Siloxanes

Deutsche Ausgabe: DOI: 10.1002/ange.201602413
Internationale Ausgabe: DOI: 10.1002/anie.201602413

Janus-Cube Octasilsesquioxane: Facile Synthesis and Structure Elucidation

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

Abstract: *A perfect "Janus-cube" octasilsesquioxane, a nanometer-scale Janus particle with two different types of substituents, was synthesized through the cross-coupling of a "half-cube" cyclic sodium siloxanolate with another half-cube cyclic fluorosiloxane. The structure was confirmed by X-ray crystallography to be a Janus cube. The overall synthesis is simple and does not require drastic separation methods compared with previous methods. The synthesis of the Janus cube demonstrates a novel siloxane bond-forming reaction involving the coupling a silanol salt and fluorosilane. The reaction is mild, does not result in acid generation, and could be applied to the construction of other novel siloxane compounds.*

Efficient bottom-up construction of complex molecules is imperative for controlling the chemical and physical properties of materials. Rigorous selection of nanoscale building blocks leads to the fine-tuning of self-assembly behavior and the development of novel material properties.[1] As nanoscale building blocks, Janus particles have considerable potential to create asymmetry and opposing chemical/physical properties in a single particle.[2] Cube-like octasilsesquioxane (T_8), an organic/inorganic hybrid molecule with cubic symmetry and octafunctionality, is attractive as a prospective nanoscale Janus particle.[3] In particular, a "Janus cube," comprising four substituents grouped into two different classes on the two opposing faces of the cube, can harness perfect cubic asymmetry (Figure 1).[3a–c]

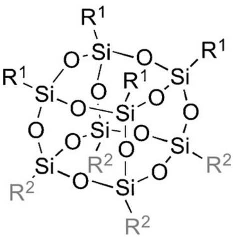


Figure 1. Structure of the Janus-cube octasilsesquioxane.

A Janus cube can be envisioned as offering a diameter of 1–2 nm with thermal robustness and a high density of organic substituents per unit volume. Therefore, Janus cubes are expected to act as silane coupling agents with high thermostability, as interlayer dielectrics, as components for constructing 2D or 3D structure networks, and more.[3b–c] In addition, Bassindale, Taylor, and co-workers have shown that the use of T_8 with long alkyl chains leads to mesogenic properties.[4] Similarly, Janus-type octasilsesquioxanes may exhibit curious solid-state structures. Although Janus cubes are expected to engender various useful applications, their isolation and crystal structure have not been reported because their synthesis is extremely challenging. Hence, establishing a decisive synthetic method for Janus cubes is attractive and of great significance.

Laine et al. reported the first method to synthesize a Janus cube through intramolecular condensation of $[R^1Si(O)OSiR^2(OMe)_2]_4$.[3b] This reaction requires acidic or basic conditions, thus resulting in many byproducts, including oligomeric and polymeric compounds, with the result that the isolation was unsuccessful. An alternative method is the cross-coupling of a "half-cube" cyclic silanol with another half-cube cyclic halosiloxane. In the last two decades, several groups have reported the stereospecific synthesis of all-*cis* cyclic silanols and their alkali-metal salts (Figure 2).[5] In 2005, our group reported all-*cis* cyclic chlorosiloxane ($(i\text{-}PrSiOCl)_4$), but the synthetic route had several problems.[6] For instance, separation of the four precursor isomers by high-performance liquid chromatography (HPLC) was necessary. Additionally, the cyclic chlorosiloxane is easily hydrolyzed, and its stereostructure is not maintained during the cross-coupling reaction, especially under acidic or basic conditions, thus resulting in extensive side products. These issues make it difficult to use cyclic chlorosiloxane in the synthesis of Janus cubes.

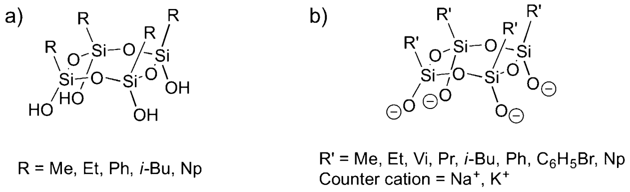


Figure 2. Suggested structures of a) the $[RSiO(OH)]_4$ half-cube; b) the $[R'SiO(OM)]_4$ half-cube salt.

