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Journal of Organometallic Chemistry 595 (2000) 241–247

Journal of Organometallic Chemistry

cyclo-Boratrisiloxane and *cyclo*-diboratetrasiloxane derivatives and their reactions with amines: crystal and molecular structure of $(p\text{-}BrC_6H_4BO)_2(Ph_2SiO)_2$

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Received 9 September 1999; accepted 14 October 1999

Abstract

The new *cyclo*-diboratetrasiloxanes $(RBO)_2(R'_2SiO)_2$ ($R = p\text{-}BrC_6H_4$, $o\text{-}MeC_6H_4$, $m\text{-}NH_2C_6H_4$, $m\text{-}NO_2C_6H_4$, Bu^n; $R'_2 = Ph_2$, $R = Ph$, $p\text{-}BrC_6H_4$, $m\text{-}NO_2C_6H_4$; $R'_2 = oct^n/Me$) and *cyclo*-boratrisiloxanes $(RBO)(R'_2SiO)_2$ ($R = p\text{-}BrC_6H_4$, $m\text{-}NH_2C_6H_4$; $R'_2 = Me_2$, Ph/Me) were prepared in high yield by condensation reactions. *cyclo*-Diboratetrasiloxane·amine adducts (1:1) were obtained for $(PhBO)_2(Ph_2SiO)_2$ with cyclohexylamine, triethylamine, piperidine, and isobutylamine and for $(o\text{-}MeC_6H_4BO)_2(Ph_2SiO)_2$ with morpholine; in contrast the *cyclo*-boratrisiloxanes were unreactive towards amines. The Lewis acidity of these borasiloxane rings was determined by the Gutmann's acceptor number (AN) method with well-defined ranges observed for the *cyclo*-diboratetrasiloxanes (46–62) and the *cyclo*-boratrisiloxanes (22–28). The crystal and molecular structure of $(p\text{-}BrC_6H_4BO)_2(Ph_2SiO)_2$ is reported. New compounds were characterised by elemental analysis, m.p., ^{1}H- and ^{11}B-NMR, and IR spectroscopy; solids were characterised by solid-state ^{11}B MAS-NMR spectroscopy.

Keywords: Borasiloxanes; Boron; Ring compounds; Silicon

1. Introduction

Compounds containing the B–O–Si linkage are well represented in the literature by the triorganosilyl esters of orthoboric [1–10], metaboric [7–9], and boronic acids [7–10], the six-, eight- and ten-membered ring *cyclo*-borasiloxane derivatives [11–17], and more recently, by borosilicate cages [18–20]. These examples all involve three-coordinate B centres but there are also a few cases where the B atoms are four-coordinate [21–24]. We are interested in assessing the effect of the proximate Si atom on the Lewis acidity at B in compounds containing B–O–Si linkages and have examined triorganosilyl esters [9]. Herein, we report the synthesis of some new and previously prepared *cyclo*-boratrisiloxane and *cyclo*-diboratetrasiloxane derivatives (Fig. 1(a, b)), an assessment of their Lewis acidities by Gutmann's method [25], and an investigation of their reactions with amines. The crystal and molecular structure of the *cyclo*-diboratetrasiloxane derivative, $(p\text{-}BrC_6H_4BO)_2(Ph_2SiO)_2$, is also reported.

2. Results and discussion

2.1. Synthesis and characterisation

Reported syntheses of borasiloxane rings have involved cyclocondensation reactions from either (i) $PhB(OH)_2$ and an α,ω-dichlorosiloxane in the presence of NEt_3 [11,12]; (ii) $PhB(OH)_2$ and a dihydroxysilane or α,ω-dihydroxysiloxane [13]; (iii) $PhBCl_2$ and a dihydroxysilane [14]; or (iv) $PhB(OH)_2$ and a diethoxysilane or α,ω-diethoxysiloxane [16,17]. The *cyclo*-boratrisilox-

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PII: S0022-328X(99)00631-2

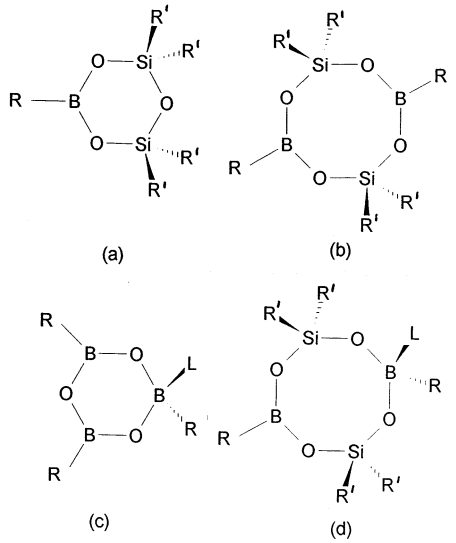

Fig. 1. Schematic drawings of the structures of derivatives of (a) a *cyclo*-boratrisiloxane; (b) a *cyclo*-diboratetrasiloxane; (c) a 1:1 adduct of a boroxine; and (d) a 1:1 adduct of a *cyclo*-diboratetrasiloxane.

