on a crystallographic 2-fold axis parallel to the y-axis. A summary of cell constants and data collection parameters is included in Table I. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables II and III, respectively.

Table I. Summary of Crystal Data and Intensity Collection Parameters

	3	8
formula	$C_{30}H_{25}BO_3Si_2$	$C_{42}H_{35}BO_4Si_3$
fw	500.5	698.79
cryst size, mm	0.3 × 0.3 × 0.5	0.2 × 0.18 × 0.21
space group	$C2/c$	$P2_1/n$
a, Å	15.703 (6)	14.6920 (20)
b, Å	10.864 (3)	13.7070 (20)
c, Å	17.733 (4)	19.932 (3)
β, Å	119.14 (2)	111.38 (1)
V, Å^3	2641(14)	3737.9 (9)
Z	4	4
D(calcd), gm/cm^3	1.26	1.24
θ range, deg	1–27	1–25
octants collected	$(\pm h,k,l)$	$(\pm h,k,l)$
μ, cm^{-1}	1.6	1.6
ω scan width ($A = 0.35 \tan \theta$), deg	0.8	0.6
total no. of data measured	2963	7073
R_{int}	0.019	0.027
no. of unique data measured	2874	6570
no. of data used [$I > 3\sigma(I)$]	2152	3558
no. of params	215	451
R, R_w	0.037, 0.048	0.048, 0.050
GOF	3.20	1.38
(Δ/σ)(max) in last cycle	0.070	0.001
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.29	0.28
final g wtg scheme	0.000 05	0.0004

Table II. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for the Non-Hydrogen Atoms of 3[a]

atom	x	y	z	U(eq)
Si	0.097 39 (3)	0.234 03 (4)	0.258 04 (3)	0.3808 (28)
O(1)	0.082 13 (9)	0.382 31 (11)	0.263 64 (9)	0.0451 (7)
O(2)	0.0	0.166 98 (14)	0.25	0.0427 (9)
B	0.0	0.444 59 (24)	0.25	0.0382 (13)
C(1)	0.0	0.588 36 (22)	0.25	0.0393 (12)
C(2)	0.086 38 (15)	0.654 60 (18)	0.279 52 (15)	0.0493 (10)
C(3)	0.086 23 (17)	0.781 19 (19)	0.280 27 (18)	0.0597 (13)
C(4)	0.0	0.844 42 (25)	0.25	0.0627 (18)
C(11)	0.206 70 (14)	0.179 47 (16)	0.355 84 (13)	0.0425 (9)
C(12)	0.203 31 (16)	0.121 58 (19)	0.424 00 (14)	0.0517 (11)
C(13)	0.287 93 (18)	0.084 38 (22)	0.496 31 (16)	0.0591 (13)
C(14)	0.376 40 (18)	0.104 81 (26)	0.501 82 (16)	0.0609 (14)
C(15)	0.382 19 (19)	0.162 4 (3)	0.435 97 (21)	0.0780 (18)
C(16)	0.297 90 (17)	0.198 73 (25)	0.363 23 (17)	0.0646 (14)
C(21)	0.110 85 (13)	0.203 99 (17)	0.161 63 (13)	0.0430 (9)
C(22)	0.103 45 (19)	0.084 63 (22)	0.131 18 (17)	0.0709 (14)
C(23)	0.116 05 (23)	0.058 10 (26)	0.060 92 (20)	0.0812 (17)
C(24)	0.136 66 (20)	0.150 12 (27)	0.020 23 (17)	0.0726 (16)
C(25)	0.145 61 (19)	0.267 67 (27)	0.049 03 (17)	0.0733 (15)
C(26)	0.132 14 (15)	0.295 18 (20)	0.119 24 (15)	0.0550 (12)

[a] $U(eq) = (U_{11} = U_{22} = U_{33})/3$.

The X-ray crystal structure of 3 confirmed the presence of a six-membered BSi_2O_3 ring. Analysis of the structural data indicates that the structural consequences of replacing a silicon atom (covalent radius 1.17 Å) by a smaller boron atom (covalent radius 0.80 Å) are very significant. This causes an appreciable decrease of 0.26 Å in the distance between the two oxygen atoms O1 and O1′ compared to the situation in $[Ph_2SiO]_3$.[23] This contraction can be readily appreciated by noting the nonparallel nature of the Si–O1 and Si′–O1′ bonds (see Figure 2). The enforced decrease in the O1–O1′ distance leads to a marked contraction of the Si–O2–Si′ bond angle to 127.1 (1)° compared to the value of 131.8 (8)° in $[Ph_2SiO]_3$. The presence of appreciable angle strain in 3 is further emphasized by a consideration of the much larger Si–O–Si bond angles found in unconstrained, linear disiloxanes such as $Me_3SiOSiMe_3$ [148.8 (1)°] or in essentially unstrained cyclic siloxanes such as $[Ph_2SiO]_4$

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(21) This ratio is based on the assumption that the trans product forms in higher yield for steric reasons.

(22) To the best of our knowledge, no X-ray crystallographic data exist for neutral, uncomplexed cyclotrisiloxanes in which a skeletal silicon atom is replaced by an atom of a heteroelement. A number of interesting metallosiloxanes have recently been studied by X-ray crystallography, but in neutral species where six-membered rings are present, coordination to skeletal oxygen atoms is observed. See, for example, ref 11d.

(23) Bokii, N. G.; Zakharova, G. N.; Struchov, Y. T. *Zh. Strukt. Khim.* **1972**, *13*, 291.

Table III. Selected Distances (Å) and Angles (deg) in the Six-Membered Ring $(PhBO)(Ph_2SiO)_2$ (**3**) with the Estimated Standard Deviations (Esd's) on the Last Figure in Parentheses

Distances			
Si–O(1)	1.6388 (13)	B–C(1)	1.562 (4)
Si–O(2)	1.6363 (9)	B–O(1)	1.3696 (20)
Si–C(11)	1.8456 (22)		
Si–C(21)	1.8509 (22)		
Angles			
Si–O(2)–Si′	127.13 (10)	O(1)–B–O(1′)	120.79 (21)
O(1)–Si–O(2)	106.55 (8)	O(1)–B–C(1)	119.61 (11)
B–O(1)–Si	128.89 (14)		

[152.3 (2)° and 167.4 (2)°].[24] Another notable feature of **3** is the significant widening of the O1–B–O1′ bond angle to 120.8 (2)° compared to the analogous value in the boroxin $[PhBO]_3$ [118.0 (6)°].[25] Interestingly, the O–Si–O bond angles in **3** [106.55 (8)°] are only slightly different from those found in $[Ph_2SiO]_3$ [107.7 (8)°]. The skeletal B–O bond lengths [1.370 (2) Å] in **3** are only slightly shorter than the average values in the boroxin $[PhBO]_3$ [1.386 (9) Å], and the average Si–O bond lengths [1.637 (1) Å] in **3** are similar to those in $[Ph_2SiO]_3$ [1.64 (1) Å]. This indicates that the appreciable structural distortion caused by the presence of the small boron atom is manifested mainly in changes in bond angles rather than bond lengths. The six-membered BSi_2O_3 ring is approximately planar, with only small (<0.07 Å) deviations from the plane noted for Si1 and O1′. Similar, small deviations from planarity were also found in $[Ph_2SiO]_3$.

Synthesis and Characterization of the Boracyclotetrasiloxane $(PhBO)(Me_2SiO)_3$ (4) and the Boracyclopentasiloxane $(PhBO)(Me_2SiO)_4$ (5). In order to also study less strained cycloborasiloxane rings, the synthesis of eight- and ten-membered rings containing a single boron atom was investigated. A single example of a boracyclotetrasiloxane, $FBO(t\text{-}Bu_2SiO)_2(Me_2SiO)$, has been previously reported, and this species was also characterized by X-ray crystallography.[26] In this case the synthesis involved the reaction of $BF_3 \cdot OEt_2$ with a dilithiated trisiloxanediol. In our work we used a similar cyclocondensation procedure to that yielding the boracyclotrisiloxanes **1**–**3**. Thus, treatment of $PhB(OH)_2$ with 1,5-dichlorohexamethyltrisiloxane in the presence of triethylamine yielded the expected boracyclotetrasiloxane **4** in 74% yield. This species was isolated as a colorless liquid after purification by vacuum distillation. The boracyclopentasiloxane **5** was similarly prepared (but in lower yield) as a colorless, vacuum-distillable liquid by using 1,7-dichlorooctamethyltetrasiloxane as the siloxane starting material.

