

Supporting Information

Janus-Cube Octasilsesquioxane: Facile Synthesis and Structure Elucidation

*Naoki Oguri, Yasunobu Egawa, Nobuhiro Takeda, and Masafumi Unno**

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Experimental Section

General

All experiments were conducted under argon atmosphere. Solvents were dried using mBRAUN purification system. Preparative recycle-type Gel permeation chromatography (GPC) was carried out with a JAI LC-9101 using a JAIGEL 20 mm × 600 mm GPC column. All melting points were determined on a Yanaco micro melting point apparatus MP-J3 and are uncorrected. The Fourier transformation nuclear magnetic resonance (NMR) spectra were obtained using a JEOL JNM-ECS 300 (^1H at 300.53 MHz, ^{13}C at 75.57 MHz, ^{29}Si at 59.71 MHz), and JEOL JNM-ECA 600 (^1H at 600.17 MHz, ^{19}F at 564.72 MHz, ^{29}Si at 119.24 MHz) NMR instruments. For ^1H NMR, chemical shifts are reported as δ units (ppm) relative to SiMe_4 and the residual solvents peaks were used as standards. For ^{19}F and ^{29}Si NMR, C_6F_6 and SiMe_4 were used as an external standard, respectively. Infrared spectra were measured with a SHIMADZU FTIR-8400S. Analysis by electron impact mass spectrometry (EI-MS) was performed on a SHIMADZU GCMS-QP2010SE/DI2010. Elemental analyses were performed by the Center for Material Research by Instrumental Analysis (CIA), Gunma University, Japan.

Preparation of sodium all-*cis*-1,3,5,7-tetraphenylcyclotetrasiloxanolate (1)

For the synthesis of this siloxanolate, we followed the procedure in the literature.^[S1] Trimethoxyphenylsilane (5.0 g, 25 mmol) was added to a solution of NaOH (1.0 g, 25 mmol) and H_2O (0.45 g, 25 mmol) in 2-propanol (25 mL). After the reaction mixture was stirred at room temperature for 3 d, the formed solid was suction filtrated, washed with hexane, and dried in vacuum to afford **1** as a white solid (3.9 g, about 6.1 mmol, >95%). This compound was used without further purification.

Preparation of all-*cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraisobutylcyclotetrasiloxane (2)

For the synthesis of this cyclic silanol, we followed the method previously reported and the spectral data were well consisted with that of them.^[S1b, S2] Isobutyltrimethoxysilane (4.5 g, 25 mmol) was added to a mixture of NaOH (1.0 g, 25 mmol) and H₂O (0.45 g, 25 mmol) in hexane (25 mL). The reaction mixture was stirred for 3 d at room temperature and a white substance precipitated. The resulting suspension was suction filtrated, washed with hexane and dried in vacuum to afford a white solid (3.6 g). To a dispersion of the white solid in Et₂O (36 mL) was added a solution of conc. hydrochloric acid (4.3 g, about 40 mmol) in water (190 mL) at 0 °C. The reaction mixture was stirred for 10 min for 0 °C. Saturated sodium bicarbonate solution was added to the mixture for neutralization. The organic layer was extracted with Et₂O, washed with water and brine, and dried over anhydrous sodium sulfate. After removing the solvent, the product was dried in vacuum to give **2** (2.2 g, 4.7 mmol, 74%). ¹H NMR (300.53 MHz, CDCl₃): δ 0.61 (d, $J_{\text{H-H}} = 6.9$ Hz, 8H), 0.94 (d, $J_{\text{H-H}} = 6.9$ Hz, 24H), 1.84 Hz (nonet, $J_{\text{H-H}} = 6.9$ Hz, 4H) ppm. ²⁹Si NMR (59.71 MHz, CDCl₃): δ -58.1 ppm.