ane and *cyclo*-diboratetrasiloxane derivatives, reported here, were prepared by cyclocondensation of appropriate stoichiometric mixtures of organoboronic acid and organosilanols in toluene using a Dean–Stark apparatus as described in Eqs. (1) and (2), respectively. Compound **7** has been previously prepared by this method and compounds **1** and **4** by the first route described above.

$$RB(OH)_2 + (R'_2SiOH)_2O \rightarrow (RBO)(R'_2SiO)_2 + 2H_2O$$

$$\{R'_2 = Me_2,\ R = Ph\ (\mathbf{1}),\ p\text{-}BrC_6H_4\ (\mathbf{2}),\ m\text{-}NH_2C_6H_4\ (\mathbf{3});$$

$$R'_2 = Me/Ph,\ R = Ph\ (\mathbf{4}),\ p\text{-}BrC_6H_4(\mathbf{5}),\ m\text{-}NH_2C_6H_4\ (\mathbf{6})\} \quad (1)$$

$$2RB(OH)_2 + 2R'_2Si(OH)_2 \rightarrow (RBO)_2(R'_2SiO)_2 + 4H_2O$$

$$\{R'_2 = Ph_2,\ R = Ph\ (\mathbf{7}),\ p\text{-}BrC_6H_4\ (\mathbf{8}),\ o\text{-}MeC_6H_4\ (\mathbf{9}),\ m\text{-}NH_2C_6H_4\ (\mathbf{10})\ m\text{-}NO_2C_6H_4\ (\mathbf{11}),\ Bu^n\ (\mathbf{12});\ R'_2 = oct^n/Me,\ R = Ph\ (\mathbf{13}),\ p\text{-}BrC_6H_4\ (\mathbf{14}),\ m\text{-}NO_2C_6H_4\ (\mathbf{15})\} \quad (2)$$

The ability of trialkyl- and triarylboroxines to react with amines [26] to form 1:1 adducts (Fig. 1(c)) prompted an investigation into the reactions of amines with these borasiloxane rings. *cyclo*-Boratrisiloxanes were found to be unreactive towards amines, but *cyclo*-diboratetrasiloxanes readily formed 1:1 adducts (Fig. 1(d)) in Et_2O at room temperature as shown in Eq. (3). These are the first reported examples of Lewis base adducts of borasiloxane rings. All new compounds were prepared in high yield as colourless, viscous liquids, or as white–colourless, crystalline solids which were generally air-stable but water-sensitive. Yields, m.p., and elemental analysis data for the new compounds are reported in Table 1.

$$(RBO)_2(Ph_2SiO)_2 + L \rightarrow (RBO)_2(Ph_2SiO)_2{\cdot}L$$

$$R = Ph,\ L = \text{cyclohexylamine}\ (\mathbf{16}),\ Et_3N\ (\mathbf{17}),\ \text{pip}\ (\mathbf{18}),\ Bu^tNH_2\ (\mathbf{19});\ R = o\text{-}MeC_6H_4,\ L = \text{morpholine}\ (\mathbf{20}). \quad (3)$$

Table 1
Yields, m.p., and elemental analysis data for borasiloxane ring derivatives

Compound	Elemental analysis [a]			Yield (%)	m.p. (°C)
	C	H	N		
2	36.2(36.3)	4.9(4.9)	–	80	Viscous liquid [b]
3	45.0(44.9)	6.8(6.8)	5.2(5.2)	84	Viscous liquid [b]
5	52.7(52.9)	4.7(4.5)	–	93	Viscous liquid [b]
6	61.4(61.4)	5.9(5.7)	3.5(3.6)	92	Viscous liquid [b]
8	56.7(56.7)	3.6(3.7)	–	83	197–201
9	72.1(72.2)	5.4(5.4)	–	92	155–158
10	68.0(68.2)	5.1(5.1)	4.2(4.4)	94	148–153
11	62.4(62.3)	4.0(4.0)	4.1(4.0)	90	172–175
12	67.9(68.1)	6.6(6.8)	–	93	Viscous liquid [b]
13	65.5(65.2)	9.3(9.1)	–	87	Viscous liquid [b]
14	50.8(50.7)	7.0(6.8)	–	90	Viscous liquid [b]
15	56.3(56.1)	7.5(7.5)	4.5(4.4)	85	Viscous liquid [b]
16	71.7(71.7)	6.1(6.2)	2.0(2.0)	86	84–87
17	71.4(71.5)	6.3(6.4)	1.7(2.0)	86	104–108
18	71.2(71.2)	5.7(6.0)	2.2(2.0)	91	128–132
19	70.9(70.8)	5.4(5.4)	4.0(3.9)	96	34–38
20	70.5(70.2)	5.9(5.9)	2.0(2.0)	87	52–55

[a] Calculated in parentheses.
[b] Did not distil at 250°C/0.1 mmHg.

