

Synthetic and X-ray diffraction studies of borosiloxane cages $[\text{R}'\text{Si}(\text{ORBO})_3\text{SiR}']$ and the adducts of $[\text{Bu}'\text{Si}\{\text{O}(\text{PhB})\text{O}\}_3\text{SiBu}']$ with pyridine or N,N,N',N' -tetramethylethylenediamine

George Ferguson^{a,*}, Simon E. Lawrence^b, Lorraine A. Neville^b,
Brian J. O'Leary^b, Trevor R. Spalding^{b,*}

^a School of Chemistry, The University of St. Andrews, Fife KY16 9ST, UK

^b Department of Chemistry, University College Cork, National University of Ireland, Cork, Ireland

Received 8 November 2006

Available online 20 January 2007

Abstract

Eleven borosiloxane $[\text{R}'\text{Si}(\text{ORBO})_3\text{SiR}']$ compounds where $\text{R}' = \text{Bu}'$ and $\text{R} = \text{Ph}$ (**1**), 4- PhC_6H_4 (**2**), 4- $\text{Bu}'\text{C}_6\text{H}_4$ (**3**), 3- $\text{NO}_2\text{C}_6\text{H}_4$ (**4**), 4- $\text{CH}(\text{O})\text{C}_6\text{H}_4$ (**5**), CpFeC_5H_4 (**6**), 4- $\text{C}(\text{O})\text{CH}_3\text{C}_6\text{H}_4$ (**7**), 4- ClC_6H_4 (**8**), 2,4- $\text{F}_2\text{C}_6\text{H}_3$ (**9**), and $\text{R}' = \text{cyclo-C}_6\text{H}_{11}$ and $\text{R} = \text{Ph}$ (**10**), and 4- BrC_6H_4 (**11**) have been synthesized and characterized by spectroscopic (IR, NMR), mass spectrometric and, for compounds where $\text{R}' = \text{Bu}'$ and $\text{R} = 4\text{-PhC}_6\text{H}_4$ (**2**), 4- $\text{Bu}'\text{C}_6\text{H}_4$ (**3**), 3- $\text{NO}_2\text{C}_6\text{H}_4$ (**4**), CpFeC_5H_4 (**6**) and 2,4- $\text{F}_2\text{C}_6\text{H}_3$ (**9**), X-ray diffraction studies. These compounds contain trigonal planar RBO_2 and tetrahedral $\text{R}'\text{SiO}_3$ units located around 11-atom “spherical” $\text{Si}_2\text{O}_6\text{B}_3$ cores. The dimensions of the $\text{Si}_2\text{O}_6\text{B}_3$ cores in compounds **2**, **3**, **4**, **6** and **9** are remarkably similar. The reaction between $[\text{Bu}'\text{Si}\{\text{O}(\text{PhB})\text{O}\}_3\text{SiBu}']$ (**1**), and excess pyridine yields the 1:1 adduct $[\text{Bu}'\text{Si}\{\text{O}(\text{PhB})\text{O}\}_3\text{SiBu}'] \cdot \text{NC}_5\text{H}_5$ (**12**) while the reaction between **1** and N,N,N',N' -tetramethylethylenediamine in equimolar amounts affords a 2:1 borosiloxane:amine adduct $[\text{Bu}'\text{Si}\{\text{O}(\text{PhB})\text{O}\}_3\text{SiBu}']_2 \cdot \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ (**13**). Compounds **12** and **13** were characterised with IR and (^1H , ^{13}C and ^{11}B) NMR spectroscopies and the structure of the pyridine complex **12** was determined with X-ray techniques.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Borosilicate; Borosiloxanes; Cage compounds; X-ray diffraction; Structures

