

## A fluorophenylboron-functionalized zirconium silsesquioxane complex

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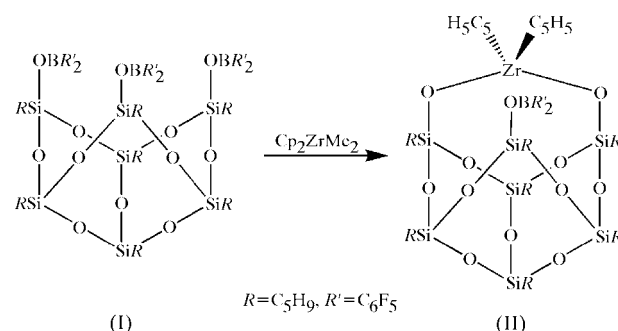
Bis( $\eta^5$ -cyclopentadienyl)[*rel*-(1*R*,5*S*,7*R*,14*S*)-(1,3,5,7,9,11,14-heptacyclopentyl-7,14-dioxidotricyclo[7.3.3<sup>1.9</sup>.1<sup>5,11</sup>]]heptasiloxan-3-yloxybis(pentafluorophenyl)borane(2-)]zirconium, [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>47</sub>H<sub>63</sub>BF<sub>10</sub>O<sub>12</sub>Si<sub>7</sub>)], consists of [ZrCp<sub>2</sub>] (Cp is cyclopentadienyl) and [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B] moieties bound to a silsesquioxane core. The silsesquioxane binds to the Zr atom through two of its O atoms to form a distorted tetrahedron. The [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B] moiety is bound to the silsesquioxane through an O atom, forming an Si—O—B bond angle of 168.4 (4)°. The steric and electronic effects of the Zr atom and the borate moieties force the silsesquioxane core to distort. These distortions can be seen by examination of the Si—O—Si bond angles.

### Comment

The use of organosilsesquioxanes as soluble models of the silanol sites on the surface of silica is well established, and this work is featured in a number of reviews (Feher & Budzichowski, 1995; Baney *et al.*, 1995; Abbenhuis, 2000; Lorenz *et al.*, 2000; Marciniec & Maciejewski, 2001; Duchateau, 2002). In particular, the use of such compounds to model the chemistry of surface-bound organometallic complexes involved in catalysis is a growing field of interest, and a number of cyclopentadienyl group 4 complexes featuring silsesquioxane ligands have been structurally characterized (Feher, 1986; Buys *et al.*, 1994; Duchateau *et al.*, 1998, 1999, 2000; Gun'ko *et al.*, 1999; Wada *et al.*, 2000; Edelmann *et al.*, 2000, 2001; Severn *et al.*, 2002, 2003).

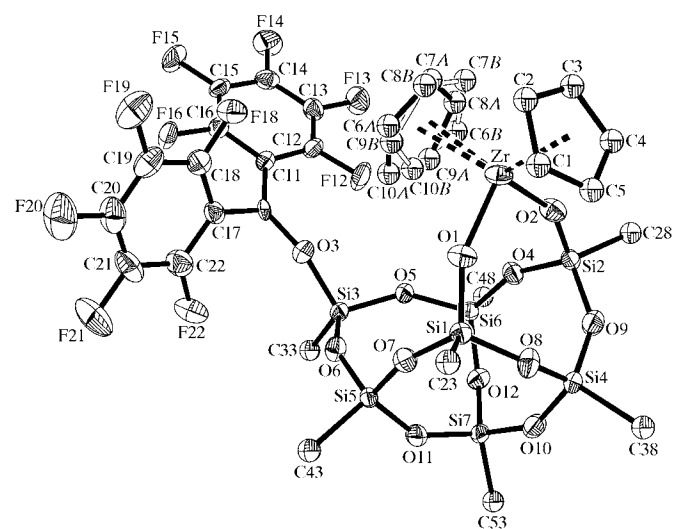
In recent work, we reported the synthesis and structural characterization of tris(boryl)silsesquioxane, (I) (Metcalf *et al.*, 2002), a model compound for hydroxylated silica modified by reactive organoboranes (Tian *et al.*, 1999), and investigated its reactivity towards a typical metallocene complex (Cp<sub>2</sub>ZrMe<sub>2</sub>) in solution by variable-temperature NMR spectroscopy. The principal product of this reaction was the title novel zirconocene-functionalized silsesquioxane, (II), which

had resisted our earlier attempts to obtain it in crystalline form. We now report the molecular structure of complex (II), which features both zirconocene and Lewis acidic borane moieties within the same silsesquioxane molecule. This appears to be the first structurally characterized compound of this kind.