Synthesis of all-*cis*-1,3,5,7-tetrafluoro-1,3,5,7-tetraisobutylcyclotetrasiloxane (**3**)

For the synthesis of **3**, we followed the procedure in the paper we previously reported and the spectral data were well consisted with that of them.^[S3] Boron trifluoride diethyl ether complex (7.8 mL, 63 mmol) was added to a dispersion of **2** (3.0 g, 6.3 mmol) in 30 mL of hexane at room temperature with vigorous stirring. After addition, compound **2** was consumed immediately and a yellow layer were emerged under the hexane layer. After 10 min, the upper layer was decanted, evaporated and dried in vacuum to afford a colorless oil (3.2 g) as a crude product, followed by separation with GPC (eluent: CHCl₃) to give a colorless oil (1.7 g, 3.5 mmol, 53%). ¹H NMR (600.17 MHz, CDCl₃): δ 0.73 (dd, $J_{\text{H-H}} = 6.8$ Hz, $J_{\text{H-F}} = 3.9$ Hz, 8H), 0.97 (d, $J_{\text{H-H}} = 6.8$ Hz, 24H), 1.87 Hz (nonet, $J_{\text{H-H}} = 6.8$ Hz, 4H) ppm. ¹⁹F NMR (564.72 MHz, CDCl₃): δ -128.95 (s) ppm. ²⁹Si NMR (59.71 MHz, CDCl₃): δ -62.87 (d, $J_{\text{Si-F}} = 272$ Hz) ppm.

Synthesis of *i*-BuPh-Janus cube (**4**)

To a dispersion of **1** (1.5 g, about 2.3 mmol) in CHCl_3 (25 mL) was added dropwise a solution of **3** (1.1 g, 2.3 mmol) in CHCl_3 (25 mL) at 0 °C. After dropping, insoluble **1** was completely consumed and the reaction mixture became a colorless solution. The solution was stirred at room temperature. After 1 d, the reaction mixture was washed with water and brine, dried over Na_2SO_4 , and evaporated to afford a crude product as a colorless solid (1.1 g), which was separated by GPC (eluent: CHCl_3). The *i*-BuPh-Janus cube (**4**) was obtained as a white solid (0.48 g, 0.48 mmol, 21%). mp over 300 °C. ^1H NMR (300.53 MHz, CDCl_3): δ 0.71 (d, $J_{\text{H-H}} = 7.2$ Hz, 8H), 0.97 (d, $J_{\text{H-H}} = 7.2$ Hz, 24H), 1.91 (nonet, $J_{\text{H-H}} = 7.2$ Hz, 4H), 7.32 (t, $J_{\text{H-H}} = 7.2$ Hz, 8H), 7.40 (m, 4H), 7.67 (m, 8H) ppm. ^{13}C NMR (75.57 MHz, CDCl_3): δ 22.37 (CH_2), 23.85 (CH), 25.72 (CH_3), 127.70 (CH), 130.49 (CH), 130.85 (CH), 134.09 (CH) ppm. ^{29}Si NMR (119.24 MHz, CDCl_3): δ -66.94, -79.12 ppm. IR (KBr): 1112, 1213, 1332, 1436, 1465, 2872, 2955, 3074 cm^{-1} . EI-MS (30 eV): m/z (%) 895 ($[\text{M} - i\text{-Bu}]^+$, 25), 819 ($[\text{M} - \text{Ph}]^+$, 10). Anal. Calcd for $\text{C}_{40}\text{H}_{56}\text{O}_{12}\text{Si}_8$: C, 50.38; H, 5.92. Found: C, 50.49; H, 5.80.

