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Synthesis and Reactivity of Nitrogen Nucleophiles-Induced Cage-Rearrangement Silsesquioxanes

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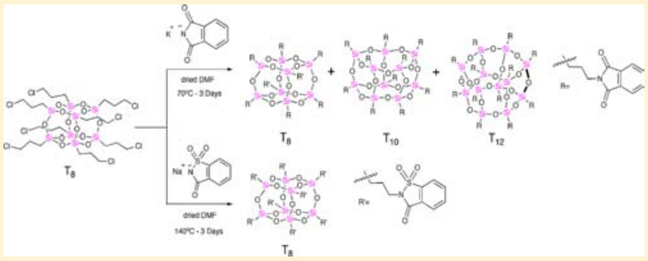
Supporting Information

ABSTRACT: Novel phthalimide and *o*-sulfobenzimide-functionalized silsesquioxanes were successfully synthesized via nucleophilic substitution reactions from octakis(3-chloropropyl)octasilsesquioxane. Surprisingly, the formation of deca- and dodecasilsesquioxanes cages was discovered during substitution with phthalimide, but only octasilsesquioxane maintained a cage in the *o*-sulfobenzimide substitution reaction. Moreover, we report the electronic effect of nitrogen nucleophiles to promote cage-rearrangement of inorganic silsesquioxane core for the first time. Structures of products were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, ESI−MS analysis, and single-crystal X-ray diffraction.



INTRODUCTION

Silsesquioxanes are a class of hybrid organic−inorganic molecules with the general formula of $[RSiO_{3/2}]_n$ (with R as alkyl, aryl, allylene functional groups, or hydrogen atom).[1] They are found in various chemical architectures such as polymeric,[2] cage-like,[3] and ladder structures.[4] Because of their highly discrete nanoscale structures of Si−O inorganic core surrounded by organic functional groups, cage-like structures or polyhedral oligomeric silsesquioxanes are of particular interest. On the basis of these characteristics, cage-like silsesquioxanes molecules could serve as an excellent nanobuilding block with fine-tunable properties via chemical modifications. Recently, applications for silsesquioxanes-based materials have been found in polymer science,[5] catalysis,[6] biomedicine,[7] nanomaterials,[8] electronic devices,[9] and electrochemistry.[10] In general, organotrihalosilanes or organotrialkoxysilanes readily undergo hydrolytic condensation reactions in the presence of basic or acidic catalysts, leading to the formation of silsesquioxanes adducts.[11] However, the hydrolytic condensation reaction of silsesquioxanes compounds is highly sensitive, and the synthetic conditions crucially affect the selectivity of product's formation. Alternatively, nucleophilic substitution reactions on silsesquioxanes molecules could be developed to achieve high yield of selective products.[12] On the basis of the aforementioned perspective, octakis(3-chloropropyl)octasilsesquioxane (abbreviated as T_8-PrCl, **1**) is considered as a promising precursor for nucleophilic substitution reactions due to its ease of synthesis from commercially available precursor. Thus, novel functionalized silsesquioxanes could be prepared facilely from this precursor.[13,14]

The Gabriel method has been known for many decades and customarily used to transform primary alkylhalides to N-alkylated phthalimide precursors via a nucleophilic substitution reaction.[15] Traditional Gabriel synthesis consists of a two-step synthesis, which was then followed by acidic hydrolysis or refluxing with hydrazine to produce primary amines. Alternatively, another chemical such as sulfonamides could be used as Gabriel reagent,[16,17] and the subsequent precursors could be readily hydrolyzed to form secondary amines. From this aspect, we strongly believe that the Gabriel method could be utilized as an effective approach to produce N-alkylated phthalimide and sulfobenzimide silsesquioxanes through nucleophilic substitution reactions on T_8-PrCl. However, our products in this study obtained from these dissimilar nitrogen nucleophiles exhibited significant diversity. The reaction with phthalimide anion surprisingly leads to the formation of a mixture (T_8R_8, $T_{10}R_{10}$, and $T_{12}R_{12}$ where T_n = $(SiO_{1.5})_n$) of octakis(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), decakis(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), and dodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)-dodecasilsesquioxane (**4**), while the reaction with *o*-sulfobenzimide anion, at harsher synthetic condition, yields only a single cubic compound of octakis(3-(1,2-benzisothiazole-3-(2*H*)-one-1,1′-dioxydyl)propyl)octasilsesquioxane (**5**). From these unexpected results, studying the effect of electronic nature on