The products **4** and **5** were readily identified by ^{11}B, ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{11}B NMR spectra showed broad resonances with chemical shifts similar to those of the six-membered rings **1**–**3**. The ^{29}Si NMR spectrum of **4** (in $CDCl_3$) showed two singlet resonances at −16.2 and −17.3 ppm with an approximate intensity ratio of 1:2. The latter resonance was therefore assigned to the silicon atoms closest to boron. The ^{29}Si NMR spectrum of **5** showed two resonances of approximately equal intensity at −18.7 and −19.7 ppm. By analogy to the spectrum of **4**, the high-field resonance was assigned to the silicon atom closest to boron. The ^{1}H and ^{13}C NMR spectra, mass spectra, and elemental analysis data for **4** and **5** were consistent with the assigned structures. For example, the electron-impact mass spectra for these species showed the presence of relatively weak molecular ions but very intense peaks corresponding to the loss of a single methyl group.

Identification of the Diboracyclohexasiloxanes $(PhBO)_2(R_2SiO)_4$ (6, R = Me; 7, R = Ph). Isolation of the Boracyclotetrasiloxane $(PhBO)(Ph_2SiO)_3$ (8). Because of the relatively low isolated yield of **1**, attempts to identify byproducts in the synthesis of this species were made. Analysis of reaction mixtures containing 1,3-dichlorotetramethyldisiloxane, phenylboric acid, and excess triethylamine by ^{29}Si NMR showed that, in addition to **1**, significant amounts of the eight-membered ring **4**, the ten-membered ring **5**, and another species (**6**) are formed. The latter comprised ca. 5% of the reaction mixture by ^{29}Si NMR and is postulated to possess a twelve-membered ring with two skeletal boron atoms. A compound with this structure would be a logical byproduct in the synthesis of **1**. However, this species could not be isolated pure and identified conclusively. Nevertheless, the ^{29}Si NMR resonance assigned to **6** consisted of a singlet resonance at −19.3 ppm, which is consistent with the presence of equivalent silicon atoms. Moreover, the chemical shift value is quite similar to that for the ^{29}Si resonance assigned to silicon atoms closest to boron in the eight-membered ring **4** (−17.3 ppm). Further evidence for the structure of **6** came from mass spectral analysis of the distillation residue after the removal of **1** and $[PhBO]_3$. This showed, in addition to peaks assigned to **4** and **5**, the presence of the molecular ion derived from **6** (*m*/*e* 504) and an intense peak assigned to the molecular ion from **6** after loss of a methyl group (*m*/*e* 489). Importantly, each of the two peaks assigned to **6** possessed the characteristic isotope pattern for a species containing two boron atoms. The preferential formation of **6** relative to **1** would be expected if the synthesis reaction solution was concentrated rather than dilute. Indeed, the yield of **6** was observed to increase to ca. 10% by ^{29}Si NMR under concentrated reaction conditions. However, the purification of this species from the other products was still not possible.

Attempts were also made to synthesize and characterize the phenylated diboracyclohexasiloxane **7**. As expected, this species was also formed in small quantities (ca. 5%) as the only borasiloxane byproduct identified by ^{29}Si NMR during the preparation of **3**. However, as was the case with the methylated diboracyclohexasiloxane **6**, compound **7**, could not be isolated in pure form. Nevertheless, the detection of a singlet ^{29}Si NMR resonance (in C_6D_6) at −43.4 ppm is consistent with this structure. Moreover, the mass spectrum of the product mixture of **3** and **7** showed, in addition to an intense peak at *m*/*e* 500 for the molecular ion derived from **3**, a peak at *m*/*e* 1000 with an isotope pattern characteristic of a species with two boron atoms. In order to facilitate the isolation of pure samples of **7**, prospective high-yield routes to this species were investigated. One route to **7** that was explored involved, first, the attempted synthesis of $PhB(OSiPh_2OSiPh_2Cl)_2$ from $PhB(OH)_2$ and 2 equiv of $ClPh_2SiOSiPh_2Cl$ in the presence of an HCl acceptor, and, second, the reaction of this species with 1 equiv of $PhB(OH)_2$. However, the reaction of $PhB(OH)_2$ with $ClPh_2SiOSiPh_2Cl$ in a 1:2 ratio in the presence of NEt_3 yielded mainly the boracyclotrisiloxane **3**, and a new product identified as the boracyclotetrasiloxane $(PhBO)(Ph_2SiO)_3$ (**8**), together with small amounts of the cyclic siloxane $[Ph_2SiO]_3$. Compound **8** was isolated from this reaction mixture in low yield (10%) by fractional crystallization from ether/hexanes as a colorless crystalline solid. This species was characterized by ^{11}B, ^{29}Si, ^{13}C, and ^{1}H NMR, mass spectrometry, elemental analysis, and X-ray diffraction (see below). The ^{29}Si NMR spectrum of **8** (in C_6D_6) consisted of two singlet resonances and was similar to that detected for the analogous species with methyl groups at silicon (**4**). Thus, the spectrum showed a downfield resonance at −40.3 ppm, and a second resonance of twice the intensity at −42.8 ppm. In a way similar to the ^{29}Si NMR assignments made for **4**, the latter resonance was assigned to the silicon atoms closest to boron.

In order to allow a comparison of the ring strain present in six- and eight-membered ring borasiloxanes, an X-ray diffraction study of the boracyclotetrasiloxane **8** was also undertaken.

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(25) Brock, C. P.; Minton, R. P.; Niedenzu, K. *Acta Crystallogr.* **1987**, *C43*, 1775.

(26) Graalmann, O.; Klingebiel, U.; Clegg, W.; Haase, M.; Sheldrick, G. M. *Z. Anorg. Allg. Chem.* **1984**, *519*, 87.

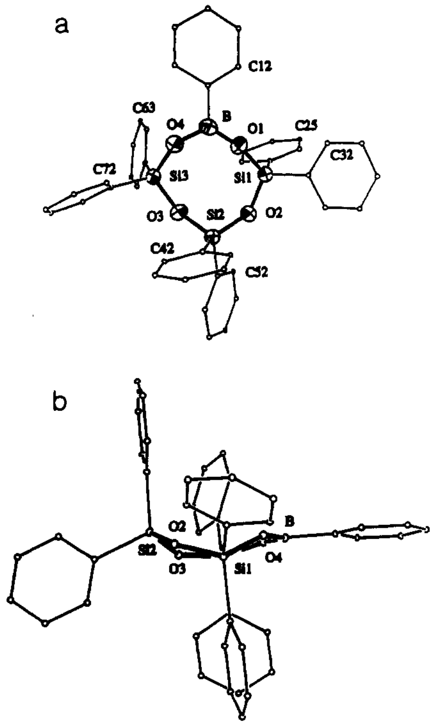

Figure 3. (a) Molecular structure of **8**. (b) A side-on view of a molecule of **8**.

X-ray Structure of $(PhBO)(Ph_2SiO)_3$ (8). Suitable single crystals of **8** were grown from a 1:1 mixture of diethyl ether/hexanes at −15 °C over 1 month.

The molecular structure of **8** is shown in Figure 3a. As the molecule is appreciably nonplanar, a side-on view of the molecule is shown in Figure 3b. A summary of cell constants and data collection parameters is included in Table I. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables IV and V, respectively.

The structural data indicate that the eight-membered ring present in **8** is appreciably less strained than the six-membered ring of **3**. Thus, the Si–O–Si bond angles of **8** [144.7 (2)° and 149.1 (2)°] are much larger than those found in **3** [127.1 (1)°] but are smaller than the Si–O–Si angles found in $[Ph_2SiO]_4$ [152.3 (2)° and 167.4 (2)°].[27] The lower values for the Si–O–Si bond angles in **8** relative to those found in $[Ph_2SiO]_4$ can be attributed to the enforced closer proximity of the two oxygens O1 and O4 bonded to boron compared to the situation where oxygens are bonded to the larger silicon atom. Thus, the oxygen atoms O1 and O4 are ca. 0.25 Å closer together in **8** compared to $[Ph_2SiO]_4$. A similar argument was also used to rationalize the small Si–O–Si angle present in **3**. However, the effect of the enforced proximity of the boron-bound oxygen atoms on the Si–O–Si bond angles in **8** is less dramatic compared to that in **3** because the ring is larger. The Si–O–Si bond angles of **8** are also smaller than those found in a species containing a titanatetrasiloxane ring [146.4 (3)° and 156.0 (3)°] and those found in the only other crystallographically characterized boracyclotetrasiloxane $(FBO)(t\text{-}Bu_2SiO)_2(Me_2SiO)$ [151.3 (1)° and 163.6 (1)°].[26,28] The O–B–O bond angle in **8** [122.1 (4)°] is slightly larger than that of **3** [120.8 (2)°]. The skeletal O–Si–O bond angles of **8** [108.7 (2)°, 110.0 (2)°, and 111.2 (2)°] are significantly larger than those found in **3** [106.55 (8)°] and those found in $[Ph_2SiO]_3$ [107.7 (8)°], but are fairly comparable to those in $[Ph_2SiO]_4$ [average, 109.7 (2)°]. The slight asymmetry of the eight-membered ring in **8** is well illustrated by the different B–O–Si bond angles which are 149.4 (3)° and 148.6 (3)°. A more marked difference in B–O–Si bond angles was found in the boracyclotetrasiloxane $(FBO)(t\text{-}Bu_2SiO)_2(Me_2SiO)$ [159.8 (2)° and 146.6 (1)°]. By contrast, the more symmetrical ring in **3** possesses a