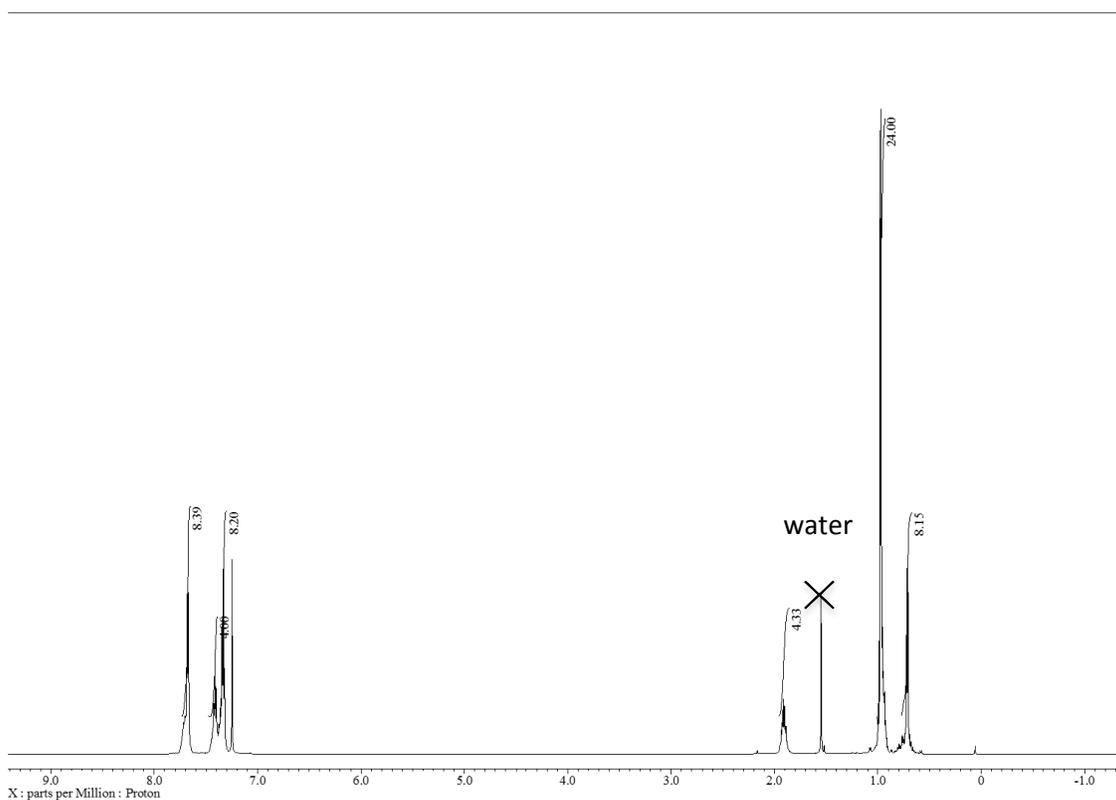


Figure S1. ^1H NMR spectrum of **4** (300.53 MHz, CDCl_3)

