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Synthesis and characterisation of *cyclo*-boratetrasiloxane, (RBO)$(Me_2SiO)_3$ (R = ^{n}Bu, Ar), derivatives

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Abstract

Low temperature reactions of dilute solutions of 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane with boronic acids {$RB(OH)_2$; R = ^{n}Bu, C_6H_4Me-2, C_6H_4Me-3, C_6H_4Me-4, C_6H_4OMe-3, C_6H_4OMe-4, C_6H_4Br-2, C_6H_4Br-3, C_6H_4Br-4} in the presence of a twofold excess of Et_3N afforded the 8-membered ring products, *cyclo*-boratetrasiloxanes, (RBO)$(Me_2SiO)_3$, in moderate yields. New compounds were colourless oils and were characterised by elemental analysis, NMR (^1H, ^{11}B, ^{13}C, ^{29}Si), IR and MS. The *cyclo*-boratetrasiloxanes are weakly Lewis acidic, with acceptor number (AN) values of ~30, but do not form adducts with amines.

Keywords: *Cyclo*-boratetrasiloxanes; B–O–Si linkages; Cyclocondensation; Lewis acidity

1. Introduction

Cyclic species containing B–O–Si linkages are represented in the literature by a number of 6-, 8- and 10-membered *cyclo*-borasiloxane ring systems [1–9]. Other compounds containing the B–O–Si linkage are the acyclic triorganosilyl esters of orthoboric [10–19], metaboric [16–18] and boronic acids [16–20], and the condensed borosilicate cage systems [21–24]. In addition to these examples, which all contain 3-coordinate B centres, there are also a few cases of compounds with B–O–Si links in which the B atom is 4-coordinate [25–28]. We are interested in assessing the Lewis acidity at 3-coordinate boron centres in compounds containing B–O–Si linkages and have previously examined triorganosilyl esters [18,29] and *cyclo*-boratrisiloxane (Fig. 1a) and *cyclo*-diboratetrasiloxane (Fig. 1b) systems [8,29]. Herein, we report the synthesis of some new *cyclo*-boratetrasiloxane (Fig. 1c) derivatives, and an assessment of their Lewis acidities by Gutmann's [30] method.

2. Results and discussion

Cyclo-borasiloxane ring systems are synthetically available by cyclocondensation reactions of appropriate B and Si containing precursors. Organoboronic acids have been successfully condensed with dihydroxysilanes, diethoxysilanes, α, ω-dihydroxysiloxanes, α, ω-diethoxysiloxanes and α, ω-dichlorosiloxanes [1–3,6,7], and dichlorophenylborane has been condensed with dihydroxysilanes [5]. The *cyclo*-boratetrasiloxanes reported here were prepared by the method of Wannagat and Eisele [3], first employed in the synthesis of (PhBO)-$(SiMe_2O)_2$, by use of an equimolar mixture of the appropriate organoboronic acid with 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane, in the presence of two molar equivalents of NEt_3 to act as HCl acceptor, as shown in Scheme 1. The new compounds **1–9** were prepared in modest to moderate yields (22–69%) as colourless oils, after filtration of the reaction mixture to

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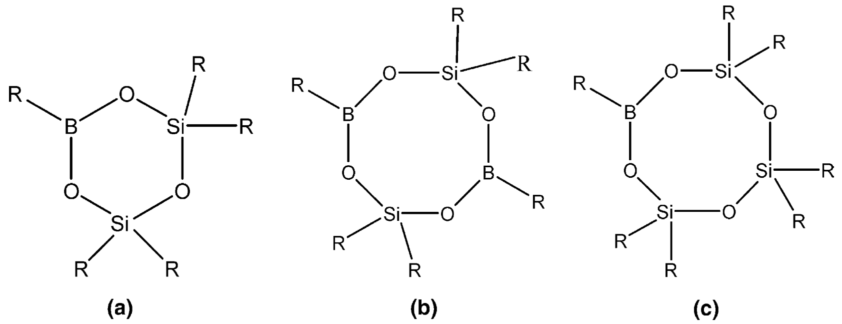
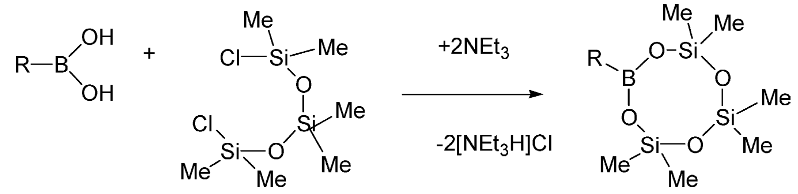


