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Selective reduction in ring size of silsesquioxane oligomers mediated by potassium metal

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Key indicators

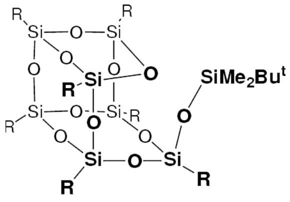
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 95%
Disorder in main residue
R factor = 0.060
wR factor = 0.163
Data-to-parameter ratio = 17.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The trisilanol (c-$C_5H_9)_7Si_7O_9(OH)_3$, generated from the hydrolytic condensation of cyclopentyltrichlorosilane, is converted in excellent yield to a new siloxane 3-*endo*-*tert*-butyldimethylsiloxy-1,3,5,7,9,11,14-heptacyclopentyltetracyclo[7.3.3.1^{3,14}.1^{5,11}]heptasiloxane [(c-$C_5H_9)_7Si_7O_9(O)(OSiMe_2Bu^t)$ or $C_{41}H_{78}O_{11}Si_8$] in two high-yield steps. It is highly unusual for a polyhedral oligosilsesquioxane to give such well diffracting crystals, and even more so for it to crystallize virtually without disorder. Molecules of this siloxane occur in the crystal as isolated units, free from the silanol hydrogen-bonding interactions that dominate the structural characteristics and associated reaction chemistry of the parent polysilanols.

Comment

Over the past year, a number of groups have found that under certain conditions lithiation of the siloxane triol (c-$C_5H_9)_7Si_7O_9(OH)_3$ proceeds smoothly, without the cage destruction which had been reported to arise during reactions to generate a sodium salt (Annand *et al.*, 1999; Feher *et al.*, 1992). The TBDMS (TBDMS is *tert*-butyldimethylsilyl) functionalization has provided us with a highly soluble, tractable disilanol, (c-$C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2{}^tBu)$, (I), which we were able to convert quantitatively to a dilithio salt using *tert*-butyl lithium (Arnold *et al.*, 2001). Treatment of a pentane or toluene solution of (I) with two equivalents of potassium metal results in dissolution of the metal over a few hours (the reaction is accelerated by sonication). This colourless solution contains the siloxane, (c-$C_5H_9)_7Si_7O_9(O)(OSiMe_2{}^tBu)$, (II), arising from the condensation of adjacent silanols to form a new six-membered siloxane ring in the complex. It is widely agreed that these classes of siloxanes crystallize readily but form poorly diffracting crystals that rarely yield satisfactory structural information (Herrmann *et al.*, 1994; Abbenhuis, 2000). This held true for (II), with further complications arising from crystals that cracked upon cooling in the cold nitrogen stream on the diffractometer. A range of morphol-



(II) **R = *c*-C_5H_9**

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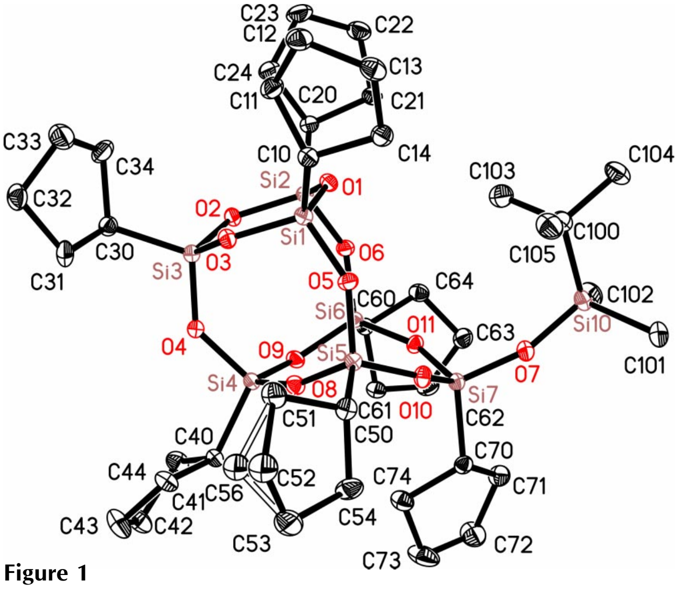

Figure 1
A view of the structure of (II) showing atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level. Atoms C52 and C56 are disorder components of the same atom, with occupancies of 0.76 (2) and 0.24 (2), respectively.

ogies of crystals was obtained from different solvents and solvent mixtures, but the only crystals that diffracted reasonably were large colourless blocks grown by ethanol diffusion into an ether solution of (II). Distances and angles for the compound are as anticipated; whilst the TBDMS anchoring vertex Si7 bends away from the cube, the *tert*-butyl group is folded back towards the siloxane oxygen O1, possibly facilitating the surprisingly highly ordered packing of the molecules.