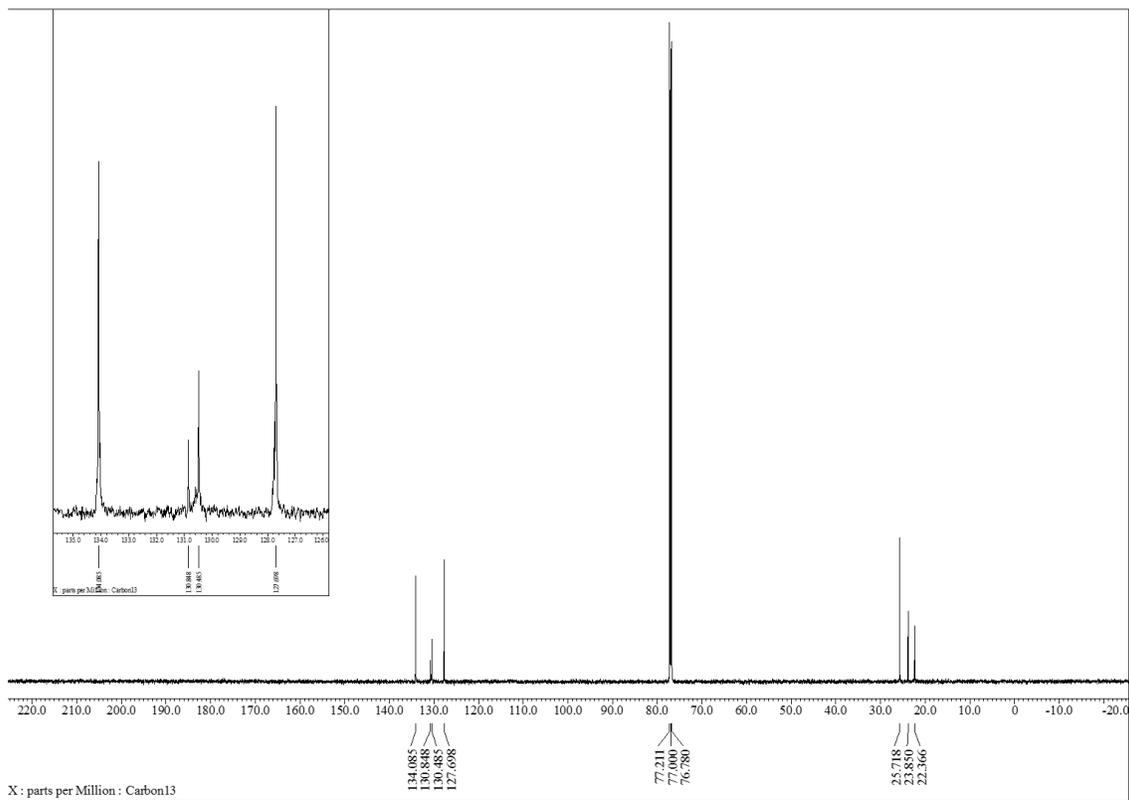


Figure S2. ^{13}C NMR spectrum of **4** (75.57 MHz, CDCl_3)

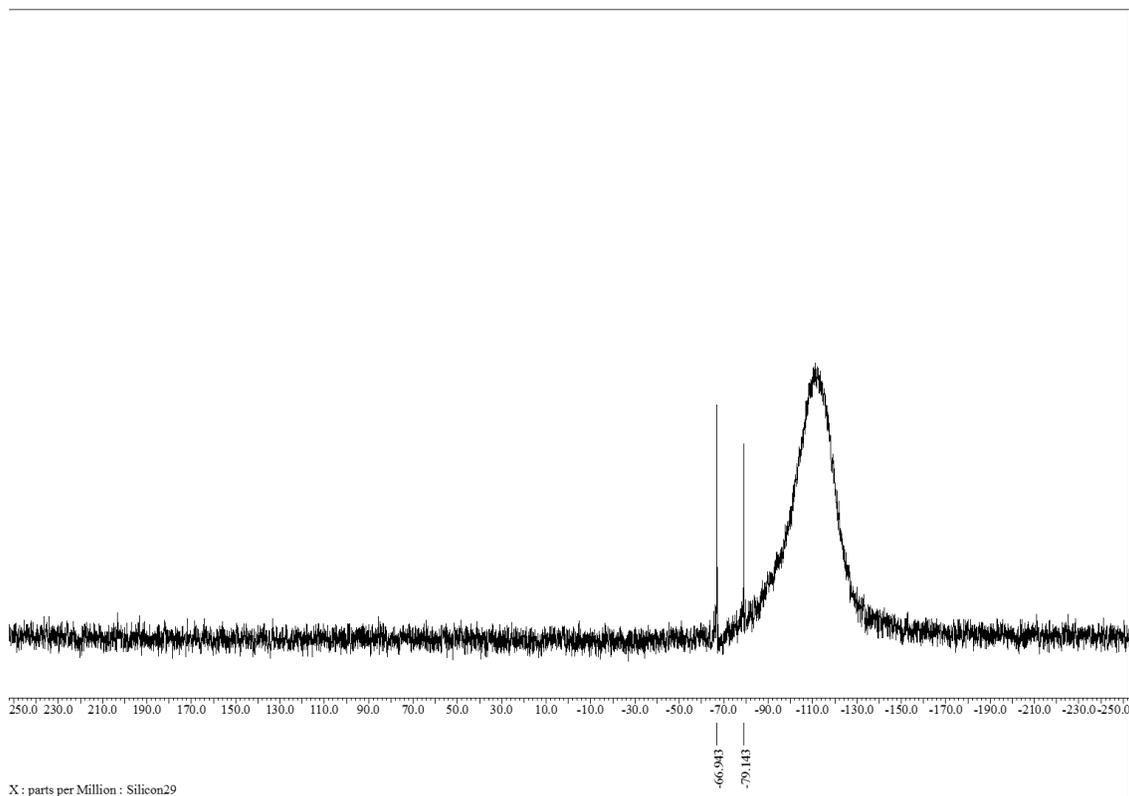


Figure S3. ^{29}Si NMR spectrum of **4** (119.24 MHz, CDCl_3)