1. Introduction

The chemistry of three-dimensional cage species containing only main group elements bonded by two center–two electron bonds is notable for the large number of silesesquioxanes $[(\text{RSi})_8\text{O}_{12}]$ which have been reported [1]. For cages containing main group 13 elements, aluminium systems are perhaps the most studied with aluminium–nitrogen compounds predominant [2]. Boron containing

species are relatively rare [3] but previously reported borosiloxane cage compounds that have been structurally characterised include $[\text{Bu}'\text{Si}\{\text{O}(4\text{-BrC}_6\text{H}_4\text{B})\text{O}\}_3\text{SiBu}']$ which contains the 11-atom “spherical” $\text{B}_3\text{Si}_2\text{O}_6$ core [4], $[\text{B}(\text{OSiPh}_2\text{SiPh}_2\text{O})_3\text{B}]$ with a “cylindrical” $\text{B}_2\text{Si}_6\text{O}_6$ core [5], “cube-based” $[(\text{Bu}'\text{Si})_4(4\text{-RC}_6\text{H}_4\text{B})_4\text{O}_{10}]$ species where $\text{R} = (\text{CH}_2=\text{CH})$ [6] or Br [7] which have $\text{B}_4\text{Si}_4\text{O}_{10}$ cores, and silesesquioxane-based species which contain “cube-based” $\text{BSi}_7\text{O}_{12}$ units [8]. One overall intention of the work carried out by our group [3–7] was to synthesise a variety of three-dimensional structures which could be reacted further to produce new molecular scaffolds in a controlled way. We now report the extension of the chemistry of the

* Corresponding authors.

E-mail addresses: gf3@st-andrews.ac.uk (G. Ferguson), t.spalding@ucc.ie (T.R. Spalding).

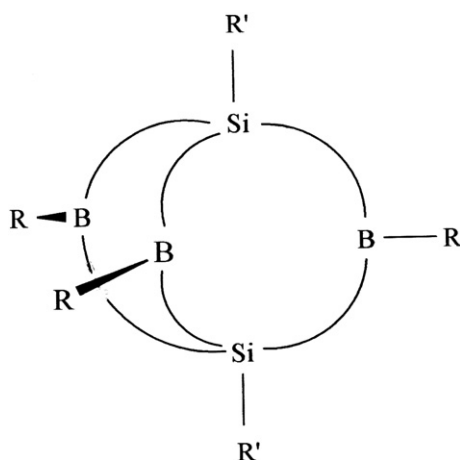


Diagram 1.

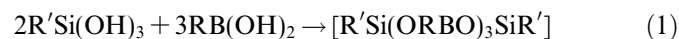
“spherical” cage borosiloxanes with the syntheses of 11 analogues of $[R'Si(OBRO)_3SiR']$ with a wide variety of R groups, Diagram 1.

The details of the structures of five of these compounds have been determined with X-ray crystallography. Additionally, we have studied the reactions between $[Bu'Si\{O(PhB)O\}_3SiBu']$ (**1**) and (a) pyridine or (b) *N,N,N',N'*-tetramethyl-ethylenediamine and established the solid-state structure of the adduct $[Bu'Si\{O(PhB)O\}_3SiBu'] \cdot NC_5H_5$ (**12**).

2. Results and discussion

2.1. Syntheses and structural studies of $[R'Si(ORBO)_3SiR']$ borosiloxanes **1** to **11**

All the borosiloxane cages with the formulae $[R'Si(ORBO)_3SiR']$ were synthesised in a Dean-Stark apparatus by water elimination reactions between $R'Si(OH)_3$ ($R' = Bu'$ or *cyclo*- C_6H_{11}) and boronic acids $RB(OH)_2$ in a 2:3 molar ratio in toluene solution heated at the reflux temperature, Eq. (1). In general the *tert*-butyl compounds were isolated in 30–40% higher yields than the corresponding *cyclohexyl* derivatives with the same R groups.



where $R' = Bu'$ and $R = Ph$ (**1**), 4- PhC_6H_4 (**2**), 4- $Bu'C_6H_4$ (**3**), 3- $NO_2C_6H_4$ (**4**), 4- $CH(O)C_6H_4$ (**5**), $CpFeC_5H_4$ (**6**), 4- $C(O)CH_3C_6H_4$ (**7**), 4- ClC_6H_4 (**8**), 2,4- $F_2C_6H_3$ (**9**), and $R' = cyclo-C_6H_{11}$ and $R = C_6H_5$ (**10**), and 4- BrC_6H_4 (**11**).

An alternative route via the reactions between *tert*-butyltrichlorosilane or *cyclohexyl*trichlorosilane and boronic acids in the presence of an amine, either Et_3N or aniline, afforded the products **1** to **9** in 5–10% lower yields and compounds **10** and **11** in ca. 30% lower yields. Attempts to use phenyl- or tolyltrichlorosilane reagents afforded boroxines as the only characterisable products.