Table 2
Acceptor number (AN) values and solution/solid state MAS ^{11}B-NMR data

	AN [a]	δ_{iso} (^{11}B) (ppm) [b]	δ (^{11}B) (ppm) [c]
1	[d]	[e]	26.8 (28.2 [Ref. [12]])
2	[d]	[e]	27.0
3	22	[e]	26.5
4	28	[e]	27.7 (28.2 [Ref. [12]])
5	27	[e]	27.8
6	28	[e]	28.4
7	59	24.3 [f]	29.1 (28.2 [Ref. [12]])
8	49	24.7 [f]	25.4
9	49	[d]	28.0
10	50	24.3 [f]	25.4
11	46	25.1 [f]	25.2
12	46	[e]	25.6
13	47	[e]	25.1
14	52	[e]	25.3
15	62	[e]	26.3
16	[d]	31.4 [g], 5.8 [h]	19.8
17	[d]	31.3 [g], 7.0 [h]	21.3
18	[d]	31.7 [g], 5.4 [h]	19.8
19	[d]	[d]	18.6
20	[d]	[d]	18.8

[a] Calculated from $\delta(^{31}P)$ of Et_3PO (50 mg) dissolved in a 1.0 ml of a THF solution containing the borasiloxane ring compound (0.61 M) using $AN = \{\delta(^{31}P) - 41\} \times 2.22$ [Ref. [30]].

[b] Solid state MAS NMR: isotropic shift, $\delta_{iso} = \delta_{cg} - \sigma_{qs}$ (δ_{cg} is the centre of gravity of the observed signal), $\sigma_{qs} = \nu_{CG} - \nu_L = -10^6(Cq)^2(1+0.33\eta^2)/40(\nu_L)^2$ ($\nu_L = 96.234$ MHz) [Ref. [29]].

[c] From proton-decoupled solution spectra in $CDCl_3$ at room temperature.

[d] Not recorded.

[e] Liquid at room temperature.

[f] Simulated data: $\sigma_{qs} = -27.2$, Cq = 3.05 MHz, $\eta = 0.5$.

[g] Simulated data: $\sigma_{qs} = -20.7$, $Cq = 2.4$ MHz, $\eta = 1.0$.

[h] Simulated data: $\sigma_{qs} = -6.4$, $Cq = 1.5$ MHz, $\eta = 0.4$

All compounds were characterised by NMR and IR spectroscopy. Solution ^{1}H data are presented in Section 3; ^nJ(HH) coupling constants were 7–10 Hz. The ^{1}H-NMR data are consistent with the structures shown in Fig. 1 and with literature data [12,13] for **1**, **4**, and **7**. The *cyclo*-boratrisiloxane derivatives **4**, **5**, and **6** and the *cyclo*-diboratetrasiloxane derivatives **13**, **14**, and **15**, presumably exist as mixtures of *cis* and *trans* isomers, but have coincidental chemical shifts at 250 MHz. The high-field (400 MHz) ^{1}H spectrum of **4** has been reported [12] and confirmed a 55/45 isomeric mixture with very similar or coincidental chemical shifts. Solution ^{11}B-NMR spectra were obtained on all compounds (Table 2) with signals for the *cyclo*-boratrisiloxane (**1**–**7**) and *cyclo*-diboratetrasiloxane (**8**–**15**) ring species at 27.1 ± 2 ppm and consistent with literature data [12] for **1** and typical of a trigonal $\{CBO_2\}$ boron environment [27]. The boron nuclei in the eight-membered diboratetrasiloxane rings are, on average, slightly less deshielded than those in the six-membered boratrisiloxane rings. The solution ^{11}B-NMR spectra of the *cyclo*-diboratetrasiloxane adducts (**16**–**20**) all showed single resonances (δ = ca. +19 ppm) upfield ($\Delta\delta \sim 9$ ppm) of the related unligated diboratetrasiloxane rings **7** and **9**. The single ^{11}B resonance for each adduct would indicate that a rapid exchange process was occurring which equilibrated the three- and four-coordinate boron centres of the adduct. Ligand dissocciation/recombination has been observed in related 1:1 triarylboroxine ligand adducts [26] and this process is also likely to be responsible for the observed boron equilibration in these adducts. Consistent with this, only one signal attributable to *o*-methyl protons was observed in the ^{1}H-NMR spectrum of adduct **20** at room temperature. Solid-state ^{11}B MAS-NMR data were obtained on most solid samples and these are reported in Table 2. All spectra were characterised by a broad complex signal which was simulated as previously described [28,29]. For the *cyclo*-boratrisiloxane and *cyclo*-diboratetrasiloxane derivatives the calculated δ_{iso} values were in good agreement with their solution δ values. The solid state ^{11}B MAS spectra of adducts **16**, **17**, and **18** were obtained and two signals at δ_{iso} values expected for three- and four-coordinate B atoms, were observed; the calculated average of these values was similar to that obtained for the adducts in solution.