Table IV. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) for the Non-Hydrogen Atoms of **8**[a]

atom	x	y	z	U(eq)
Si(1)	0.987 53 (9)	0.132 37 (9)	0.262 59 (6)	0.039 2 (7)
Si(2)	0.998 03 (8)	0.292 42 (9)	0.156 20 (6)	0.034 6 (7)
Si(3)	1.085 35 (9)	0.420 95 (8)	0.295 06 (6)	0.037 8 (7)
O(1)	0.962 10 (21)	0.209 22 (21)	0.315 43 (15)	0.049 87 (19)
O(2)	0.986 42 (20)	0.187 50 (19)	0.190 47 (14)	0.044 50 (18)
O(3)	1.067 26 (20)	0.362 07 (19)	0.220 26 (13)	0.041 67 (17)
O(4)	1.027 85 (21)	0.369 43 (21)	0.341 61 (15)	0.041 14 (19)
B	0.989 1 (3)	0.287 4 (4)	0.359 7 (3)	0.038 7 (3)
C(11)	0.972 0 (3)	0.285 7 (3)	0.432 32 (22)	0.042 3 (3)
C(12)	0.930 0 (4)	0.206 9 (4)	0.452 73 (24)	0.059 3 (3)
C(13)	0.916 9 (4)	0.203 9 (4)	0.517 7 (3)	0.079 3 (4)
C(14)	0.948 1 (5)	0.279 9 (5)	0.564 9 (3)	0.090 0 (5)
C(15)	0.990 6 (5)	0.358 7 (4)	0.546 7 (3)	0.095 0 (5)
C(16)	1.002 4 (4)	0.361 8 (4)	0.481 1 (3)	0.068 0 (3)
C(21)	1.110 9 (3)	0.083 0 (3)	0.311 99 (21)	0.042 67 (28)
C(22)	1.191 5 (4)	0.144 5 (3)	0.331 0 (3)	0.055 3 (3)
C(23)	1.284 8 (4)	0.114 1 (4)	0.369 4 (3)	0.069 3 (4)
C(24)	1.300 4 (4)	0.018 6 (5)	0.390 0 (3)	0.071 0 (4)
C(25)	1.224 0 (5)	−0.045 6 (4)	0.372 3 (3)	0.069 0 (4)
C(26)	1.130 0 (4)	−0.013 8 (3)	0.334 06 (25)	0.055 7 (3)
C(31)	0.891 3 (3)	0.037 7 (3)	0.235 2 (3)	0.045 3 (3)
C(32)	0.863 1 (4)	−0.011 3 (4)	0.285 8 (3)	0.070 0 (4)
C(33)	0.793 2 (4)	−0.084 0 (4)	0.266 0 (4)	0.087 3 (4)
C(34)	0.749 3 (4)	−0.107 5 (4)	0.195 4 (5)	0.085 7 (5)
C(35)	0.773 6 (4)	−0.061 6 (4)	0.143 6 (3)	0.074 0 (4)
C(36)	0.844 8 (4)	0.010 7 (4)	0.164 1 (3)	0.062 0 (4)
C(41)	0.876 7 (3)	0.347 9 (3)	0.112 52 (21)	0.042 13 (28)
C(42)	0.864 1 (4)	0.447 5 (4)	0.099 5 (3)	0.055 3 (3)
C(43)	0.774 2 (4)	0.488 4 (4)	0.064 4 (3)	0.069 3 (4)
C(44)	0.692 4 (4)	0.431 8 (5)	0.040 1 (3)	0.075 3 (4)
C(45)	0.701 6 (4)	0.333 8 (5)	0.052 2 (3)	0.079 7 (5)
C(46)	0.792 2 (4)	0.293 2 (4)	0.088 2 (3)	0.063 3 (3)
C(51)	1.059 0 (3)	0.270 3 (3)	0.090 84 (21)	0.036 80 (27)
C(52)	1.135 6 (3)	0.205 1 (3)	0.105 72 (25)	0.056 3 (3)
C(53)	1.181 8 (4)	0.188 2 (4)	0.057 4 (3)	0.074 3 (4)
C(54)	1.150 4 (5)	0.236 7 (5)	−0.007 2 (3)	0.081 3 (4)
C(55)	1.074 2 (4)	0.300 9 (4)	−0.023 7 (3)	0.067 7 (4)
C(56)	1.028 9 (3)	0.317 2 (3)	0.024 72 (23)	0.048 7 (3)
C(61)	1.217 1 (3)	0.417 9 (17)	0.348 81 (22)	0.041 03 (28)
C(62)	1.253 8 (4)	0.401 5 (4)	0.422 9 (3)	0.063 3 (4)
C(63)	1.352 1 (5)	0.400 3 (4)	0.462 3 (3)	0.072 3 (4)
C(64)	1.418 6 (4)	0.415 4 (4)	0.430 1 (3)	0.062 7 (4)
C(65)	1.385 4 (4)	0.432 8 (4)	0.357 5 (3)	0.064 3 (4)
C(66)	1.286 9 (4)	0.433 3 (4)	0.317 93 (24)	0.054 3 (3)
C(71)	1.037 8 (3)	0.546 8 (3)	0.273 25 (22)	0.041 0 (3)
C(72)	0.942 0 (4)	0.571 7 (4)	0.263 4 (3)	0.063 7 (4)
C(73)	0.905 9 (4)	0.664 3 (5)	0.241 3 (3)	0.076 0 (4)
C(74)	0.965 1 (5)	0.733 7 (4)	0.229 2 (3)	0.073 0 (4)
C(75)	1.059 6 (5)	0.712 0 (4)	0.239 7 (3)	0.075 0 (4)
C(76)	1.095 4 (4)	0.619 7 (3)	0.261 3 (3)	0.060 0 (3)

[a] $U(\mathrm{eq}) = (U_{11} = U_{22} = U_{33})/3$.

Table V. Selected Distances (Å) and Angles (deg) in the Eight-Membered Ring $(PhBO)(Ph_2SiO)_3$ (**8**) with the Estimated Standard Deviations (Esd's) on the Last Figure in Parentheses

	Distances		
Si(1)–O(1)	1.627 (3)	Si(1)–C(21)	1.848 (4)
Si(1)–O(2)	1.619 (3)	Si(1)–C(31)	1.850 (4)
Si(2)–O(2)	1.628 (3)	B–O(1)	1.352 (6)
Si(2)–O(3)	1.622 (3)	B–O(4)	1.366 (6)
Si(3)–O(3)	1.630 (3)	B–C(11)	1.557 (6)
Si(3)–O(4)	1.626 (3)		
	Angles		
Si(1)–O(2)–Si(2)	144.74 (19)	B–O(1)–Si(1)	148.6 (3)
Si(2)–O(3)–Si(3)	149.12 (20)	B–O(4)–Si(3)	149.4 (3)
O(1)–Si(1)–O(2)	110.02 (15)	O(1)–B–O(4)	122.1 (4)
O(2)–Si(2)–O(3)	108.74 (15)	O(1)–B–C(11)	119.1 (4)
O(3)–Si(3)–O(4)	111.19 (15)	O(4)–B–C(11)	118.8 (4)

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(27) Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr.* **1979**, *B35*, 522.