Essentially, the synthesis and isolation of Janus cubes is difficult because cage synthesis is typically accompanied by numerous byproducts, thus making separation impossible. As seen above, selective construction of the Si-O-Si framework is still challenging, and this prevents the utilization of siloxane compounds with complex skeletons, which could have various applications. More moderate synthetic methods that minimize the generation of byproducts are desired not only for synthesizing Janus cubes, but also for making siloxane compounds with intricate frameworks.

In this work, we designed a new Si-O-Si bond-forming reaction from fluorosilane, which is suitable for preparing well-defined siloxanes, while suppressing the generation of

---

[*] N. Oguri, Dr. Y. Egawa, Prof. Dr. N. Takeda, Prof. Dr. M. Unno
Department of Chemistry and Chemical Biology
Graduate School of Science and Technology, Gunma University
Kiryu 376-8515, Gunma (Japan)
E-mail: unno@gunma-u.ac.jp

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201602413.

byproducts. Recently, we accomplished the facile stereospecific synthesis of cyclic fluorosiloxanes $(RSiOF)_4$ [R = *i*-Bu, Ph],[7] and we now utilize this as a Janus-cube precursor. This fluorosiloxane is stable to moisture, and no hydrolysis was observed in air or even water. Sodium cyclosiloxanolate was selected as the other half-cube compound because it can be prepared in high yield.

We herein report a facile route to a Janus cube, its isolation, and the elucidation of its structure by X-ray crystallography. Initially, we prepared phenyl-substituted cyclosiloxanolate (**1**) through a hydrolytic reaction of $PhSi(OMe)_3$ according to a reported method.[5d,i,8] Next, we synthesized isobutyl-substituted cyclic silanol (**2**) in 74 % yield through the hydrolysis of *i*-$BuSi(OMe)_3$.[5i,9] Subsequently, the cyclic fluorosiloxane (**3**) was prepared in 53 % yield through a quick and mild fluorination reaction with boron trifluoride by using a method we reported elsewhere.[7] Finally, we performed the cross-coupling of compounds **1** and **3** in $CHCl_3$ at room temperature (Scheme 1). This reaction did not require acid or base. The starting materials were completely consumed after one day, to afford the desired Janus cube (**4**) in 21 % yield, with polymeric condensation byproducts. Only the polymers and **4** were observed in the NMR spectra. Klingebiel previously reported siloxane bond formation in the reaction of a simple lithium silanolate with fluorosilane;[10] however, this is the first example of fluorosiloxane being utilized as a precursor for the construction of a well-defined siloxane skeleton.

The Janus cube was isolated by gel-permeation chromatography (GPC; eluent, $CHCl_3$). Peaks corresponding to the polymeric compounds and **4** were separated after three cycles (Figure 3). The target compound could be successfully separated because the cyclic fluorosiloxane was stable and had moderate reactivity towards the cyclic sodium siloxanolate, and because the coupling reaction did not afford an acid. The lack of acid suppresses the generation of byproducts such as polymeric and oligomeric compounds, as well as breaking of the cubic framework.

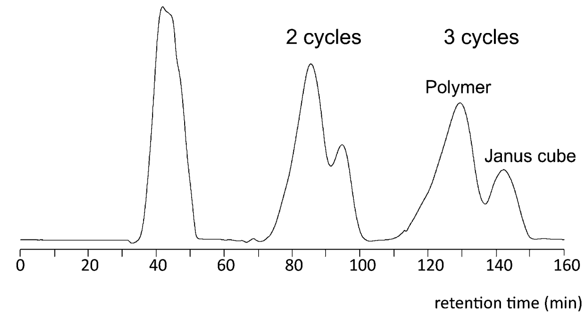
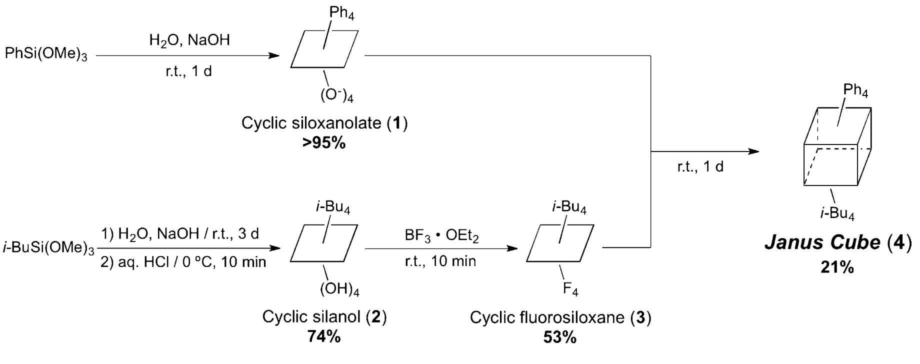


Figure 3. GPC chart of the reaction mixture (eluent: $CHCl_3$).