IR spectra of all compounds were characterised by very strong absorptions in 1440–1260 cm^{-1} and 1150–1050 cm^{-1} regions due to B–O and Si–O stretching modes, respectively, and ν_{max} for these absorptions are given in Section 3. Additional strong bands were observed at ca. 1530 and 1345 cm^{-1} in **11** and **15**, which may be assigned to the $-NO_2$ group. Inspection of the data for **16**–**19** did not reveal any distinguishable trends occurring for the B–O or Si–O stretches upon coordination of amine ligands to the *cyclo*-diboratetrasiloxane, **7**.

2.2. Acceptor number (AN) data

A quantitative parameter (acceptor number, AN), derived from the ^{31}P-NMR shift obtained for Et_3PO by electrophilic solvent interactions, has been described by Gutmann and co-workers as a measure of solvent Lewis acidity [25]. The AN scale has arbitrary fixed points of 0 and 100 for hexane and $SbCl_5$, respectively, and on this scale, BF_3 has a value of 89 [30]. The relative reactivities of the boratrisiloxane and diboratetrasiloxane rings towards amines was confirmed by AN values for these derivatives (Table 2). *cyclo*-Diboratetrasiloxanes have AN values in the range 46–62, are moderately strong Lewis acids and comparable in acid strength to triorganoboroxines ($AN \sim 50$ [31]) which also form isolatable amine adducts. *cyclo*-Boratrisiloxanes have AN values considerably lower (22–28) and are comparable in acid strength to trialkylorthoborate esters (18–30 [30]) which in general do not form isolat-

able amine adducts [32]. The relative reactivity of these borasiloxane rings towards Lewis bases (hence their ANs) needs to be considered. One possible explanation is that there might be aromatic stabilization of the *cyclo*-boratrisiloxanes since they are formally 6π-electron ring systems, whereas the *cyclo*-diboratetrasiloxanes formally have 8π electrons. However, this explanation must be discounted since theoretically any such an effect would be weak [13] and empirically the formally 6π-electron organoboroxines (*cyclo*-triboratrisiloxanes) do form adducts [31]. The Lewis acidity of these borasiloxane rings must depend upon the extent of π-electron density made available to B from the adjacent O atoms, and this in turn must be determined by the donor–acceptor nature of the other atom, affected by substituent effects, attached to the O. The electronic influence of Si on increasing the Lewis acidity at B in triorganosilyl esters of orthoboric, metaboric and arylboronic acids has been attributed to competitive O–Si π-bonding [9], and O–Si bond lengths in borasiloxane rings are consistent with bond orders of greater than one (see below) indicating that the competitive O–Si π-bonding must be considered. *cyclo*-Borasiloxanes contain {RB} and {R_2Si} ring π-acceptor fragments sandwiched by an equal number of annular O π-donor atoms. The {RB} fragment is the more strongly π-accepting and the six- and eight-membered ring derivatives have B:Si ratios of 1:2 and 1:1, respectively. Thus, the {RB} fragment has a greater relative share of available O π-electron density when in the boratrisiloxane ring. Structurally, the *cyclo*-boratrisiloxane ring contains a unique O atom which is part of a {–SiR_2–O–SiR_2–} link and *trans*-annular to {RB}. These {R_2Si} fragments, whose π-acceptor requirements are effectively satisfied by this O atom, allow more of the π-electron density of the O atoms in the adjacent {–RB–O–SiR_2–} linkages to reside on {RB}. Such a situation cannot occur in the eight-membered *cyclo*-diboratetrasiloxane rings where the O atoms always bridge the {RB} and {R_2Si} fragments. AN measurements would indicate that the electronic effects of {–SiR_2OSiR_2–} towards {RBO_2} is comparable to that found for two {–SiR_3} groups in bis(triorganosilyl)boronate esters [9].