Fig. 1. Schematic structures of (a) *cyclo*-boratrisiloxanes, (b) *cyclo*-diboratetrasiloxanes, and (c) *cyclo*-boratetrasiloxanes. R = alkyl or aryl.



Scheme 1. Synthesis of *cyclo*-boratetrasiloxane derivatives, $Me_6Si_3O_4BR$ {R = C_6H_4Me-2 (**1**), C_6H_4Me-3 (**2**), C_6H_4Me-4 (**3**), C_6H_4OMe-3 (**4**), C_6H_4OMe-4 (**5**), C_6H_4Br-2 (**6**), C_6H_4Br-3 (**7**), C_6H_4Br-4 (**8**), ^{n}Bu (**9**)}.

remove the solid $[NEt_3H]Cl$, and removal of all volatiles from the filtrate under reduced pressure. Low temperature reagent addition and dilute reaction mixtures were essential in obtaining the desired *cyclo*-boratetrasiloxanes by limiting polymer formation. Manners and co-workers [7] have previously prepared the *cyclo*-boratetrasiloxane, $(PhBO)(SiMe_2O)_3$, in 74% by this method.

Compounds **1**–**9** were relatively air-stable but were susceptible to hydrolysis and hence were stored under dry N_2. Satisfactory elemental (C, H) analysis data were obtained on all compounds, and mass spectrometry and spectroscopic (NMR, IR) data were consistent with the 8-membered ring *cyclo*-boratetrasiloxane formulation. Additionally, the molecular weight of **3**, as determined by freezing point depression of camphor, was also fully consistent with the 8-membered ring formulation.

Thermal analysis over the temperature range 20–750 °C was undertaken on **3** in order to ascertain whether these *cyclo*-boratetrasiloxanes were possible precursors to Si–O–B ceramics. The TGA trace revealed significant (>80%) weight loss from the sample between 180 and 260 °C, with ~100% weight loss by 300 °C. There was no observable sample residue, and the DSC trace displayed an endothermic peak at 220 °C, consistent with vaporisation of the sample. Clearly, **3** was not a potential thermal precursor to Si–O–B ceramics.

Mass spectra were obtained for all compounds except **7** and **9**. Molecular ions were observed in all cases and breakdown patterns were all generally very similar, and consistent with breakdown patterns reported for other *cyclo*-borosiloxanes [3,5,7]. In particular, all spectra showed intense peaks at $M^+ - CH_3$ (base peaks for **1**, **2**, **3** and **5**) with generally relatively weak molecular ion peaks. All spectra also displayed strong signals at *m/e* $M^+ - 57$ ($M^+ - SiMe_2 + H$), and at *m/e* 207 (M^+–Me–ArBO). IR spectra of all compounds were characterised by very strong absorptions in the 1302–1356 cm^{-1} and 1049–1078 cm^{-1} regions due to B–O and Si–O stretching modes, respectively, with additional strong signals at 2962 (C–H), 1261 (B–O), and 808 (O–Si–O bend? [31]) cm^{-1}. ^{11}B NMR spectra all showed one signal in the range expected [32] for trigonal CBO_2 centres with the butyl derivative **9** having a resonance significantly to higher frequency of resonances for the aryl derivatives, **1**–**8**. ^{29}Si spectra show two signals at ca. δ −17 separated by ca. 1.5 ppm, with the low frequency signal being approximately of double intensity and assigned to the Si atoms linked via O to B. These observations are in accord with those reported for (PhBO) $(SiMe_2O)_3$ [7]. The ^{29}Si signals for the butyl derivative (**9**) are at lower frequency by ca. 1.5 ppm relative to the aryl derivatives **1**–**8**. The number of signals and their relative intensities observed in ^1H NMR spectra of **1**–**9** were all consistent with their formulations as *cyclo*-boratetrasiloxanes and were characterised by two almost coincidental signals of relative intensity 1:2 centred at ca. 0.2 ppm, associated with the $SiMe_2$ protons, in proportion to additional signals associated with the organo-B functionality.