Scheme 1. Overall synthetic route to **4**. Si-O-Si bonds are represented as lines for clarity.

The formation of **4** was confirmed by NMR (^1H, ^{13}C, and ^{29}Si), electron ionization mass spectrometry (EI-MS), and FTIR spectroscopy, as well as elemental analysis (see Supporting Information). The ^1H NMR spectrum showed the presence of isobutyl and phenyl groups with an integral intensity ratio of 9:5, thus suggesting that compound **4** contains isobutyl and phenyl groups in a 1:1 ratio. The ^{29}Si NMR spectrum displayed only two singlets at $\delta = -66.9$ and -79.1 ppm, which correspond to isobutyl- and phenyl-substituted silicon, respectively (Figure 4). These chemical shifts were consistent with previously reported octaisobutyloctasilsesquioxane and octaphenyloctasilsesquioxane ($\delta = -67.9$[11] and -79.7 ppm,[12] respectively). EI-MS results further supported the formation of **4** (m/z 895 $[M-i\text{-Bu}]^+$, 819 $[M-\text{Ph}]^+$).

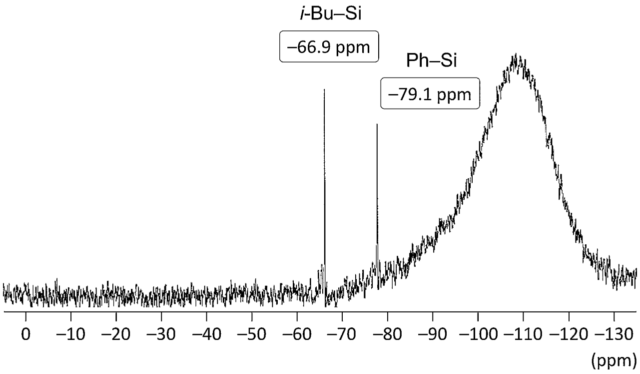


Figure 4. ^{29}Si NMR spectrum of Janus cube **4**.

Compound **4** was isolated as a white solid and was soluble in common polar organic solvents, such as THF, $CHCl_3$, and CH_2Cl_2, and insoluble in nonpolar solvents, such as hexane, benzene, and toluene. Single crystals of **4** were acquired through slow evaporation from a CH_3Cl/hexane solution. The crystal structure was confirmed by X-ray crystallography (Figure 5),[13] which showed unequivocally that exactly four phenyl groups and four isobutyl groups were attached to the two opposite faces. This is the first report of an X-ray crystallographic analysis of a Janus-type T_8.

In conclusion, we synthesized and isolated a Janus cube bearing phenyl and isobutyl groups, and determined its crystal structure, thereby confirming it to be a Janus-type octasilsesquioxane.[14] Since the synthesis of half-cube compounds with various substituents has been established, our novel method makes it possible to prepare a wide variety of Janus

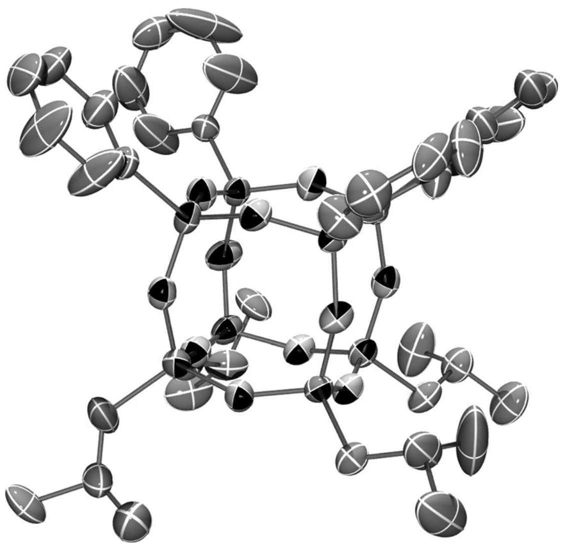


Figure 5. ORTEP diagram of Janus cube **4**, with the thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Si or O black, C gray.

cubes. For example, a Janus cube with a vinyl group could undergo many transformations, such as cross coupling reactions, olefin metathesis, hydrosilylation, epoxidation, and the thiol–ene reaction, and could thus contribute to the construction of multifunctional Janus cubes, such as amphipathic molecules and nanoscale building blocks for precisely controlling the chemical/physical properties of materials. More fundamentally, in this synthesis, we established a new siloxane bond-forming reaction by coupling fluorosiloxane with siloxanolate. This reaction appeared to be mild and generated no acid, thus indicating that it could be applied to constructing siloxane frameworks that are sensitive to acids or bases. We believe that this Si-O-Si bond-forming reaction will contribute to the synthesis of a new class of siloxanes with intricate frameworks.