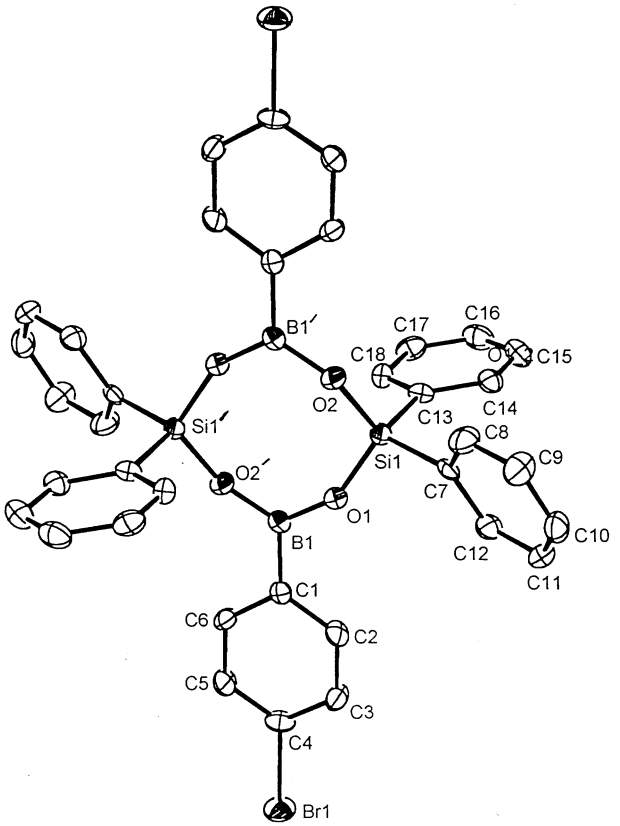

Fig. 2. ORTEP plot of the molecular structure of (p-$BrC_6H_4BO)_2(Ph_2SiO)_2$ (**8**) showing atomic numbering scheme. The structure is centrosymmetric. Thermal ellipsoids are drawn at 50% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for (p-$BrC_6H_4BO)_2(Ph_2SiO)_2$ (**8**)

Bond lengths			
Br(1)–C(4)	1.900(4)	Si(1)–O(2)	1.622(3)
Si(1)–O(1)	1.626(3)	Si(1)–C(13)	1.851(4)
Si(1)–C(7)	1.853(5)	B(1)–O(1)	1.359(6)
B(1)–O(2′) [a]	1.375(6)	B(1)–C(1)	1.552(7)
Bond angles			
O(2)–Si(1)–O(1)	111.9(2)	O(2)–Si(1)–C(13)	110.4(2)
O(1)–Si(1)–C(13)	107.1(2)	O(2)–Si(1)–C(7)	107.8(2)
O(1)–Si(1)–C(7)	108.4(2)	C(13)–Si(1)–C(7)	111.2(2)
B(1)–O(1)–Si(1)	150.7(3)	B(1′)–O(2)–Si(1)	144.7(3)
O(1)–B(1)–O(2′)	120.7(4)	O(1)–B(1)–C(1)	119.4(4)
O(2′)–B(1)–C(1)	119.9(4)	C(6)–C(1)–C(2)	116.3(4)
C(6)–C(1)–B(1)	121.8(4)	C(2)–C(1)–B(1)	121.7(4)
C(5)–C(4)–C(3)	120.9(4)	C(5)–C(4)–Br(1)	120.1(3)
C(3)–C(4)–Br(1)	119.1(4)	C(8)–C(7)–C(12)	117.3(4)
C(8)–C(7)–Si(1)	123.3(4)	C(12)–C(7)–Si(1)	119.3(3)
C(14)–C(13)–C(18)	117.2(4)	C(14)–C(13)–Si(1)	121.7(3)
C(18)–C(13)–Si(1)	121.1(3)		

[a] The primed atoms belong to one and the same molecule and are generated by the symmetry: $(-x, 1-y, 1-z)$.