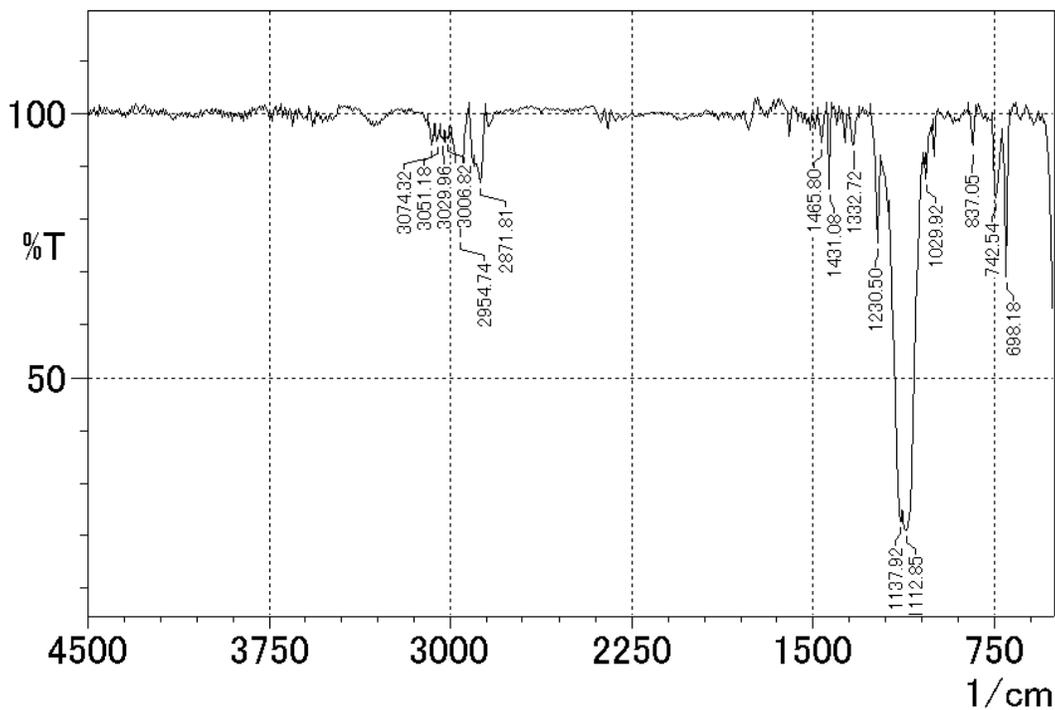


Figure S4. IR spectrum of **4** (KBr)

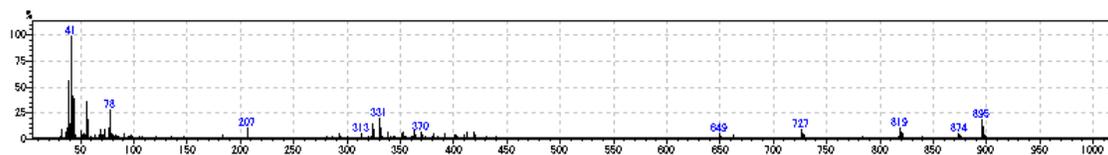


Figure S5. EI-MS spectrum of **4** (30 eV)

X-ray Crystallographic Analysis of **4**

White crystals were obtained from CHCl_3 /hexane solution, which was suited for X-ray analysis. The intensity data were collected on a Rigaku XtaLab P200 diffractometer with multi-layer mirror monochromated Mo $K\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). The structures was solved by direct methods (SHELXS-97⁴), and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97^[S4]). All the non-hydrogen atoms were refined anisotropically. All hydrogens were placed using AFIX instructions. All calculations were carried out using Yadokari-XG2009.^[S5] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-1446733 for compound **4**. Copies of the data can be obtained free of charge via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **4** (123 K): C₄₀H₅₆O₁₂Si₈, fw 953.57, triclinic, space group *P*-1, white crystals, *a* = 10.637(3), *b* = 11.086(3), *c* = 20.880(7) Å, $\alpha = 93.679(7)^\circ$, $\beta = 93.938(7)^\circ$, $\gamma = 96.230(8)^\circ$, *V* = 2435.5(13) Å³, *Z* = 2, *D*_{calcd} = 1.300 Mg/m³, *R*1 = 0.0735 (*I* > 2σ), *wR*2 = 0.2157 (all data), GOF = 0.945.

References

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