We have previously noted that whereas *cyclo*-boratrisiloxanes were unreactive towards amines, *cyclo*-

diboratetrasiloxanes were sufficiently Lewis acidic to form adducts [8,29]. The reaction of the *cyclo*-boratetrasiloxanes **1**–**9** with amines was attempted but adducts were not obtained, indicating that they were poor Lewis acids. This was further quantified on selected examples by use of Gutmann's [30,33] method, which confirmed their weak Lewis acidity and gave acceptor number (AN) values of 29, 30 and 30, for **1, 3** and **9**, respectively. For comparison, we have previously reported that *cyclo*-diboratetrasiloxanes had AN values of 47–62 and *cyclo*-boratrisiloxanes had values of 22–28, and an explanation on their relative Lewis acidities has been offered in terms of competitive O–Si and O–B π-bonding, and the different B:Si ratios within the ring systems [8]. The electronic effect of the {$-SiMe_2OSiMe_2-$} and {$-SiMe_2OSiMe_2OSiMe_2-$} fragments towards {RBO_2} must be very similar and this is reflected in their AN values. The slightly higher value (i.e., more acidic nature) of the *cyclo*-boratetrasiloxane compared to the *cyclo*-boratrisiloxane may not be significant but is opposite to that expected from the increased Si:B ratio. Ring strain may be an important factor here since adduct formation would lead to a reduction of the ring angle at B, and this is more easily accommodated in an 8-membered ring. Alternatively, it may be that the *cyclo*-boratrisiloxane has reduced Lewis acidity, when compared to other *cyclo*-borasiloxanes, since it is formally a 6π-electron system.

3. Experimental

3.1. General

Reactions were carried out under N_2 in dried solvents. The boronic acids and $Si_3Me_6O_2Cl_2$ were obtained commercially and used as supplied. IR spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer as thin films between NaCl plates. TGA-DSC analysis on **3** was undertaken on a TA Instruments SDTQ600 thermal analyser. Multi-element solution NMR was recorded on a Bruker AC 250 CP/MAS NMR spectrometer operating at 250.0 MHz for ^1H, 80.25 MHz for ^{11}B, 62.90 MHz for ^{13}C, 101.25 MHz for ^{31}P and 49.66 MHz for ^{29}Si. Chemical shifts (δ) are given in ppm with positive values towards high frequency from $SiMe_4$ (^1H, ^{13}C, ^{29}Si), BF_3OEt_2 (^{11}B), and 85% H_3PO_4 (^{31}P). Elemental analyses were obtained on a Carlo Erba EA-1108 (C, H, N) instrument using helium as carrier gas. AN values were obtained as described previously [33] and were referenced against PPh_3 ($\delta = -6.0$) dissolved in $CDCl_3$ and used a lock. EI (70 eV) MS spectra were obtained on a Finnigan 4500 instrument.

3.2. Synthesis

Boratetrasiloxanes were all prepared by an adaptation of a literature method [3,7], with the procedure described below for $Me_6Si_3O_4B(C_6H_4Me\text{-}2)$ (**1**).