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much smaller B–O–Si angle of 128.9 (1)° which provides further evidence for the presence of additional bond angle strain in this species. The B–O bond lengths in **8** [1.352 (6) and 1.366 (6) Å] are similar to that in **3** [1.370 (2) Å] but differ significantly from those in $(FBO)(t\text{-}Bu_2SiO)_2(Me_2SiO)$ [1.313 (2) and 1.320 (3) Å]. The Si–O bonds of **8** vary from 1.619 (3) to 1.628 (3) Å and are therefore slightly shorter in length than that found in **3** [1.6388 (13) Å] but slightly longer than those found in $[Ph_2SiO]_4$ [1.604 (3)–1.623 (4) Å]. The ring in **8** is appreciably nonplanar, and the ring conformation can be best described as a distorted boat, with the Si1 and Si3 atoms forming the base and the Si2 atom along with the BO_2 fragment forming the stern and bow. The nonplanarity of the ring is illustrated by the very high value of χ^2 of 108 565 for the weighted least-squares plane through the eight ring atoms. The most significant deviations from the plane are for O4 [0.486 (3) Å], O1 [0.597 (3) Å], and B [0.676 (6) Å]. By contrast, much smaller deviations from planarity are present in $[Ph_2SiO]_4$, with no deviations from the mean plane of the eight-membered ring greater than 0.1 Å.

In summary, comparison of the structure of **8** to that of **3** indicates that the additional strain present in **3** is manifested mainly in bond angle distortion rather than in changes in bond lengths. Thus, the values of the Si–O–Si, B–O–Si, O–B–O, and O–Si–O bond angles are all appreciably smaller in **3** compared to the corresponding values in **8**.

Polymerization Behavior of the Boracyclosiloxanes. Many cyclic siloxanes are known to undergo ring-opening polymerization in the presence of acidic or basic catalysts.[3] We were therefore interested in studying the behavior of the boracyclosiloxanes using conditions under which conventional cyclic siloxanes are known to polymerize. Polymerization experiments were carried out with the six-membered rings **1** and **3** and also the eight-membered ring **4**. These involved reactions either in the melt or in solution and were carried out either in the presence or in the absence of externally added acid or base initiators.

Polymerization Behavior of the Boracyclotrisiloxanes 1 and 3. In order to investigate the polymerization behavior of the boracyclosiloxanes **1** and **3**, thermal reactions in the melt were carried out in the presence of $K[OSiMe_3]$, a well-known catalyst for cyclic siloxane ring-opening polymerization.[3] When **1** or **3** was heated in a sealed tube at elevated temperatures in the presence of small quantities of $K[OSiMe_3]$, analysis of the products by ^{29}Si NMR showed that ring–ring transformation reactions had taken place. The silicon-containing products mainly consisted of larger rings containing a single boron atom. In addition, significant quantities of the cyclic boroxin $[PhBO]_3$ were isolated and identified by ^{13}C NMR and mass spectrometry. For example, in a typical experiment, compound **3** was heated for 3 days at 200 °C in the presence of 1.0 mol % $K[OSiMe_3]$. The ^{29}Si NMR spectrum of the reaction products (Figure 4) showed the presence of unreacted **3** (27%) together with large amounts of the eight-membered ring **8** (42%) and smaller quantities of a new product identified as the ten-membered ring **9** (24%). The ^{29}Si NMR resonances assigned to **9** consisted of two singlets of equal intensity located at slightly higher field than those of the eight-membered ring **8**. This is analogous to the situation for the fully characterized methylated ten-membered ring **5** with respect to the detected ^{29}Si NMR resonance pattern and position relative to the eight-membered ring **4**. The presence of all of the species **3**, **8**, and **9** in the product mixture was confirmed by mass spectrometry which showed molecular ions corresponding to each compound. Very small amounts of the cyclic siloxanes $[Ph_2SiO]_3$ and $[Ph_2SiO]_4$ and the diboracyclohexasiloxane **7** were also detected by ^{29}Si NMR (total ca. 8%; see Figure 4). A similar range of rings was formed when the methylated cyclic **1** was heated in the presence of $K[OSiMe_3]$ at elevated temperatures. However, the equilibration process was found to be significantly more rapid for **1** than for **3**, and lower reaction temperatures were therefore used.

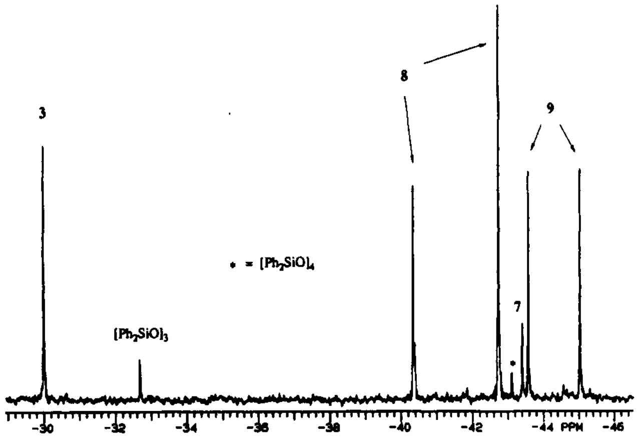

Figure 4. ^{29}Si NMR spectrum (39.7 MHz) (in C_6D_6) of the reaction products after heating compound **3** at 200 °C for 3 days in the presence of 1.0 mol % $K[OSiMe_3]$.

Furthermore, larger quantities of siloxane products were formed. For example, when **1** was heated with 1.0 mol % $K[OSiMe_3]$ at 150 °C for 1.5 h, the products detected by ^{29}Si NMR included unreacted **1** (31%), the eight-membered ring **4** (36%), the ten-membered ring **5** (15%), the cyclic siloxanes $[Me_2SiO]_3$ (3%) and $[Me_2SiO]_4$ (2%), and the diboracyclohexasiloxane **6**, higher cyclic siloxanes, and the polymer $[Me_2SiO]_n$ (in total, ca. 10%). In order to investigate whether the siloxanes together with $[PhBO]_3$ were the thermodynamic products of these equilibration reactions, a sample of **1** was heated with 1.0 mol % $K[OSiMe_3]$ at 150 °C for 7 days. The detected products consisted almost entirely of $[Me_2SiO]_3$, $[Me_2SiO]_4$, and the polymeric siloxane $[Me_2SiO]_n$, together with $[PhBO]_3$. In addition, mainly siloxane and boroxin products were detected when **1** was heated with an increased concentration of $K[OSiMe_3]$ initiator (10 mol %) at 150 °C for 1.5 h. These experiments strongly suggest that the larger ring borasiloxanes detected in the reactions of the six-membered ring species when shorter reaction periods or small amounts of initiator were used are intermediates in the process of ultimately forming siloxanes and extruding boron–oxygen units as $[PhBO]_3$.

Ring–ring transformation reactions were also detected for **1** and **3** in solution in the presence of base. For example, reaction of **1** with 1.0 mol % of either $K[OSiMe_3]$ or BuLi in THF at -80 °C followed by warming to room temperature yielded distributions of ring–ring transformation products by ^{29}Si NMR similar to those formed by **1** in the analogous melt reaction at elevated temperatures. By contrast, reaction of **1** with 1.0 mol % triflic acid in CH_2Cl_2 at -80 °C followed by warming to room temperature yielded the siloxanes $[Me_2SiO]_3$, $[Me_2SiO]_4$, and $[Me_2SiO]_n$ together with $[PhBO]_3$.[29] No larger borasiloxane rings were detected as intermediates. This suggests that cationic initiation is more effective than initiation with base for the redistributive ring–ring transformation reactions of **1** as the reaction proceeds more rapidly to the thermodynamically favored siloxane and boroxin products.

Ring–ring transformation reactions were also detected for **1** and **3** in the melt or in solution in the absence of any externally added initiator. However, in these cases the rates of the reactions were considerably slower. For example, the half-life of **1** in $CDCl_3$ is of the order of a few days whereas for **3** 50% loss of starting material requires several weeks. It is likely that, in the absence of externally added initiator, spurious traces of acid or base function as the redistribution reaction catalysts.

Polymerization Behavior of the Boracyclotetrasiloxane 4. Compound **4** was also heated at elevated temperatures in the

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(29) The reaction of **3** with triflic acid was not explored as the replacement of phenyl groups by triflate groups is likely using this reagent. See: Matyjaszewski, K.; Hrkach, J.; Kim, H. K.; Ruehl, K. *Adv. Chem. Ser.* **1990**, *224*, 285.