Experimental

A toluene solution of (I) (317 mg, 0.32 mmol, 10 ml) was added to high purity K lumps (25.0 mg, 0.64 mmol) and either sonicated or stirred vigorously for 4 h, or until no K was visible. Removal of volatiles under reduced pressure afforded a colourless solid. Extraction with pentane, followed by concentration and cooling to 243 K afforded highly crystalline (II) (yield 231 mg, 74%). Crystals were grown at room temperature by ethanol diffusion into a diethyl ether solution.

Crystal data

$C_{41}H_{78}O_{11}Si_8$
$M_r = 971.75$
Triclinic, $P\overline{1}$
$a = 11.9992$ (8) Å
$b = 14.6230$ (9) Å
$c = 15.0146$ (13) Å
$\alpha = 75.182$ (3)°
$\beta = 89.959$ (3)°
$\gamma = 89.793$ (2)°
$V = 2546.9$ (3) Å^3

$Z = 2$
$D_x = 1.267$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26509 reflections
$\theta = 2.9$–27.5°
$\mu = 0.26$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.25 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.87$, $T_{\max} = 0.99$
19 540 measured reflections

9603 independent reflections
5603 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\max} = 26.0$°
$h = -15 \rightarrow 15$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.163$
$S = 1.00$
9603 reflections
541 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Si1—O1	1.629 (3)	Si4—O9	1.621 (3)
Si1—O3	1.632 (3)	Si5—O5	1.622 (2)
Si1—O5	1.613 (3)	Si5—O8	1.613 (3)
Si2—O1	1.636 (3)	Si5—O10	1.611 (3)
Si2—O2	1.626 (3)	Si6—O6	1.624 (2)
Si2—O6	1.617 (2)	Si6—O9	1.624 (3)
Si3—O2	1.634 (3)	Si6—O11	1.609 (3)
Si3—O3	1.635 (3)	Si7—O7	1.590 (3)
Si3—O4	1.619 (2)	Si7—O10	1.618 (3)
Si4—O4	1.630 (2)	Si7—O11	1.625 (3)
Si4—O8	1.618 (3)	Si10—O7	1.634 (3)
O1—Si1—O3	106.48 (14)	O6—Si6—O11	107.92 (13)
O1—Si1—O5	109.47 (14)	O9—Si6—O11	109.20 (14)
O3—Si1—O5	108.77 (13)	O7—Si7—O10	107.89 (15)
O1—Si2—O2	106.68 (14)	O7—Si7—O11	109.41 (15)
O1—Si2—O6	108.78 (14)	O10—Si7—O11	109.48 (14)
O2—Si2—O6	108.67 (13)	Si1—O1—Si2	129.99 (16)
O2—Si3—O3	106.40 (13)	Si1—O3—Si3	130.97 (17)
O2—Si3—O4	108.37 (13)	Si1—O5—Si5	146.39 (17)
O3—Si3—O4	109.18 (14)	Si2—O2—Si3	130.55 (17)
O4—Si4—O8	108.75 (13)	Si2—O6—Si6	148.56 (18)
O4—Si4—O9	108.90 (14)	Si3—O4—Si4	136.23 (16)
O8—Si4—O9	108.71 (14)	Si7—O7—Si10	160.06 (19)
O5—Si5—O8	109.46 (14)	Si4—O8—Si5	155.73 (18)
O5—Si5—O10	108.01 (14)	Si4—O9—Si6	144.47 (17)
O8—Si5—O10	109.08 (14)	Si5—O10—Si7	144.31 (18)
O6—Si6—O9	110.35 (13)	Si6—O11—Si7	156.54 (18)

Although the crystal has a unit cell which is metrically close to monoclinic, merging of the data under $2/m$ symmetry gave a very high merging R of 0.584; we accordingly adopted the lower triclinic system where the corresponding value was 0.070. For its class, compound (II) displays a surprisingly low level of disorder in the peripheral groups. Positional disorder of one cyclopentyl group was modelled and refined satisfactorily upon application of geometric similarity restraints: the major and minor components comprise 0.76 (2) and 0.24 (2), respectively. H atoms were refined riding on their parent atoms with $U_{\rm iso}({\rm H}) = xU_{\rm eq}({\rm C})$, where $x = 1.5$ for methyl H atoms and 1.2 for all others; C—H distances were restrained to 0.98, 0.99 and 1.00 Å for methyl, methylene and methine H atoms, respectively.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2000).

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