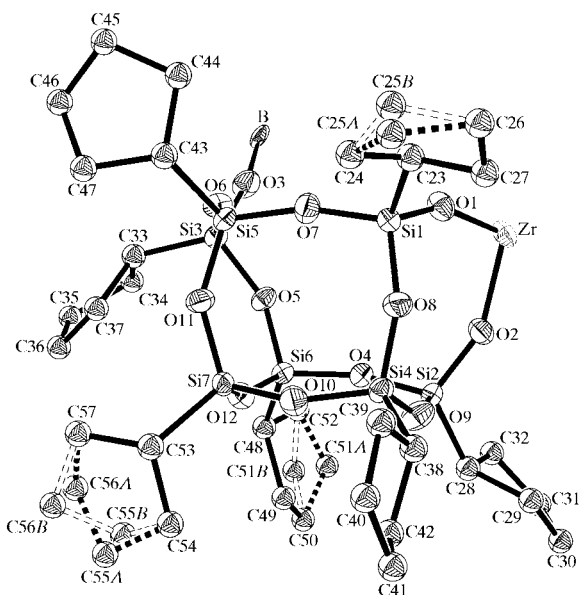
A view of complex (II) is depicted in Fig. 1, and a plot of the silsesquioxane cage and the attached cyclopentyl rings is shown in Fig. 2. The silsesquioxane core refined without difficulty. Despite the low temperature used for data collection, the quality of the result was limited by the relatively poor quality of the crystals available, which scattered weakly beyond  $2\theta = 50^\circ$ . The structural refinement of (I), which is the precursor to (II), did not have the same refinement problems as compound (II).

The Zr atom is bound to two silsesquioxane O atoms and two cyclopentadiene rings in a distorted tetrahedral geometry. The two Zr—O bond lengths are equal within experimental error. The occupancies in the disordered cyclopentadiene (Cp) ring were found to be 66% for the C6A—C10A ring and 34% for the C6B—C10B ring. Zr—centroid distances for the cyclopentadiene rings are 2.246 (6), 2.248 (11) and



**Figure 1**

The molecular structure of (II), showing 50% probability displacement ellipsoids. Cyclopentadiene rings are shown with artificially low isotropic displacement parameters, and the cyclopentane rings have been omitted for clarity, except for the C atoms directly attached to the Si atoms, which are shown with artificially low isotropic displacement parameters.


**Figure 2**

The silsesquioxane cage of (II), showing the cyclopentane rings, depicted at the 50% probability level. The cyclopentadiene and fluorophenyl rings have been omitted for clarity. The cyclopentane rings are shown with artificially low isotropic displacement parameters.

2.213 (17) Å for rings C1–C5, C6A–C10A and C6B–C10B, respectively. The bond angles between the cyclopentadiene centroids and the Zr atom are 129.7 (3) and 127.9 (5)° for (C1–C5)–Zr–(C6A–C10A) and (C1–C5)–Zr–(C6B–C10B), respectively. The geometrical parameters associated with the zirconocene moiety are similar to those found in the related compound  $\{[(C_5H_9)Si]_7O_6(O_2ZrCp_2)(OSiMePh_2)\}$ , recently reported and structurally characterized by Duchateau and co-workers (Skowronska-Ptasinska *et al.*, 2001).

The silsesquioxane in (II) is also functionalized with a bis(perfluorophenyl)borane moiety. The geometrical parameters associated with this moiety are similar to those observed in the structure of (I), where the average B–O distance is 1.330 (1) Å and the B–O–Si angles are 143.8 (1), 169.0 (1) and 170.7 (1)°. Although these B–O bonds are short and the angles at O in general are obtuse, the extent of a  $\pi$ -type interaction between B and O remains to be proven. In particular, unlike the compound  $(C_6F_5)_2BOH$ , in which there is restricted rotation about the B–O bond in solution (Beringhelli *et al.*, 2003), the  $^{19}F$  NMR spectra of either (I) or (II) do not vary over the temperature range 193–298 K in solution. The above borinic acid is trimeric in the solid state, featuring trigonal–pyramidal O and tetrahedral B atoms, with long B–O distances of 1.526 (6) Å (Beringhelli *et al.*, 2003), and so cannot be structurally compared with (I) or (II).

Despite the close proximity of the Lewis acidic borane moiety to the Zr–O groups in (II), there is no evidence of a dative interaction between B and either O1 or O2; these B–O distances are in excess of 6 Å. In fact, the only intramolecular contacts which are within the van der Waals radii of the respective elements are those between B and the C9A–H10A

bond of the endocyclic Cp ring, where the B–C10A distance is 3.78 (1) Å. While these contacts are suggestive of a weak dative interaction between the B atom and the  $\pi$  cloud of this Cp ring, the fact that the bond angles at the B atom sum to 360.0 (5)° suggests that these close contacts do not really represent bonding interactions but are caused by structural constraints of the silsesquioxane cage.