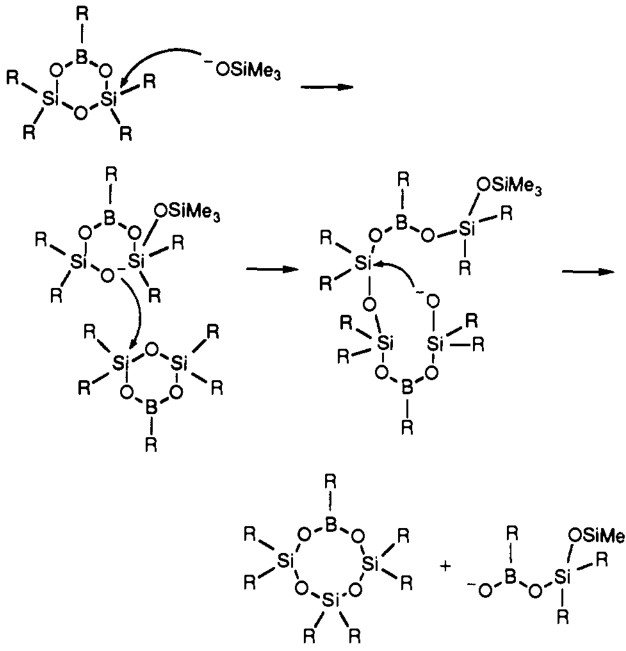
presence or absence of small amounts of K[$OSiMe_3$]. For this species, which contains a less strained eight-membered borasiloxane ring, the equilibration reactions were noticeably slower than for **1** and higher temperatures were required for appreciable rates of reaction. For example, when **4** was heated at 225 °C for 3 h in the presence of 1.0 mol % K[$OSiMe_3$], analysis of the reaction products by ^{29}Si NMR showed that the major components consisted of unreacted **4** (62%) and the ten-membered ring **5** (16%). Interestingly, small amounts (ca. 9%) of the ring contraction product **1** were also detected. The other major redistribution product was the phenylboroxin $[PhBO]_3$ (detected by ^{13}C NMR and mass spectrometry). The ring–ring equilibration process was very slow in the absence of added K[$OSiMe_3$]. Thus, when **4** was heated alone at 225 °C for 4 h, analysis of the product mixture by ^{29}Si NMR showed the major components to be unreacted **4** (ca. 84%) together with a small amount of the ten-membered ring **5** (ca. 10%).

Implications of the Results. Ring–ring transformation reactions have been previously detected in heterosiloxane chemistry. For example, treatment of $TiCl_4$ with $LiOSiPh_2OSiPh_2OLi$ affords an isolated product containing eight-membered titanatetrasiloxane rings rather than the expected six-membered ring product. Such reactions have been attributed to the release of strain energy present in the expected six-membered ring which is believed to be initially formed.[20] To our knowledge, the results described in this paper represent the first detected examples of ring–ring transformation reactions involving isolated, well-characterized heterosiloxane rings. Furthermore, the X-ray structural data for **3** and **8** and the observation that the ring–ring equilibration process for **1** is much faster than that of **4** clearly support the idea that significant strain exists in six-membered heterosiloxane rings, at least where relatively small heteroatoms such as boron are present. The release of ring strain is clearly one of the driving forces behind the ring-expansion reactions detected for **1** and **3**. Another driving force is the formation of cyclic and polymeric siloxanes and the stable six-membered ring $[PhBO]_3$. This accounts for the detection of redistributive ring–ring transformation products consisting of larger rings which contain relatively less boron than the starting material. The detection of small quantities of the diboracyclohexasiloxanes **6** and **7** indicates that nonredistributive ring–ring transformation reactions can also occur, but to a very limited extent. By contrast, nonredistributive ring–ring transformations are dominant with many other inorganic ring systems.[6–8]

Mechanisms for Borasiloxane Ring–Ring Transformation Reactions. Any detailed mechanism for the equilibration reactions detected for boracyclosiloxanes must explain both the formation of larger borasiloxane rings in the intermediate stages of the equilibration process and also the formation of cyclic and polymeric siloxanes and the cycloboroxin $[PhBO]_3$ as the thermodynamically favored products. As most of the experiments carried out utilized the anionic initiator K[$OSiMe_3$], possible mechanisms for the reactions involving this species are considered. Reactions carried out in the presence of triflic acid probably proceed via mechanisms similar to those with base initiator except that ring-opened cationic intermediates formed after the initial protonation at borasiloxane skeletal oxygen atoms are involved.

Using K[$OSiMe_3$], two initial steps can be considered. By analogy with the accepted mechanism for the base-catalyzed ring-opening polymerization of cyclic siloxanes such as $[Me_2SiO]_4$, the reaction might be expected to initially proceed via attack of the $[OSiMe_3]^-$ anion at silicon.[3] On the other hand, in view of the presence of a sextet boron atom, attack at boron is also a possibility. Moreover, bearing in mind the formation of the thermodynamically favored cycloboroxin product, it is probable that attack at boron by boron oxyanions also takes place at some stage of the mechanism as the generation of boroxins requires the formation of new B–O–B bonds. Because of the range of mechanistic possibilities, it is not possible to be certain of all the pathways taking place in detail. However, it appears likely that the ring–ring transformation process involves a complex series of interrelated steps in which the products of each individual step are able to further participate in redistribution reactions.

Scheme I. A Possible Mechanism for Boracyclosiloxane Ring-Expansion Reactions



One possible mechanism which accounts for the formation of larger borasiloxane rings containing a single boron atom is shown in Scheme I. This involves initial attack of $[OSiMe_3]^-$ at the silicon atom of a boracyclotrisiloxane which induces ring-opening to generate an anionic, open-chain species. Attack of the latter on another cyclic borasiloxane molecule would then yield a longer chain. Cyclization of this species via a back-biting reaction could then afford a larger boracyclosiloxane ring and would also generate a new anionic species which might initiate further ring–ring transformation reactions. The mechanism in Scheme I also accounts for the formation of the ten-membered ring equilibration product assuming that eight-membered rings as well as six-membered rings can participate in the first or second steps.

Because of the probable overall complexity of the equilibration process, we do not speculate on detailed mechanisms for siloxane and cycloboroxin formation. However, we attribute the ultimate formation of these species to the imposition of thermodynamic factors. The formation of small, but significant, quantities of the more strained six-membered ring species **1** in the equilibration process for the boracyclotetrasiloxane **4** suggests that this species is formed as a kinetic product. The formation of **1** from **4** might proceed via attack of the silanolate anion at a skeletal silicon atom of **4** to generate an anionic, ring-opened species which subsequently yields the ring-contracted species **1** (together with a new silanolate anion) via a back-biting step.[30]

Conclusions

The combination of additional strain arising from the presence of a small skeletal boron atom and relative lability to traces of acid or base leads to facile ring–ring transformation reactions for six-membered ring boracyclosiloxanes such as **1** and **3**. The eight-membered ring species **4** also undergoes ring–ring transformation reactions, but the process is slower as the ring is less strained. The main products arise from redistributive ring–ring transformations

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[30] Interestingly, significant quantities of the strained cyclic siloxane $[Me_2SiO]_3$ are also formed in the equilibration of **4** which suggests that this compound is also a kinetic product.

which yield species in which the boron to silicon ratio is different from that in the starting material. Only very small amounts of the nonredistributive ring–ring transformation products **6** and **7** were detected. This indicates that ring-expansion reactions without the relative loss of boron constitute only a very minor pathway. The redistributive ring–ring transformation reactions predominantly yield eight- and ten-membered rings, presumably as the tendency to extrude boron limits the size of the borasiloxane rings formed. It therefore appears that the formation of the boroxin $[\mathrm{PhBO}]_3$ presents a significant thermodynamic barrier to polyborasiloxane formation using ring-opening methods. We are now turning our attention to the incorporation of other elements and moieties into the cyclic siloxane ring structure and studies of the polymerization behavior of these species.

Experimental Section

Materials. Halogenated siloxanes were purchased from Huls and were either distilled or used as provided. Dimethyldichlorosilane (Aldrich) was distilled or used as provided. Phenylboric acid was either prepared by the method of Bean[31] or used as received (Aldrich). Triflic acid (Aldrich), 1.6 M butyllithium in hexanes (Aldrich), and potassium trimethylsilanolate (Huls) were used as received. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres). Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves.

Equipment. ^{1}H NMR spectra (200 or 400 MHz) and ^{13}C NMR spectra (50.3 or 100.5 MHz) were recorded on either a Varian Gemini 200 or Varian XL 400 spectrometer, while ^{11}B NMR spectra (64.2 MHz) (using $\mathrm{BF_3/Et_2O}$ as an external reference) were obtained on either a Varian XL 200 or a Varian Gemini 300 instrument. The ^{29}Si NMR spectra (39.7 MHz) were referenced externally to $\mathrm{(CH_3)_4Si}$ and were recorded on a Varian XL 400 spectrometer utilizing either a normal (proton coupled) or a DEPT pulse sequence (proton decoupled) with a $^{2}J_{\mathrm{Si-H}}$ coupling of 6.7 Hz. ^{29}Si/^{1}H 2D HETCOR experiments were performed using a $^{1}J_{\mathrm{Si-H}}$ coupling of 10 Hz with the BIRD pulse sequence removed. Where product weights are not reported, yields have been estimated using ^{29}Si NMR integration. The latter values are corrected to the nearest percent, and therefore the total of the percentage yields for any reaction may be slightly more or slightly less than 100%. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in either an electron impact (EI) or fast atom bombardment (FAB) mode. Elemental analyses were performed by Canadian Microanalytical Services, Delta, BC, Canada.