$Me_6Si_3O_4B(C_6H_4Me\text{-}2)$ (**1**). *ortho*-Tolylboronic acid, $(C_6H_4Me\text{-}2)B(OH)_2$, (1.0 g, 7.4 mmol) was dissolved in anhydrous Et_2O (1000 cm^3). NEt_3 (1.56 g, 15.5 mmol) was added and the solution was cooled to −78 °C by means of a dry ice/acetone bath. 1,5-Dichloro-1,1,3,3,5,5-hexamethyltrisiloxane, $ClSiMe_2OSiMe_2OSiMe_2Cl$, (2.04 g, 7.4 mmol) was added via a dropping funnel over a 1 h period, maintaining the stirred reaction temperature at −78 °C. The reaction mixture was then allowed to warm to room temperature and was stirred for a further 24 h. Filtration of the reaction mixture removed $[NEt_3H]Cl$, and removal of the Et_2O from the filtrate, under reduced pressure, afforded the product as a *colourless oil* (1.5 g). Yield 59%. NMR (ppm): $\delta(^1H)$: 7.5 (d, 7.7 Hz, 1H), 7.0 (m, 3H), 2.4 (s, 3H), 0.1 (s, 12H), 0.0 (s, 6H); $\delta(^{11}B)$: 24.6; $\delta(^{13}C)$: 144.8, 136.5, 130.4, 130.1, 124.7, 22.8, 0.6, 0.4; $\delta(^{29}Si)$: −16.5, −17.7. IR (cm^{-1}): 2962s, 1599m, 1439m, 1329brs, 1261s, 1143m, 1074brs, 887m, 857s, 808s, 730m, 653m. MS (EI, 70 eV) *m/z* (%): 340 (20, M^+), 325 (100, $M^+ - CH_3$), 283 (60), 251 (20), 207 (45, $M^+ - Me - ArBO$), 163 (25), 133 (30). Elemental analysis. Found: C, 45.7; H 7.5%; required for $C_{13}H_{25}BO_4Si_3$: C, 45.9, H, 7.4%.

$Me_6Si_3O_4\ B(C_6H_4Me\text{-}3)$ (**2**). Yield 64%, colourless oil. NMR (ppm): $\delta(^1H)$: 7.7 (m, 2H), 7.35 (m, 2H), 2.4 (s, 3H), 0.3 (s, 12H), 0.2 (s, 6H); $\delta(^{11}B)$: 25.1; $\delta(^{13}C)$: 136.7, 135.8, 134.4, 132.3, 131.7, 127.4, 21.3, 0.6, 0.3; $\delta(^{29}Si)$: −16.5, −17.7. IR (cm^{-1}): 2963s, 1423m, 1335s, 1310brs, 1261s, 1214m, 1128m, 1078brs, 885m, 858m, 844m, 808s, 709s. MS (EI, 70 eV) *m/z* (%): 340 (15, M^+), 325 (100, $M^+ - CH_3$), 283 (48, $M^+ - SiMe_2 + H$), 251 (14), 207 (36, $M^+ - Me - ArBO$), 191 (35), 163 (16), 133 (29). Elemental analysis. Found: C, 45.6; H, 7.5%; required for $C_{13}H_{25}BO_4Si_3$: C, 45.9; H, 7.4%.

$Me_6Si_3O_4B(C_6H_4Me\text{-}4)$ (**3**). Yield 35%, colourless oil. NMR (ppm): $\delta(^1H)$: 7.6 (d, 7.7 Hz, 2H), 7.1 (d, 7.7 Hz, 2H), 2.3 (s, 3H), 0.2 (s, 12H), 0.1 (s, 6H); $\delta(^{11}B)$: 25.2; $\delta(^{13}C)$: 141.1, 135.4, 134.7, 128.4, 21.7, 0.7, 0.4; $\delta(^{29}Si)$: −16.6, −17.8. IR (cm^{-1}): 2962m, 1610m, 1400m, 1315brs, 1261s, 1141m, 1075brs, 885m, 858m, 807s. MS (EI, 70 eV) *m/z* (%): 340 (25, M^+), 325 (100, $M^+ - CH_3$), 283 (73, $M^+ - SiMe_2 + H$), 251 (10), 207 (50, $M^+ - Me - ArBO$), 191 (52), 163 (40), 133 (48). Elemental analysis. Found: C, 45.7; H, 7.4%; required for $C_{13}H_{25}BO_4Si_3$: C, 45.9; H, 7.4%. Rast's method for molecular weight determination: **3** (0.021 g) was dissolved in molten camphor (0.4958 g) and allowed to solidify. M. pt 173 °C. Calculated Molecular weight, 336 g/mol [34].