2.3. Molecular structure of (p-$BrC_6H_4BO)_2(Ph_2SiO)_2$ (**8**)

A drawing of the molecular structure of **8** is given in Fig. 2 and selected bond lengths and bond angles are given in Table 3; crystallographic data and structure refinement methods are given in Section 3. The structure of **8** may be discussed in relation to the previously determined structures of the non-brominated derivative $(PhBO)_2(Ph_2SiO)_2$ [13], the related borasiloxane ring species $(PhBO)(Ph_2SiO)_2$ [12,13], $(PhBO)_2(^tBu_2SiO)_2$ [14], and $(PhBO)(Ph_2SiO)_3$ [12], and the borosilicate cage compounds $^tBuSi\{O(BC_6H_4Br)O\}_3Si^tBu$ [18],

$B\{OSiPh_2OSiPh_2O)_3B$ [19], and $\{(cyclo\text{-}C_6H_{11})_7Si_7O_{12}B\}_2$ [20]. The overall molecular dimensions and the bond angle and bond length parameters obtained for **8** are similar to those reported previously for $(PhBO)_2(Ph_2SiO)_2$ [13] with the exception of the bond angles about the annular O atoms and the planarity of the ring. Compound **8** is centrosymmetric and displays an eight-membered ring structure with four annular O atoms bridging alternating $\{p\text{-}BrC_6H_4B\}$ and $\{Ph_2Si\}$ fragments. The ring is non-planar and deviations of the unique Si(1), B(1), O(1) and O(2) atoms from the mean plane of the ring are −0.162(2), 0.038(2), 0.112(2) and 0.167(2) Å, respectively. The B atoms are three-coordinate and are each bound to two O atoms and one C atom with the sum of the angles at B at 360° confirming their trigonal planar geometry and with an internal ring O–B–O angle of 120.7(4)°. The *para*-substituted phenyl ring is nearly co-planar with the plane containing the *cyclo*-diboratetrasiloxane ring atoms B(1), O(1), and O(2′) as shown by the O(1)–B(1)–C(1)–C(2) torsion angle of 1.3(6)°. The B–O distances {1.359(6) and 1.375(6), av. 1.367(6) Å} are similar to those observed for $(PhBO)_2(Ph_2SiO)_2$ {av. 1.347(5) Å [13]} and are within, or slightly extend, the range observed previously for similar bonds {1.313(2)–1.374(7) Å} [18]. The Si atoms are four-coordinate with approximate tetrahedral geometry {bond angles at Si: 107.1(2)–111.9(2)°, av. 109.5 (2)°} and the Si atoms are bound to two C and two O atoms with the internal ring O–Si–O angle at 111.9(2)°; the Si–O bond lengths {1.626(3) and 1.622(3), av. 1.624(5) Å} are within ranges observed previously for similar bonds {1.615(3)–1.655(5) Å} [18]. The B–O and Si–O bond lengths within the ring are all shorter than the sum of their covalent radii {1.91 Å for SiO, 1.54 Å for BO [33]} indicative of π-bonding interactions within the ring and bond orders of greater than 1. The B–O–Si angles within the ring are 144.7(3) and 150.7(3)° and the latter is significantly different to that reported for a corresponding angle in $(PhBO)_2(Ph_2SiO)_2$ {145.3(3) and 160.9(3)°} [13]. However, it has been noted previously that the B–O–Si angle in structurally characterised compounds show considerable variations {128.9–160.9°} and distortions about O are also common in siloxane chemistry [10]. The internal ring angles at B and Si are close to those expected for sp^2 and sp^3 hybridised centres and it appears that the ring angles at O have increased from that expected for sp^2 hybridisation in a (failed) attempt accommodate a planar ring structure. The sum of the internal angles for an idealised planar eight-membered ring structure is 1080° and the total for **8** is 1056.0°; the internal angles for $(PhBO)_2(Ph_2SiO)_2$ {Σ 1078.8°} indicate a more planar structure. Presumably, the low energy deformations of the B–O–Si bond angles are balanced in this case by crystal packing forces. The C(4)–Br(1) bond length and the remaining bond angles and distances within the phenyl rings are unexceptional.

3. Experimental

3.1. General

Reactions were carried out under N_2 in dried solvents. IR spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer as KBr discs or as thin films between NaCl plates. Multi-element solution NMR were recorded on a Bruker AC 250 CP/MAS NMR spectrometer operating at 250 MHz for ^1H, 101.25 MHz for $^{31}P\text{-}\{^1H\}$, and 80.2 MHz for $^{11}B\text{-}\{^1H\}$. Chemical shifts (δ) are given in ppm with positive values towards high frequency (downfield) from $SiMe_4$ (^1H), $BF_3{\cdot}OEt_2$ (^{11}B) or 85% H_3PO_4 (^{31}P). Elemental analysis (C, H, N) were obtained on a Carlo Erba MOD-1106 instrument using helium as carrier gas. AN numbers were obtained as described previously [30] and were referenced against PPh_3 ($\delta = -6.0$) dissolved in the $CDCl_3$ used as a lock. The following compounds were obtained commercially and used as supplied: $Oct^nMeSiCl_2$, Me_2SiCl_2, $PhMeSiCl_2$, Ph_2SiCl_2, $Ar\text{-}B(OH)_2$ (Ar = Ph, *p*-BrC_6H_4, *m*-$NH_2C_6H_4$, *m*-$NO_2C_6H_4$), $Bu^nB(OH)_2$, and Et_3PO. The amines used as ligands were obtained commercially and distilled before use. $Oct^nMeSi(OH)_2$, $Ph_2Si(OH)_2$, $\{MePhSi(OH)\}_2O$, $\{Me_2Si(OH)\}_2O$ and *o*-$MeC_6H_4B(OH)_2$ were prepared by literature procedures [34,35]. Details of the preparations of **8**, and **16**, typical of those shown in Eqs. (1)–(3), are given below together with ^1H and IR data for all new compounds. Yields, m.p. and elemental analysis data for new compounds are given in Table 1, and ^{11}B-NMR data are given in Table 2.