Synthesis of $\mathbf{(PhBO)(Me_2SiO)_2}$ (1). This compound was prepared via the previously reported method[18] and was purified by vacuum distillation: bp 77 °C (0.7 mmHg); yield 32%; ^{29}Si NMR ($\mathrm{CDCl_3}$) δ -3.3, ($\mathrm{C_6D_6}$) -3.0 (s) ppm; ^{11}B NMR ($\mathrm{CH_2Cl_2}$) δ 28.2 (br s) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 135.6 (s, meta BPh), 131.7 (s, para BPh), 128.0 (s, ortho BPh), 0.73 (s, $\mathrm{CH_3}$) ppm; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.86 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 8.2 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 2.0 Hz, 2 H, ortho BPh), 7.44 (tt, $^{3}J_{\mathrm{HH}}$(m,p) = 7.3 Hz, 1 H, para BPh), 7.35 (t, 2 H, meta BPh), 0.27 (s, 6 H, $\mathrm{C}H_3$) ppm.

Synthesis of $\mathbf{(PhBO)(MePhSiO)_2}$ (2) and $\mathbf{(PhBO)(Ph_2SiO)_2}$ (3). These compounds were prepared by similar methods, and therefore the procedure is only described for **3**.

To a cooled (–78 °C) solution of phenylboric acid (3.0 g, 25 mmol) and excess triethylamine (5.5 g, 55 mmol) in diethyl ether (1000 mL) was added slowly, dropwise, a solution of 1,3-dichlorotetraphenyldisiloxane (11.3 g, 25 mmol) in the same solvent (50 mL). After being warmed to room temperature, the reaction mixture was allowed to stir overnight. Filtration (to remove $\mathrm{[NEt_3H]Cl}$), followed by solvent removal and recrystallization of the residue from $\mathrm{CH_2Cl_2}$/hexanes at –6 °C, afforded colorless crystals of **3**: yield 8.1 g (65%); ^{29}Si NMR ($\mathrm{CDCl_3}$) δ -30.8 (s), ($\mathrm{C_6D_6}$) -30.0 (s) ppm; ^{11}B NMR ($\mathrm{CH_2Cl_2}$) δ 28.2 (br s) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 136.1 (s, meta BPh), 135.1 (s, meta SiPh), 134.7 (br m, ipso BPh), 133.7 (s, ipso SiPh), 132.4 (s, para BPh), 131.6 (s, para SiPh), 128.7 (s, ortho SiPh), 128.4 (s, ortho BPh) ppm; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.23 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 7.8 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.7 Hz, 2 H, ortho BPh), 7.88 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 7.7 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.8 Hz, 8 H, ortho SiPh), 7.67 (m, 1 H, para BPh), 7.6–7.4 (m, 14 H, para, meta SiPh, meta BPh) ppm; MS (EI, 70 eV) *m/z* (%) = 500 (100, $\mathrm{M^+}$), 423 (97, $\mathrm{M^+ - Ph}$), 345 (53, $\mathrm{M^+ - 2Ph}$). Anal. Calcd for $\mathrm{C_{30}H_{25}BO_3Si_2}$: C, 71.99; H, 5.03. Found: C, 71.75; H, 5.17.

Compound **2** was prepared by the above procedure using 1,3-dichlorodimethyldiphenyldisiloxane in the place of 1,3-dichlorotetraphenyldisiloxane. Purification was achieved by vacuum distillation (bp 247 °C (0.03 mmHg)) to give a clear, partially solid product: yield 5.5 g (59%); ^{29}Si NMR ($\mathrm{CDCl_3}$) δ -16.5 (s) ppm; ^{11}B NMR ($\mathrm{CH_2Cl_2}$) δ 28.4 (br s) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 135.23 (s, meta, trans BPh), 135.21 (s, meta, cis BPh), 133.40 (s, ipso, cis SiPh), 133.35 (s, ipso, trans SiPh), 133.3 (s, meta, trans SiPh), 133.2 (s, meta, cis SiPh), 131.4 (s, para BPh), 130.6 (s, para, cis SiPh), 130.5 (s, para, trans SiPh), 128.1 (s, ortho BPh), 127.9 (s, ortho, cis SiPh), 127.9 (s, ortho, trans SiPh), –0.74 (s, trans $\mathrm{CH_3}$), –0.91 (s, cis $\mathrm{CH_3}$) ppm; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.84 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 8.0 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.6 Hz, 2 H, ortho BPh), 7.61 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 8.0 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.6 Hz, 4 H, ortho, cis SiPh), 7.48 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 7.0 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.2 Hz, 4 H, ortho, trans SiPh), 7.38–7.18 (m, 9 H, para, meta, cis and trans SiPh and BPh), 0.50 (s, 6 H, trans $\mathrm{C}H_3$), 0.43 (s, 6 H, cis $\mathrm{C}H_3$) ppm; MS (EI, 70 eV) *m/z* (%) = 376 (31, $\mathrm{M^+}$), 361 (100, $\mathrm{M^+ - CH_3}$), 283 (26, $\mathrm{M^+ - CH_3 - Ph}$), 257 (43, $\mathrm{M^+ - CH_3 - PhBO}$). Anal. Calcd for $\mathrm{C_{20}H_{21}BO_3Si_2}$: C, 63.82; H, 5.63. Found: C, 63.89; H, 5.60.

Synthesis of $\mathbf{(PhBO)(Me_2SiO)_3}$ (4) and $\mathbf{(PhBO)(Me_2SiO)_4}$ (5). These compounds were prepared by a similar method, and therefore the procedure is only described for **4**.

To a cooled (–78 °C) solution of phenylboric acid (3.16 g, 26 mmol) and excess triethylamine (5.5 g, 55 mmol) in diethyl ether (1000 mL) was added slowly, dropwise, a solution of 1,5-dichlorohexamethyltrisiloxane (7.21 g, 26 mmol) in the same solvent (50 mL). After being warmed to room temperature, the reaction mixture was allowed to stir overnight. Filtration (to remove $\mathrm{[NEt_3H]Cl}$), followed by solvent removal and vacuum distillation (bp 80 °C (0.1 mmHg)), afforded **4** as a colorless liquid: yield 6.2 g (74%); ^{29}Si NMR ($\mathrm{CDCl_3}$) δ -16.2 (s, 1 Si, β-Si), -17.3 (s, 2 Si, α-Si) ppm; ^{11}B NMR ($\mathrm{CH_2Cl_2}$) δ 27.9 (br s) ppm; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 135.3 (s, meta BPh), 131.0 (s, para BPh), 127.6 (s, ortho BPh), 0.73 (s, β-Si$\mathit{C}\mathrm{H_3}$), 0.40 (s, α-Si$\mathit{C}\mathrm{H_3}$) ppm; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 8.03 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 7.8 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.7 Hz, 2 H, ortho BPh), 7.30–7.25 (m, 3 H, para, meta BPh), 0.20 (s, 12 H, α-SiCH_3), 0.11 (s, 6 H, β-SiCH_3) ppm; MS (EI, 70 eV) *m/z* (%) = 326 (3, $\mathrm{M^+}$), 311 (100, $\mathrm{M^+ - CH_3}$), 269 (74, $\mathrm{M^+ - Si - 2CH_3}$). Anal. Calcd for $\mathrm{C_{12}H_{23}BO_4Si_3}$: C, 44.16; H, 7.10. Found: C, 43.07; H, 6.83.