$Me_6Si_3O_4B(C_6H_4OMe\text{-}3)$ (**4**). Yield 65%, colourless oil. NMR (ppm): $\delta(^1H)$: 7.4 (m, 3H), 7.1 (m, 1H), 3.9 (s, 3H), 0.4 (s, 12H), 0.2 (s, 6H); $\delta(^{11}B)$: 24.8; $\delta(^{13}C)$: 159.1,

136.0, 128.7, 127.7, 120.4, 116.6, 55.1, 0.7, 0.4; $\delta(^{29}\mathrm{Si})$: −16.6, −17.6. IR (cm^{-1}): 2961s, 1596m, 1575m, 1485m, 1464m, 1446m, 1421s, 1309brs, 1261s, 1243s, 1182m, 1122s, 1049brs, 944m, 884s, 858s, 805s, 708s, 685m, 673m. MS (EI, 70 eV) *m/z* (%): 356 (85, M^{+}), 341 (60, $\mathrm{M}^{+}-\mathrm{CH_3}$), 299 (65, $\mathrm{M}^{+}-\mathrm{SiMe_2}+\mathrm{H}$), 207 (70, $\mathrm{M}^{+}-\mathrm{Me}-\mathrm{ArBO}$), 91 (100), 73 (88). Elemental analysis. Found: C, 43.6; H, 7.2%; required for $\mathrm{C_{13}H_{25}BO_5Si_3}$: C, 43.8; H, 7.1%.

$Me_6Si_3O_4B(C_6H_4OMe\text{-}4)$ (**5**). Yield 69%, colourless oil. NMR (ppm): $\delta(^{1}\mathrm{H})$: 7.6 (d 7.7 Hz, 2H), 6.9 (d, 7.7 Hz, 2H), 3.7 (s, 3H), 0.15 (s, 12H), 0.05 (s, 6H); $\delta(^{11}\mathrm{B})$: 24.7; $\delta(^{13}\mathrm{C})$: 162.1, 137.1, 126.2, 113.1, 55.1, 0.7, 0.4; $\delta(^{29}\mathrm{Si})$: −16.2, −17.7. IR (cm^{-1}): 2961s, 1603s, 1408m, 1316brs, 1261s, 1174m, 1143m, 1075brs, 885m, 858m, 808s, 649m. MS (EI, 70 eV) *m/z* (%): 356 (100, M^{+}), 341 (83, $\mathrm{M}^{+}-\mathrm{CH_3}$), 299 (100, $\mathrm{M}^{+}-\mathrm{SiMe_2}+\mathrm{H}$), 207 (74, $\mathrm{M}^{+}-\mathrm{Me}-\mathrm{ArBO}$), 91 (98), 73 (28). Elemental analysis. Found: C, 43.5; H, 7.2%; required for $\mathrm{C_{13}H_{25}BO_5Si_3}$: C, 43.8; H, 7.1%.

$Me_6Si_3O_4B(C_6H_4Br\text{-}2)$ (**6**). Yield 49%, colourless oil. NMR (ppm): $\delta(^{1}\mathrm{H})$: 7.54 (m, 1H), 7.49 (m, 1H), 7.1 (m, 2H), 0.9 (s, 12H), 0.1 (s, 6H); $\delta(^{11}\mathrm{B})$: 24.3; $\delta(^{13}\mathrm{C})$: 138.2, 135.7, 132.6, 130.0, 127.2, 3.3, −0.2; $\delta(^{29}\mathrm{Si})$: −15.8, −17.6. IR (cm^{-1}): 2962s, 1588m, 1557m, 1425m, 1356brs, 1307s, 1261s, 1143m, 1055brs, 881m, 805s. MS (EI, 70 eV) *m/z* (%): 406 (8, M^{+}), 391 (58, $\mathrm{M}^{+}-\mathrm{CH_3}$), 349 (25, $\mathrm{M}^{+}-\mathrm{SiMe_2}+\mathrm{H}$), 267 (70), 207 (60, $\mathrm{M}^{+}-\mathrm{Me}-\mathrm{ArBO}$), 191 (63), 147 (100), 91 (68). Elemental analysis. Found: C, 35.3; H, 5.6%; required for $\mathrm{C_{12}H_{22}BBrO_4Si_3}$: C, 35.6; H, 5.5%.