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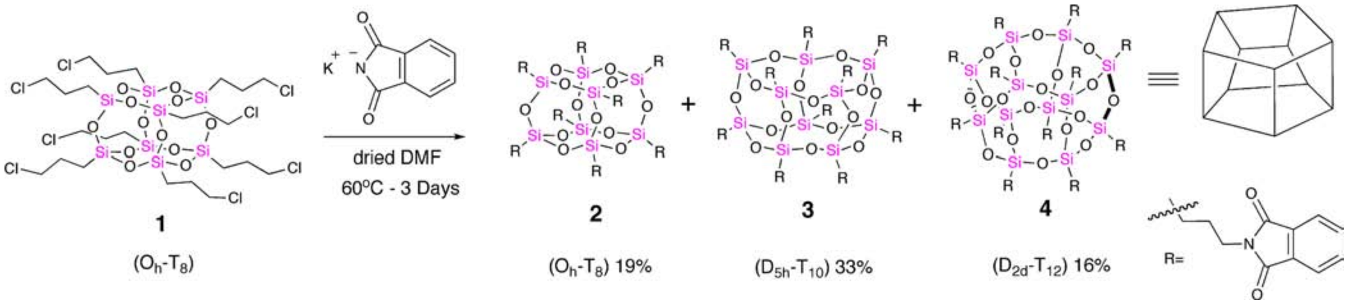
Scheme 1. Synthetic Approach for Preparation of Cage-Rearrangement Octa-, Deca-, and Dodeca-phthalimide-Functionalized Silsesquioxanes



nitrogen nucleophiles toward a selective formation of silsesquioxanes products should reveal the insightful knowledge about the selectivity in cage-rearrangement or cage-degradation phenomena.

■ RESULTS AND DISCUSSION

Preparation and Characterization of Cage-Rearrangement Silsesquioxanes. To investigate the nucleophilic substitution reactions, ^{1}H NMR spectroscopy was used to monitor the reaction's progress. After a mixture of **1** and potassium phthalimide salt was heated in dried DMF solution at 60 °C for 3 days (Scheme 1), the ^{1}H NMR spectrum of the crude product revealed a complete disappearance of the 3-chloropropyl's signals and the appearance of five new signals at 0.55, 1.65, 3.53, 7.59, and 7.67 ppm. The first three signals are consistent with protons in propylene linkages, while the multiplet signals within aromatic regions arise from phthalimide moieties. However, the spectrum shows broad signals with clear splitting patterns, possibly indicating cage decomposition products. Surprisingly, the ^{29}Si{^{1}H} NMR spectrum of crude product gives distinguishably four singlet signals at −67.10, −68.71, −68.94, and −71.43 ppm that can be attributed to the cage-rearrangement products[19] (T_8, T_{10}, and T_{12}; Figure 1), along with a large peak of glass wall between −80 and −120 ppm. Following the satisfactory chromatographic analysis, their separations to obtain each pure compound were further undertaken. We observed that the crude product (1.00 g) by using only conventional column chromatography in a mixture solvent of ethyl acetate/hexane (4.0:1.0) could be easily separated into T_{10}, **3** (0.33 g; R_f = 0.33) as a major product, while T_8, **2** (0.19 g; R_f = 0.45) and T_{12}, **4** (0.16 g; R_f = 0.23) are obtained as minor products.

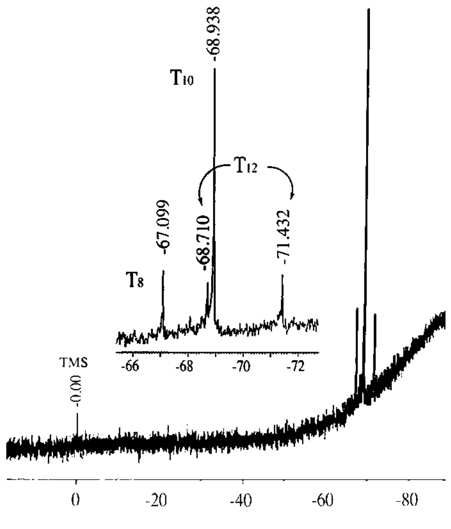


Figure 1. ^{29}Si{^{1}H} NMR spectrum of phthalimide-functionalized silsesquioxanes crude product.