Compound **5** was prepared by the above procedure using 1,7-dichlorooctamethyltetrasiloxane in the place of 1,5-dichlorohexamethyltrisiloxane. Purification was achieved by vacuum distillation to yield **5** as a colorless liquid: yield 3.4 g (34%). ^{29}Si NMR ($\mathrm{CDCl_3}$) δ -18.7 (s, 2 Si, β-Si), -19.7 (s, 2 Si, α-Si) ppm; ^{11}B NMR ($\mathrm{CH_2Cl_2}$) δ 27.8 (br s) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 135.8 (s, meta BPh), 131.4 (s, para BPh), 128.1 (s, ortho BPh), 1.22 (s, β-Si$\mathit{C}\mathrm{H_3}$), 0.99 (s, α-Si$\mathit{C}\mathrm{H_3}$) ppm; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.77 (dd, $^{3}J_{\mathrm{HH}}$(o,m) = 7.8 Hz, $^{4}J_{\mathrm{HH}}$(o,p) = 1.7 Hz, 2 H, ortho BPh), 7.41–7.35 (m, 3 H, para BPh, meta BPh), 0.24 (s, 12 H, α-SiCH_3), 0.08 (s, 12 H, β-SiCH_3) ppm; MS (EI, 70 eV) *m/z* (%) = 400 (8, $\mathrm{M^+}$), 385 (100, $\mathrm{M^+ - CH_3}$), 343 (99, $\mathrm{M^+ - Si - 2CH_3}$). Anal. Calcd for $\mathrm{C_{14}H_{29}BO_5Si_4}$: C, 41.98; H, 7.30. Found: C, 41.17; H, 7.23.

Synthesis of $\mathbf{(PhBO)_2(Me_2SiO)_4}$ (6) and $\mathbf{(PhBO)_2(Ph_2SiO)_4}$ (7). Compounds **6** and **7** are formed in 5–10% yield (by ^{29}Si NMR) in the synthesis of **1** and **3**, respectively. Attempts to isolate pure samples of these compounds were unsuccessful.

Data for **6** (as a mixture with **1**, **4**, and **5**): ^{29}Si NMR ($\mathrm{C_6D_6}$) δ -19.3 (s) ppm; MS (EI, 70 eV) *m/z* (%) = 504 (10, $\mathrm{M^+}$), 489 (100, $\mathrm{M^+ - CH_3}$), 459 (9, $\mathrm{M^+ - 3CH_3}$). The observed isotope pattern was characteristic of a species containing two boron atoms. All peak intensities are relative to 489 amu, which represents 4.5% of the maximum ion intensity detected at 237 amu (**1**, $\mathrm{M^+ - CH_3}$).

Data for **7** (as a mixture with **3**): ^{29}Si NMR ($\mathrm{C_6D_6}$) δ –43.4 (s) ppm; MS (EI, 70 eV) *m/z* (%) = 1000 (48, $\mathrm{M^+}$), 923 (37, $\mathrm{M^+ - Ph}$), 845 (100, $\mathrm{M^+ - 2Ph}$). The observed isotope pattern was characteristic of a species containing two boron atoms. All peak intensities are relative to 845 amu, which represents 8.5% of the maximum ion intensity detected at 500 amu (**3**, $\mathrm{M^+}$).

Synthesis of $\mathbf{(PhBO)(Ph_2SiO)_3}$ (8). To a diethyl ether (1000 mL) solution containing phenylboric acid (1.5 g, 12.5 mmol) and excess triethylamine (5.5 g, 55 mmol) at –78 °C was added, dropwise, a cold (–78 °C) solution of 1,3-dichlorotetraphenyldisiloxane (11.3 g, 25 mmol) in the same solvent (50 mL). After being warmed to room temperature, the reaction mixture was allowed to stir overnight. Filtration (to remove $\mathrm{[NEt_3H]Cl}$), followed by several fractional crystallizations from a mixture of diethyl ether/hexane (1:1) at –15 °C to remove first triphenylborox-

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(31) Bean, F. R.; Johnson, J. R. *J. Am. Chem. Soc.* **1932**, *54*, 4415.

ine, compound **3**, and then hexaphenyltrisiloxane, finally yielded clear, colorless clusters of crystals of **8**: yield 0.9 g (10%); ^{29}Si NMR (C_6D_6) δ –40.3 (s, 1 Si, β-Si), –42.8 (s, 2 Si, α-Si) ppm; ^{11}B NMR (CH_2Cl_2) δ 31.1 (br s) ppm; ^{13}C NMR ($CDCl_3$) δ 136.4 (s, meta BPh), 135.1 (s, meta β-SiPh), 135.0 (s, meta α-SiPh), 134.9 (ipso β-SiPh), 134.6 (ipso α-SiPh), 132.3 (s, para BPh), 131.0 (s, para α-SiPh), 130.5 (s, para β-SiPh), 128.5 (s, ortho BPh), 128.5 (s, ortho α-SiPh), 127.5 (s, ortho β-SiPh) ppm; ^{1}H NMR (C_6D_6) δ 8.24 (dd, $^3J_{HH}$(o,m) = 7.8 Hz, $^4J_{H\text{-}H}$(o,p) = 1.7 Hz, 2 H, ortho BPh), 7.82–7.50 (m, 12 H, ortho α- and β-SiPh), 7.67 (tt, 1 H, para BPh), 7.3–7.0 (m, 20 H, para, meta α,β-SiPh, meta BPh) ppm; MS (EI, 70 eV) m/z (%) = 698 (14, M$^+$), 543 (67, M$^+$ – 2Ph), 439 (100, M$^+$ – 2Ph – PhBO). Anal. Calcd for $C_{42}H_{35}BO_4Si_3$: C, 72.17; H, 5.05. Found: C, 72.00; H, 5.04.

Synthesis of (PhBO)($Ph_2SiO)_4$ (9). Compound **9** was identified as a ring–ring transformation product when **3** was heated at 200 °C for 3 days in the presence of 1.0 mol % K[$OSiMe_3$] as initiator. The product was characterized by ^{29}Si NMR and mass spectrometry as a component which comprised 23% of a mixture containing mainly unreacted **3** (22%), the eight-membered ring **8** (48%), and the twelve-membered ring **9** (4%).

Data for **9** (as a mixture with **3** and **8**): ^{29}Si NMR (C_6D_6) δ –43.6 (s, 2 Si, α-Si), –45.0 (s, 2 Si, β-Si) ppm; MS (EI, 70 eV) m/z (%) = 897 (25, M$^+$), 820 (67, M$^+$ – Ph), 742 (100, M$^+$ – 2Ph). All peaks are relative to 742 amu, which represents 7.6% of maximum ion intensity at 439 amu. m/z (%) = (M$^+$ – 2Ph – PhBO) for **8**. These peaks had the correct isotope pattern for a species containing a single boron atom.

Ring–Ring Redistribution Reactions of the Boracyclotrisiloxanes 1 and 3 and the Boracyclotetrasiloxane 4. Ring–Ring Redistribution Reactions of 1, 3, and 4 in the Absence of Added Initiator. Melt ring–ring redistribution reactions for **1**, **3**, or **4** were carried out by heating ca. 0.5-g samples of the purified boracyclosiloxanes at 150 °C (**1**), 200 °C (**3**), or 225 °C (**4**) in an evacuated sealed Pyrex tube. The products were then dissolved in dry diethyl ether, and the resulting solution was filtered to remove $[PhBO]_3$. The solvent was then removed carefully under low vacuum (100 mmHg) and the residue dissolved in C_6D_6 and analyzed by ^{29}Si NMR spectroscopy.

For **1**, the major silicon-containing reaction products identified by ^{29}Si NMR after 3 h were unreacted starting material (**1**, 72%), **4** (9%), **5** (11%), **6** (8%), a small amount of $[Me_2SiO]_4$ (1%), and a trace of $[Me_2SiO]_n$ (<1%).

For **3**, after 72 h the main silicon-containing products by ^{29}Si NMR were unreacted starting material (**3**, 7%), **8** (64%), **9** (14%), and **7** (2%), together with the cyclic siloxanes $[Ph_2SiO]_3$ (9%) and $[Ph_2SiO]_4$ (3%).

For **4**, the major silicon-containing products after 4 h by ^{29}Si NMR were unreacted starting material (**4**, 84%), together with **5** (10%), **1** (3%), $[Me_2SiO]_3$ (3%), traces of $[Me_2SiO]_4$ and polymer $[Me_2SiO]_n$ (total <1%).

Ring–Ring Redistribution Reactions of 1, 3, and 4 Using K[$OSiMe_3$] as Initiator. Ring–ring redistribution reactions in the melt were carried out by heating 0.2–0.5-g samples of **1**, **3**, or **4** at 150 °C (for **1**), 200 °C (for **3**), or 225 °C (for **4**) in the presence of 1.0 mol % K[$OSiMe_3$] (or 10.0 mol % K[$OSiMe_3$] for **1**) in a sealed glass tube. The reaction products were dissolved in diethyl ether, and the resulting solution was filtered to remove triphenylboroxin, and any unreacted K[$OSiMe_3$]. The solvent was then removed carefully under low vacuum (100 mmHg) and the residue dissolved in C_6D_6 and analyzed by ^{29}Si NMR spectroscopy.

The following were observed for **1**.