$Me_6Si_3O_4B(C_6H_4Br\text{-}3)$ (**7**). Yield 41%, colourless oil. NMR (ppm): $\delta(^{1}\mathrm{H})$: 7.9 (m, 1H), 7.7 (m, 1H), 7.6 (m, 1H), 7.3 (m, 1H), 0.3 (s, 12H), 0.16 (s, 6H); $\delta(^{11}\mathrm{B})$: 23.9 ; $\delta(^{13}\mathrm{C})$: 138.0, 133.8, 133.6, 129.4, 122.4, 0.7, 0.4; $\delta(^{29}\mathrm{Si})$: −16.4, −17.3. IR (cm^{-1}): 2963s, 1302brs, 1261s, 1147m, 1075brs, 910m, 882m, 855s, 808s, 704m. Elemental analysis. Found: C, 35.3; H, 5.7%; required for $\mathrm{C_{12}H_{22}BBrO_4Si_3}$: C, 35.6; H, 5.5%.

$Me_6Si_3O_4B(C_6H_4Br\text{-}4)$ (**8**). Yield 30%, colourless oil. NMR (ppm): $\delta(^{1}\mathrm{H})$: 7.5 (d, 7.7 Hz, 2H), 7.35 (d, 7.7 Hz, 2H), 0.1 (s, 12H), 0.0 (s, 6H); $\delta(^{11}\mathrm{B})$: 24.9 ; $\delta(^{13}\mathrm{C})$: 136.9, 136.3, 132.4, 130.8, 126.0, 0.6, 0.3; $\delta(^{29}\mathrm{Si})$: −16.3, −17.3. IR (cm^{-1}): 2962s, 1586s, 1387s, 1340brs, 1310s, 1262s, 1138s, 1069brs, 1012s, 883m, 856s, 807s, 725m, 643m. MS (EI, 70 eV) *m/z* (%): 406 (10, M^{+}), 391 (58, $\mathrm{M}^{+}-\mathrm{CH_3}$), 349 (12, $\mathrm{M}^{+}-\mathrm{SiMe_2}+\mathrm{H}$), 281 (5), 249 (32), 207 (100, $\mathrm{M}^{+}-\mathrm{Me}-\mathrm{ArBO}$), 177 (38), 133 (65), 91 (64). Elemental analysis. Found: C, 35.4; H, 5.8%; required for $\mathrm{C_{12}H_{22}BBrO_4Si_3}$: C, 35.6; H, 5.5%.

$Me_6Si_3O_4BBu^{n}$ (**9**). Yield 22%, colourless oil. NMR (ppm): $\delta(^{1}\mathrm{H})$: 1.3 (m, 4H), 0.85 (t, 7.7 Hz, 3H), 0.69 (m, 2H), 0.15 (s, 12H), 0.1 (s, 6H); $\delta(^{11}\mathrm{B})$: 31.3; $\delta(^{13}\mathrm{C})$: 26.8, 25.4, 14.0, 0.9, 0.7. 0.3; $\delta(^{29}\mathrm{Si})$: −17.1, −19.3. IR (cm^{-1}): 2961s, 2928m, 2873m, 1329brs, 1284m, 1260s, 1052brs, 891m, 855m, 803s. Elemental analysis. Found: C, 39.4; H, 8.8%; required for $\mathrm{C_{10}H_{27}BO_4Si_3}$: C, 39.2; H, 8.9%.

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