Initial characterisation of **1–11** by chemical analysis was followed by spectroscopic (FT-IR, NMR) and, in some cases, mass spectrometric analysis. For the compounds with $R' = Bu'$ and $R = 4-PhC_6H_4$ (**2**), 4- $Bu'C_6H_4$ (**3**), 3- $NO_2C_6H_4$ (**4**), $CpFeC_5H_4$ (**6**), and 2,4- $F_2C_6H_3$ (**9**), single-crystal X-ray diffraction studies were carried out. A summary of crystal data for these compounds is given in Section 4.

2.2. Crystal and molecular structures of $[Bu'Si\{O(4-PhC_6H_4B)O\}_3SiBu']$ (**2**), $[Bu'Si\{O(4-Bu'C_6H_4B)O\}_3SiBu']$ (**3**), $[Bu'Si\{O(3-NO_2C_6H_4B)O\}_3SiBu']$ (**4**), $[Bu'Si\{O(CpFeC_5H_4B)O\}_3SiBu']$ (**6**), and $[Bu'Si\{O(2,4-F_2C_6H_3B)O\}_3SiBu']$ (**9**)

Comparison of the structures of compounds $[Bu'Si(OBRO)_3SiBu']$ where $R = 4-PhC_6H_4$ (**2**), 4- $Bu'C_6H_4$ (**3**), 3- $NO_2C_6H_4$ (**4**), $CpFeC_5H_4$ (**6**) and 2,4- $F_2C_6H_3$ (**9**) reveals that the structural details of the $Si_2O_6B_3$ cages are remarkably similar, Table 1.

All five compounds contain two tetrahedral $Bu'SiO_3$ -units and three trigonal planar RBO_2 -units held together by an 11-atom $Si(OBO)_3Si$ framework. Figs. 1–3 show ORTEP views of molecules with $R = 4-PhC_6H_4$ (**2**), 4- $Bu'C_6H_4$ (**3**) and $CpFeC_5H_4$ (**6**) from a general perspective.

The structures of compounds **2** and **6** are shown viewed along the axes passing through both silicon atoms in Figs. 4 and 5, respectively. The *tert*-butyl groups attached to the silicon atoms in compounds **2** and **6** are in “eclipsed” arrangements. The same structural motif is found in **3**, **4**, **6** and **9**.

The C_6 -rings attached to the boron atoms in **2** and **3** are arranged in a “paddlewheel” formation, see Fig. 4, and are almost co-planar with the adjacent $Si-O-B-O-Si$ bonded sequence. The same structural motif was observed in **3**, **4**, and **9**, and in the compound $[Bu'Si\{O(4-BrC_6H_4B)O\}_3SiBu']$ [**4**]. A similar situation is observed in the ferrocenyl compound $[Bu'Si\{O(CpFeC_5H_4B)O\}_3SiBu']$ (**6**), where the C_5H_4 ring is almost co-planar with the attached borosiloxane group, Fig. 5. The reason for the preference for co-planarity may reside in a partial overlap of the π system of the aromatic C_6 -ring and some delocalised bonding in the $Si-O-B-O-Si$ sequence. However, it is also possible that the co-planarity is due to “crystal packing” forces. It is interesting to note that in the case of **6** the ferrocenyl groups are not all arranged to give a pseudo- D_{3h} molecular symmetry. The reasons are unclear but may be due either to weak intramolecular $H \cdots \pi-C_5H_5$ ring interactions or more general “crystal packing” forces.

The B–O lengths in **2**, **3**, **4**, **6** and **9** range from 1.348(5) to 1.380(4) and are at the upper end of the reported range for trigonal boron species with $Si-O-B$ bonds i.e. 1.313(2) in $(OBF)(OSiBu'_2)_2(OSiMe_2)$ (**13**) [**9**] to 1.374(7) Å in $[B(OSiPh_2SiPh_2O)_3B]$ (**14**) [**5**]. They are similar to B–O distances in the previously reported spherical cage $[Bu'Si\{O-(4-BrC_6H_4B)O\}_3SiBu']$ (**15**) [**4**], which were

Download English Version:

<https://daneshyari.com/en/article/1339800>

Download Persian Version:

<https://daneshyari.com/article/1339800>

[Daneshyari.com](https://daneshyari.com)