3.2. Preparation of $(p\text{-}BrC_6H_4BO)_2(Ph_2SiO)_2$ (8)

$Ph_2Si(OH)_2$ (1.0 g, 5.0 mmol) was added to *p*-$BrC_6H_4B(OH)_2$ (0.93 g, 5.0 mmol) in $C_6H_5CH_3$ (100 ml) and heated to reflux in a Dean–Stark apparatus for 20 h. The H_2O-rich layer (0.18 ml, 99.9% H_2O, 10 mmol) which formed during the reflux/azeotropic distillation was discarded. The reaction solution was allowed to cool and a small quantity of solid residue which formed was removed by filtration and discarded. The $C_6H_5CH_3$ was removed from the reaction mixture by use of a rotary evaporator at reduced pressure (20 mmHg), and the residual solid was recrystallised from Et_2O–60–80°C petroleum ether (1:3) to afford the product as a white solid (1.46 g, 83%). Crystals suitable for X-ray diffraction were grown by diffusion of 60–80°C petroleum ether into a layered solution of the compound in $CHCl_3$.

3.3. Preparation of $(PhBO)_2(Ph_2SiO)_2 \cdot C_6H_{11}NH_2$ (16)

At room temperature $C_6H_{11}NH_2$ (0.082 g, 0.83 mmol) in Et_2O (20 ml) solution was added to a stirred suspension of $(PhBO)_2(Ph_2SiO)_2$ (0.5 g, 0.83 mmol) in Et_2O (20 ml). The diboracyclotetrasiloxane dissolved after a few minutes stirring and the resultant solution was filtered. The product, a white air-stable analytically pure solid (0.5 g, 86%), was obtained after evaporation of the solvent and oven drying (50°C) of the residue.

3.4. ^{1}H-NMR data ($CDCl_3$/r.t. 250 MHz)

2: 0.2 (s, 12H), 7.4 (d, 2H), 7.65 (d, 2H); **3**: 0.3 (s, 12H), 3.65 (br s, 2H), 6.8 (d, 1H), 7.25 (m, 3H); **5**: 0.55 (s, 6H), 7.2–7.45 (m, 10H), 7.5 (d, 2H), 7.75 (d, 2H); **6**: 0.5 (s, 6H), 3.6 (br s, 2H), 6.7 (d, 1H), 7.05–7.4 (m, 11H), 7.7 (m, 2H); **8**: 7.3–7.5 (m, 12H), 7.6 (d, 4H), 7.75 (m, 8H), 7.97 (d, 4H); **9**: 2.6 (s, 6H), 7.15–7.5 (m, 18H), 7.6 (m, 8H), 8.05 (d, 2H); **10**: 3.7 (s, 4H), 6.9 (d, 2H), 7.3 (t, 2H), 7.35 (t, 12H), 7.5 (m, 2H), 7.55 (d, 2H), 7.75 (m, 8H); **11**: 7.35–7.55 (m, 12H), 7.6 (t, 2H), 7.75 (m, 8H), 8.4 (m, 4H), 8.85 (s, 2H); **12**: 1.0 (t, 6H), 1.15 (m, 4H), 1.45 (m, 4H), 1.6 (q, 4H), 7.35–7.55 (m, 12H), 7.7 (m, 8H); **13**: 0.4 (s, 6H), 0.9 (m, 10H), 1.3 (m, 24H), 7.45 (m, 6H), 7.9 (m, 4H); **14**: 0.3 (s, 6H), 0.9 (m, 10H), 1.2 (m, 24H), 7.45 (d, 4H), 7.6 (d, 4H); **15**: 0.4 (s, 6H), 0.75 (m, 10H), 1.15 (m, 24H), 7.5 (t, 2H), 8.05 (d, 2H), 8.25 (d, 2H), 8.55 (s, 2H); **16**: 1.25 (m, 6H), 1.7–1.95 (m, 4H), 2.5 (br s, 2H), 2.9 (m, 1H), 7.15–7.55 (m, 18H), 7.7 (m, 8H), 8.0 (m, 4H); **17**: 1.1 (t, 9H), 2.7 (q, 6H), 7.1–7.6 (m, 26H), 7.95 (m, 4H); **18**: 1.35 (m, 6H), 2.05 (br s, 1H), 2.75 (t, 4H), 7.05–7.35 (m, 18H), 7.55 (m, 8H), 7.8 (m, 4H); **19**: 0.8 (d, 6H), 1.6 (sept, 1H), 2.55 (d, 2H), 2.65 (br s, 2H), 7.15–7.5 (m, 18H), 7.6–7.75 (m, 8H), 8.05 (m, 4H); **20**: 1.0 (br s, 1H), 2.65 (s, 6H), 2.8 (t, 4H), 3.5 (t, 4H), 7.3 (m, 18H), 7.6 (m, 8H), 7.9 (m, 2H).