According to our previous report,[18] the cage-rearrangement of **1** under the reaction with azide anion in a solution of DMF at elevated temperature also yields a mixture (T_8, T_{10}, and T_{12}) of azido-functionalized silsesquioxane products. Similarly, the decasilsesquioxane T_{10} cage was reported as a major form. Our hypothesis predicts that a cage-rearrangement mechanism would be reasonable only when the nucleophilicity of nitrogen anions is strong enough to induce the cleavage of silicon−oxygen bonds in the core network to produce particular fragments. Nitrogen−silicon bonds formed during substitution reactions and the subsequent molecular self-assembly of these fragments would allow the formation of thermodynamically favorable cage-like silsesquioxanes.

Moreover, ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **2**, T_8 and **3**, T_{10} exhibit identical patterns, and thus cannot be distinguished. In this study, further characterizations by ^{29}Si{^{1}H} NMR and mass spectrometry enable the determination of the identity of each compound. ^{29}Si{^{1}H} NMR spectra for both pure **2** and **3** exhibit only singlet signals at −67.11 and −68.95 ppm (Figure 2a and 2b), respectively. A symmetrical environment for silicon atoms on each structure (T_8 and T_{10}) would be predicted. Nevertheless, the ^{29}Si{^{1}H} NMR spectrum of **4** (T_{12}) produces double singlet signals at −68.74 and −71.46 ppm (Figure 2c), corresponding to the two different types of silicon atoms in a dodecasilsesquioxane cage. Among the twelve silicon atoms in dodeca-structure, eight atoms are present in the interior within two 10- and one 8-membered fused rings, but another four atoms are in two 8- and one 10-membered fused rings. These differences in the chemical shift are attributed to a ring-strain on the silsesquioxane cages (T_8, T_{10}, and T_{12}). This interpretation is consistent with the studies by Marsmann and Kawakami et al.,[18,19] as well as Rikowski[19a] proposed the electron withdrawing group (chlorine atom) on octakis(3-chloropropyl)-octasilsesquioxane effects to the cage-rearrangement reaction under basic conditions. As a result, the ^{13}C{^{1}H} NMR spectrum of **4** shows doubly singlet signals for each carbon in propylene linkages, which are strong evidence to confirm the presence of two distinct environments in the dodecasilsesquioxanes cage.

Preparation and Characterization of Cubic Octasilsesquioxane. The reaction of *o*-sulfobenzimide salt on **1** was shown in Scheme 2. From the observation, even a minuscule amount of water crucially affected the reaction, leading to the

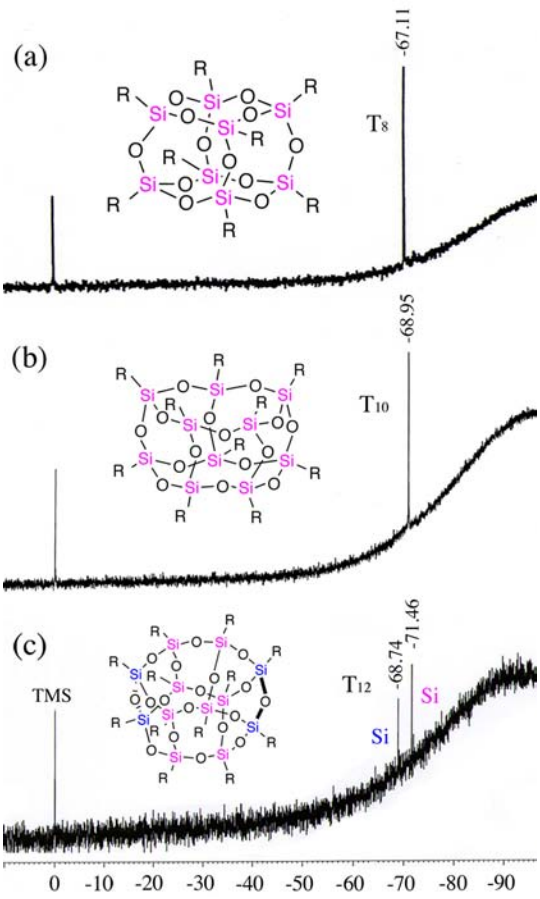
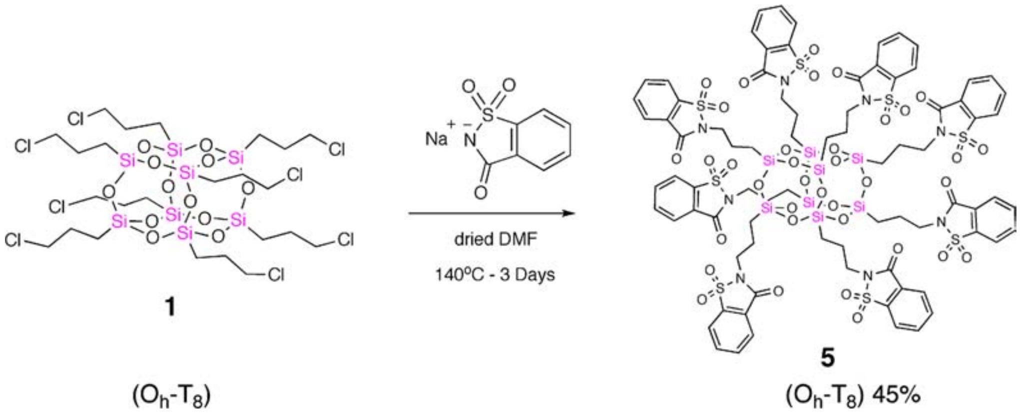