(a) When **1** was heated in the melt for 1.5 h in the presence of 1.0 mol % K[$OSiMe_3$], the products identified by ^{29}Si NMR spectroscopy were unreacted starting material (**1**, 31%), **4** (36%), **5** (15%), **6** (2%), $[Me_2SiO]_3$ (3%), $[Me_2SiO]_4$ (2%), and polymer $[Me_2SiO]_n$ (δ = –21.4 ppm, 3%). In addition, an unidentified resonance at δ = 7.58 ppm (8%) was detected.

(b) When **1** was heated for 7 days at 150 °C using 1.0 mol % K[$OSiMe_3$], the products identified by ^{29}Si NMR spectroscopy were the polymer $[Me_2SiO]_n$ (δ = –21.4 ppm, 85%), $[Me_2SiO]_4$ (δ = –18.6 ppm, 2%), $[Me_2SiO]_5$ (δ = –21.0 ppm, 4%), and $[Me_2SiO]_6$ (δ = –21.6 ppm, 3%). In addition, an unidentified resonance at δ = 7.58 ppm (6%) was detected.

(c) When **1** was heated in the melt for 1.5 h at 150 °C using 10.0 mol % K[$OSiMe_3$], the products identified by ^{29}Si NMR were **4** (4%), **5** (5%), **6** (2%), $[Me_2SiO]_4$ (5%), $[Me_2SiO]_5$ (δ = –21.0 ppm, 5%), $[Me_2SiO]_6$ (δ = 21.6 ppm, 3%), and $[Me_2SiO]_n$ (δ = –21.4 ppm, 56%). In addition, an unidentified resonance at δ = 7.58 ppm (19%) was detected. Several small unidentified peaks clustered around the $[Me_2SiO]_n$ resonance were also detected. These might arise from linear oligosiloxanes formed in the reaction.

(d) Solution ring–ring redistribution reactions of **1** (0.2–0.5 g) using 1.0 mol % K[$OSiMe_3$] were carried out at –80 °C in CH_2Cl_2. The reactions were stirred at –80 °C for 3 h, and allowed to warm to room temperature. The solution was then filtered to remove unreacted K[$OSiMe_3$] as well as triphenylboroxin, and the residue analyzed by ^{29}Si NMR spectroscopy. The main silicon-containing products identified by ^{29}Si NMR were **4** (13%), **5** (7%), and the siloxanes $[Me_2SiO]_4$ (10%), $[Me_2SiO]_5$ (δ = –21.0 ppm, 6%), $[Me_2SiO]_6$ (δ = –21.6 ppm, 4%), and $[Me_2SiO]_n$ (δ = –21.4 ppm, 60%).

(e) Solution ring–ring redistribution reactions of **1** (0.2–0.5 g) using 10.0 mol % K[$OSiMe_3$] were carried out at –80 °C in CH_2Cl_2. The reactions were stirred at –80 °C for 3 h, the solution was filtered to remove unreacted K[$OSiMe_3$] as well as triphenylboroxin, and the residue was analyzed by ^{29}Si NMR. The products consisted of the polymer $[Me_2SiO]_n$ (δ = –21.4 ppm, 51%), $[Me_2SiO]_4$ (<1%), $[Me_2SiO]_5$ (δ = –21.0 ppm, 11%), and $[Me_2SiO]_6$ (δ = –21.6 ppm, 9%). In addition, an unidentified resonance at δ = 7.58 ppm (29%) was detected.

For **3**, the major silicon-containing products by ^{29}Si NMR spectroscopy after 3 days at 200 °C using 1.0 mol % K[$OSiMe_3$] were the unreacted starting material (**3**, 27%), **8** (42%), **9** (24%), and **7** (4%), along with the cyclic siloxanes $[Ph_2SiO]_3$ (3%) and $[Ph_2SiO]_4$ (1%). A mass spectrum of the product mixture provided evidence for all of these species.

For **4**, the major silicon-containing products by ^{29}Si NMR after 3 h in the melt at 225 °C using 1.0 mol % K[$OSiMe_3$] were unreacted starting material (**4**, 62%), **5** (16%), **1** (9%), $[Me_2SiO]_3$ (8%), and $[Me_2SiO]_4$ (5%), as well as a small trace of the polymer $[Me_2SiO]_n$ (<1%).

Ring–Ring Redistribution Reactions of 1 Initiated by CF_3SO_2OH. Compound **1** (0.2–0.5 g, 1.8–4.4 mmol) was dissolved in CH_2Cl_2 (10 mL) and the solution cooled to –80 °C. Approximately 1.0 mol % CF_3SO_2OH was then added. The temperature of the solution was maintained at –80 °C for 3 h, and the reaction mixture was then allowed to warm to room temperature. After 3 h, the solvent was removed under low vacuum (100 mmHg) and the residue was redissolved in dry diethyl ether and filtered to remove $[PhBO]_3$. The solvent was then removed carefully under low vacuum (100 mmHg) and the residue dissolved in C_6D_6 and analyzed by ^{29}Si NMR spectroscopy.

The products were identified as $[Me_2SiO]_n$ (δ = –21.4 ppm, 75%), $[Me_2SiO]_4$ (14%), $[Me_2SiO]_5$ (δ = –21.0 ppm, 8%), and $[Me_2SiO]_6$ (δ = –21.6 ppm, 3%).

Ring–Ring Redistribution Reactions of 1 Initiated by BuLi. This reaction was carried out in a way similar to that using CF_3SO_2OH as the initiator except that THF was used as solvent. The products were analyzed by ^{29}Si NMR spectrometry.

For **1**, the products were identified as the borasiloxanes **4** (15%) and **5** (9%) and the siloxanes $[Me_2SiO]_4$ (10%), $[Me_2SiO]_5$ (δ = –21.0 ppm, 7%), $[Me_2SiO]_6$ (δ = –21.6 ppm, 3%), and $[Me_2SiO]_n$ (δ = –21.4 ppm, 57%).

X-ray Structure Determination Technique. Intensity data for both compounds were collected on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The $\omega/2\theta$ scan technique was applied with variable scan speeds. Intensities of three standard reflections measured every 2 h showed no decay. The space groups were determined from systematic absences. For compound **3** the space group could be *Cc* or *C*2/*c*. *C*2/*c* was chosen and confirmed by the successful refinement. With $Z = 4$ in *C*2/*c* the molecules must lie across the 2-fold axes parallel to *y*, or the centers of symmetry. An empirical absorption correction[32] was applied to the data for **3** (maximum and minimum corrections 1.504 and 0.775) but not for **8**.

The structures were solved by direct methods using SHELX86.[33] Refinement was by a full-matrix least-squares method to minimize $\sum w(F_o - F_c)^2$ with, where $w = 1/(\alpha^2(F_o) + gF_o^2)$, anisotropic thermal parameters for non-hydrogen atoms. Difference maps showed maxima in positions consistent with the expected locations of hydrogen atoms. In compound **3** the hydrogen atoms were refined with isotropic thermal parameters, and in compound **8** the hydrogen atoms were positioned on geometric grounds (C–H 0.95 Å, $U(H) = U(C) + 0.01$ Å^2) and included in the calculations as riding atoms. Crystal data, details of data collection, and least-squares parameters for **3** and **8** are given in Table I. All calculations

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(32) Walker, N. *DIFFABS. Empirical Absorption Correction Program*; Queen Mary College, London, England, 1983.

(33) (a) Sheldrick, G. M. *SHELXS86. Program for crystal structure determination*; University of Gottingen, Federal Republic of Germany, 1986. (b) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

were performed using SHELX76,[34] SHELXS86,[33] and NRCVAX[35] on a 486-33 PC and an Apollo computer.

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Supplementary Material Available: Figures showing the molecular structures of **3** and **8** and tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, torsion angles, and least-squares plane data for **3** and **8** and hydrogen atom coordinates for **8** (16 pages); listings of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Registry No. **1**, 67133-55-5; **2**, 7236-95-5; **3**, 136745-52-3; **4**, 141613-68-5; **5**, 141613-69-6; **6**, 141613-70-9; **7**, 141613-71-0; **8**, 141613-72-1; **9**, 141613-73-2; K[OSiMe$_3$], 10519-96-7; CF$_3$SO$_2$OH, 1493-13-6; BuLi, 109-72-8; phenylboric acid, 98-80-6; dichlorotetraphenyldisiloxane, 7756-87-8; 1,3-dichlorodimethyldiphenyldisiloxane, 3582-72-7; 1,5-dichlorohexamethyltrisiloxane, 3582-71-6; 1,7-dichlorooctamethyltetrasiloxane, 2474-02-4.

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