3.5. Selected IR data (ν_{max}(strong)/cm^{-1}, thin films on NaCl plates or KBr discs[a])

1: 1438, 1316, 1261, 1070; **2**: 1391, 1315, 1261, 1067; **3**: 1439, 1340, 1310, 1260, 1066; **4**: 1438, 1429, 1318, 1262, 1190, 1070; **5**: 1390, 1361, 1317, 1261, 1124, 1104, 1068; **6**: 1440, 1317, 1261, 1123, 1072; **7**[a]: 1441, 1388, 1180, 1132, 1071; **8**[a]: 1390, 1308, 1148, 1130, 1118, 1067; **9**[a]: 1439, 1429, 1352, 1303, 1275, 1150, 1117; **10**[a]: 1440, 1357, 1315, 1255, 1128, 1118; **11**[a]: 1429, 1374, 1340,1300, 1268, 1153, 1129; **12**: 1430, 1364, 1283, 1254, 1198, 1128, 1118; **13**: 1441, 1363, 1306, 1261, 1142; **14**: 1392, 1270, 1342, 1306, 1262,1139, 1012; **15**: 1478, 1427, 1387, 1350, 1302, 1270, 1149; **16**: 1443, 1429, 1403, 1332, 1285, 1252, 1123, 1028; **17**: 1446, 1423, 1297, 1271, 1252, 1118, 1087; **18**: 1429, 1283, 1234, 1184, 1149, 1120, 1064, 1028; **19**: 1441, 1430, 1400, 1313, 1258, 1191, 1119, 1070, 1027; **20**: 1447, 1429, 1389, 1314, 1279, 1127, 1096, 1039.

3.6. X-ray structure of $(p\text{-}BrC_6H_4BO)_2(Ph_2SiO)_2$ (8)

Crystallographic measurements were made using a FAST area detector diffractometer and Mo–K_α radiation following previously described procedures [36]. The data were corrected for absorption (DIFABS) [37].

Crystal data: $C_{36}H_{28}B_2Br_2O_4Si_2$, formula weight = 762.20, triclinic, space group $P\bar{1}$, $a = 8.5613(11)$, $b = 10.1141(6)$, $c = 10.2200(7)$ Å, $a = 71.068(12)$, $b = 81.91(2)$, $\gamma = 86.902(9)°$, $U = 828.71(13)$ Å^3, $Z = 1$, λ(Mo–K_α) = 0.71069 Å, $\mu = 25.58$ cm^{-1}, crystal size $0.35 \times 0.30 \times 0.25$ mm, colourless prism, $T = 150$ K, 3430 data collected [$2.12 \leq \theta \leq 24.87°$; $-8 \leq h \leq 9$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$], 2276 unique with $F_o > 0$ ($R_{int} = 0.0739$). The structure was solved by direct methods (SHELXS-86 [38]) and refined on F^2 by full-matrix least-squares (SHELXL-96 [39]) using all unique data to final wR (on F^2) = 0.0921 (all 2276 data and 208 parameters) and R [on F, $F_o > 4\sigma(F_o)$] = 0.0403. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms included in calculated positions (riding model) with U_{iso} set at 1.2 times the U_{eq} of the parent atom.

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 119653. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ [fax: +44-1223-336033 or e-mail: deposit @ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

Acknowledgements

We thank Dr D. Apperley at the EPSRC solid state NMR service centre (Durham University) for spectra. We also acknowledge the EPSRC X-ray Crystallographic service at UWC.

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