The Si–O bond distances within the structure of (II) show considerable variation, ranging from 1.588 (4) to 1.629 (4) Å. As might be expected, the Si–O bond lengths associated with the cage respond to changes in those Si–O bonds associated with the two different exocyclic substituents. Thus, while the shortest Si–O distances in the structure are those associated with the zirconocene group, the average lengths of the remaining Si–O bonds about these Si atoms are significantly longer in comparison [Si1 1.622 (4) Å and Si2 1.624 (4) Å] and are, in fact, somewhat longer than the average length of the Si–O bonds associated with the non-peripheral Si atoms of the cage [1.615 (4) Å for atoms Si4 to Si7]. Similarly, the long exocyclic Si3–O3 bond involving the borane moiety is counterbalanced by the relatively short remaining Si–O lengths involving this Si atom [1.609 (4) Å].

The Si–O–Si angles in (II), which range from 145.2 (3) to 163.0 (3)°, reveal distortions of the silsesquioxane cage due to the steric and electronic requirements of both the zirconocene and borane groups. This is evident from both the progressive increase in average Si–O–Si bond angles as one moves from the unique vertex Si atom [Si7 with 147.3 (3)°] outwards [Si4, Si5 and Si6 with 150.5 (3)°] to the edges [Si1, Si2 and Si3 with 152.0 (3)°] of the cage, where the variation in these last Si–O–Si angles is considerable [Si1 157.0 (3)°, Si2 151.0 (3)° and Si3 148.2 (3)°].

## Experimental

The synthesis, isolation and characterization of compound (II) have been reported in detail elsewhere (Metcalfe *et al.*, 2002). Single crystals of this compound suitable for X-ray analysis were obtained by slow cooling of a concentrated hexane–acetonitrile mixture (5:1 v/v). Initially, compound (II) was dissolved in the minimal quantity of hexane in a vial and then acetonitrile was added dropwise to this hexane solution. The final solution separated into two phases which were cooled slowly to 243 K. Crystals of compound (II) grew at the interface and after 3 d these began to separate and were isolated by decantation of the mother liquor.

**Table 1**

Selected geometric parameters (Å, °).

Zr–O1	1.983 (4)	Si3–O3	1.625 (4)
Zr–O2	1.978 (4)	O3–B	1.330 (7)
Si1–O1	1.593 (4)	C11–B	1.555 (9)
Si2–O2	1.588 (4)	C17–B	1.582 (8)
O2–Zr–O1	98.16 (15)	Si7–O11–Si5	145.2 (3)
Si1–O1–Zr	154.4 (2)	O3–B–C11	119.3 (5)
Si2–O2–Zr	153.7 (2)	O3–B–C17	119.1 (6)
B–O3–Si3	168.4 (4)	C11–B–C17	121.6 (5)
Si5–O7–Si1	163.0 (3)		

## Crystal data

[Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>47</sub>H<sub>63</sub>BF<sub>10</sub>O<sub>12</sub>Si<sub>7</sub>)]  
*M<sub>r</sub>* = 1438.81  
 Triclinic, *P* $\bar{1}$   
*a* = 11.0484 (17) Å  
*b* = 11.3415 (18) Å  
*c* = 25.919 (4) Å  
 $\alpha$  = 82.620 (3)°  
 $\beta$  = 86.414 (3)°  
 $\gamma$  = 82.697 (3)°  
*V* = 3191.2 (9) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.497 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6719 reflections  
 $\theta$  = 2.4–27.3°  
 $\mu$  = 0.39 mm<sup>-1</sup>  
*T* = 100 (2) K  
 Plate, colorless  
 0.20 × 0.10 × 0.05 mm

## Data collection

Bruker APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 20 985 measured reflections  
 11 091 independent reflections  
 6812 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.092  
 $\theta_{\max}$  = 25.0°  
*h* = -13 → 12  
*k* = -13 → 13  
*l* = -30 → 30

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.069  
*wR* (*F*<sup>2</sup>) = 0.160  
*S* = 0.93  
 11 091 reflections  
 780 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$   
 $\Delta\rho_{\max} = 1.22 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$

Disorders were originally modeled without restraints. This produced unreasonable bond distances and angles for the 3,4-position of some cyclopentane rings. Distance restraints were thus applied to the 3,4-positions of the disordered cyclopentane rings. Similarity restraints were applied to the various disordered cyclopentane rings and the disordered cyclopentadiene ring. Refining the anisotropic displacement parameters of the disordered atoms yielded high *U*<sub>eq</sub> values; therefore, the disordered portions were refined isotropically. All H atoms were calculated and their positions refined based on a riding model. Bond lengths and angles for H atoms were idealized (cyclopentadiene C–H = 1.00 Å and secondary C–H = 0.99 Å) upon refinement. *U*<sub>iso</sub>(H) values were fixed at 1.2*U*<sub>eq</sub>(C). The occupancy of each disordered H atom was set according to the occupancy of its parent C atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1472). Services for accessing these data are described at the back of the journal.

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