Acknowledgements

This work was supported by the "Development of Innovative Catalytic Processes for Organosilicon Functional Materials" project (PL: K. Sato) from the New Energy and Industrial Technology Development Organization (NEDO).

Keywords: Janus particles · materials science · siloxanes · siloxane bond formation · silsesquioxanes

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9336–9339
Angew. Chem. **2016**, *128*, 9482–9485

---

[1] a) G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418–2421; b) D. A. Tomalia, A. Jensen, *Periodic Patterns, Relationships and Categories of Well-Defined Nanoscale Building Blocks,* National Science Foundation Workshop Report, **2007**; c) D. A. Tomalia, J. B. Christensen, U. Boas, *Dendrimers, Dendrons, and Dendritic Polymers: Discovery, Application, and the Future,* Cambridge University Press, Cambridge, **2012**; d) M. Huang, C.-H. Hsu, J. Wang, S. Mei, X, Dong, Y. Li, M. Li, H. Liu, W. Zhang, T. Aida, W.-B. Zhang, K. Yue, S. Z. D. Cheng, *Science* **2015**, *348*, 424–428.

[2] a) P. G. De Gennes, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 842–845; *Angew. Chem.* **1992**, *104*, 856–859; b) A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194–5261; c) A. Perro, S. Reculusa, S. Ravaine, E. Bourgeat-Lami, E. Duguet, *J. Mater. Chem.* **2005**, *15*, 3745–3760; d) S. Reculusa, C. Poncet-Legrand, A. Perro, E. Duguet, E. Bourgeat-Lami, C. Mingotaud, S. Ravaine, *Chem. Mater.* **2005**, *17*, 3338–3344; e) K. H. Roh, D. C. Martin, J. Lahann, *Nat. Mater.* **2005**, *4*, 759–763; f) S. C. Glotzer, M. J. Solomon, *Nat. Mater.* **2007**, *6*, 557–562; g) L. C. Palmer, Y. S. Velichko, M. O. De La Cruz, S. I. Stupp, *Philos. Trans. R. Soc. London Ser. A* **2007**, *365*, 1417–1433; h) I. Kretzschmar, J. H. Song, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 84–95; i) E. Duguet, A. Désert, A. Perro, S. Ravaine, *Chem. Soc. Rev.* **2011**, *40*, 941–960.

[3] a) R. M. Laine, M. Roll, M. Z. Asuncion, S. Sulaiman, V. Popova, D. Bartz, D. J. Krug, P. H. Mutin, *J. Sol-Gel Sci. Technol.* **2008**, *46*, 335–347; b) M. Z. Asuncion, M. Ronchi, H. Abu-Seir, R. M. Laine, *C. R. Chim.* **2010**, *13*, 270–281; c) H. W. Ro, V. Popova, D. J. Krug, A. M. Forster, R. M. Laine, C. L. Soles, *Appl. Organomet. Chem.* **2013**, *27*, 652–659; d) Y. Li, W.-B. Zhang, I.-F. Hsieh, G. Zhang, Y. Cao, X. Li, C. Wesdemiotis, B. Lotz, H. Xiong, S. Cheng, *J. Am. Chem. Soc.* **2011**, *133*, 10712–10715.

[4] a) A. R. Bassindale, H. Chen, Z. Liu, I. A. MacKinnon, D. J. Parker, P. G. Taylor, Y. Yang, M. E. Light, P. N. Horton, M. B. Hursthouse, *J. Organomet. Chem.* **2004**, *689*, 3287–3300; b) Y. El Aziz, A. R. Bassindale, P. G. Taylor, R. A. Stephenson, M. B. Hursthouse, R. W. Harrington, W. Clegg, *Macromolecules* **2013**, *46*, 988–1001; c) E. L. Heeley, D. J. Hughes, Y. El Aziz, P. G. Taylor, A. R. Bassindale, *Macromolecules* **2013**, *46*, 4944–4954; d) E. L. Heeley, D. J. Hughes, Y. El Aziz, I. Williamson, P. G. Taylor, A. R. Bassindale, *Phys. Chem. Chem. Phys.* **2013**, *15*, 5518–5529; e) E. L. Heeley, D. J. Hughes, Y. El Aziz, P. G. Taylor, A. R. Bassindale, *Eur. Polym. J.* **2014**, *51*, 45–56.

[5] a) F. J. Feher, J. J. Schwab, D. Soulivong, J. W. Ziller, *Main Group Chem.* **1997**, *2*, 123–132; b) M. Unno, K. Takada, H. Matsumoto, *Chem. Lett.* **1998**, 489–490; c) M. Unno, A. Suto, K. Takada, H. Matsumoto, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 215–220; d) O. I. Shchegolikhina, Y. Pozdniakova, M. Antipin, D. Katsoulis, N. Auner, B. Herrschaft, *Organometallics* **2000**, *19*, 1077–1082; e) O. I. Shchegolikhina, Y. A. Pozdnyakova, Y. A. Molodtsova, S. D. Korkin, S. S. Bukalov, L. A. Leites, K. A. Lyssenko, A. S. Peregudov, N. Auner, D. E. Katsoulis, *Inorg. Chem.* **2002**, *41*, 6892–6904; f) Y. A. Pozdniakova, K. A. Lyssenko, A. A. Korlyukov, I. V. Blagodatskikh, N. Auner, D. Katsoulis, O. I. Shchegolikhina, *Eur. J. Inorg. Chem.* **2004**, 1253–1261; g) M. Ronchi, M. Pizzotti, A. Orbelli Biroli, P. Macchi, E. Lucenti, C. Zucchi, *J. Organomet. Chem.* **2007**, *692*, 1788–1798; h) O. I. Shchegolikhina, Y. A. Pozdnyakova, A. A. Chetverikov, A. S. Peregudov, M. I. Buzin, E. Matukhina, *Russ. Chem. Bull.* **2007**, *56*, 83–90; i) R. Ito, Y. Kakihana, Y. Kawakami, *Chem. Lett.* **2009**, *38*, 364–365; j) Y. A. Pozdnyakova, A. A. Korlyukov, E. G. Kononova, K. A. Lyssenko, A. S. Peregudov, O. I. Shchegolikhina, *Inorg. Chem.* **2010**, *49*, 572–577.

[6] M. Unno, Y. Kawaguchi, Y. Kishimoto, H. Matsumoto, *J. Am. Chem. Soc.* **2005**, *127*, 2256–2263.

[7] N. Oguri, N. Takeda, M. Unno, *Chem. Lett.* **2015**, *44*, 1506–1508.

[8] M. Unno, H. Endo, N. Takeda, *Heteroat. Chem.* **2014**, *25*, 525–532.

[9] H. Endo, N. Takeda, M. Takanashi, T. Imai, M. Unno, *Silicon* **2015**, *7*, 127–132.

[10] U. Klingebiel, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 678–679; *Angew. Chem.* **1981**, *93*, 696–697.

[11] A. R. Bassindale, Z. Liu, I. A. MacKinnon, P. G. Taylor, Y. Yang, M. Light, P. N. Horton, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **2003**, *14*, 2945–2949.

[12] A. R. Bassindale, D. J. Parker, M. Pourny, P. G. Taylor, P. N. Horton, M. B. Hursthouse, *Organometallics* **2004**, *23*, 4400–4405.

[13] Crystal data for **4** (123 K): $C_{40}H_{56}O_{12}Si_8$, fw 953.57, triclinic, space group $P\bar{1}$, white crystals, $a = 10.637(3)$, $b = 11.086(3)$, $c = 20.880(7)$ Å, $\alpha = 93.679(7)$, $\beta = 93.938(7)$, $\gamma = 96.230(8)$°, $V = 2435.5(13)$ Å^3, $Z = 2$, $D_{calcd} = 1.300\ \mathrm{Mg\,m^{-3}}$, $R1 = 0.0735$ ($I > 2\sigma$), $wR2 = 0.2157$ (all data), GOF = 0.945. CCDC 1446733 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[14] During the submission process, the synthesis of Janus-cube octasilsesquioxanes by an alternative approach was published: A. Blazquez-Moraleja, M. E. Pérez-Ojeda, J. R. Suarez, M. L. Jimeno, J. L. Chiara, *Chem. Commun.* **2016**, *52*, 5792–5795.

Received: March 9, 2016