Figure 2. ^{29}Si{^{1}H} NMR spectra of purified compounds (a) octa-, (b) deca-, and (c) dodeca-phthalimide-functionalized silsesquioxanes (**2**, **3**, and **4**).

decomposition of precursor **1** and yielding various unwanted by-products. Because commercial *o*-sulfobenzimide salt attains a large amount of water, removal of water molecules in the lattice salt is necessary prior to performing the reaction. It is also worth noting that the regioselectivity in the reaction must be taken into account, because *o*-sulfobenzimide anion is an ambident nucleophile with the possibility to be alkylated at both nitrogen and oxygen atoms.[20] Several reports have indicated the effects of solvent, temperature, and catalyst toward regioselectivity of O- and N-alkylations on sulfobenzimide.[21] In dried DMF solution, the thermal transformation of O-alkylated into more stable N-alkylated products proceeds via a Chapman−Mumm rearrangement mechanism.[22] Interestingly, our harsh conditions were also capable for both O- and N-alkylations, depending mainly on the synthetic temperature. At 100 °C, the substitution conversion was found in 87% with the 1:10 ratio of O-alkylated to N-alkylated products. The explanation for the O-/N-alkylated proportion arises from the fact that stronger nucleophile of nitrogen anion reacts more rapidly than weaker nucleophile of oxygen anion (kinetic factors). Nevertheless, after the synthetic temperature was elevated to 140 °C, ^{1}H NMR spectrum of crude product reveal >99% substitution. The O-alkylation was negligibly detected, while the N-alkylation was mainly perceived. We propose that a less stable O-alkylation product transforms reversibly into a more stable N-alkylated product at higher temperature (thermodynamic factors). From chromatographic analysis of crude product in the solvent mixture of ethyl acetate/hexane (19.0:1.0), three major fractions were identified. The first two fractions at R_f = 0.34 and 0.42 appear as broad stains, which may likely represent a tangible evidence, later confirmed by ^{29}Si{^{1}H} NMR analysis, of incomplete substitutions and decompositions of oligomeric fragments. By means of conventional column chromatography, pure compound of **5** (R_f = 0.23) was obtained in 45% yield. ^{1}H NMR analysis of **5** reveals three new signals of aliphatic protons on propylene linkages at 0.77, 1.97, and 3.76 ppm, and additional two multiplet signals of aromatic protons on *o*-sulfobenzimide moieties at 7.75 and 7.95 ppm. In addition, the ^{29}Si{^{1}H} NMR spectrum displays only one singlet at −67.12 ppm, and high-resolution mass analysis detects a molecular ion at *m*/*z* 2247.1077. According to this analysis, we conclude that, under this synthetic condition, the octasilsesquioxane cage was obtained as a major compound without the occurrence of additional cage-rearrangement products.

To testify the validity of our presumption, we analyzed the mass spectrum of crude product from *o*-sulfobenzimide substitution reaction and found that the highest molecular ion falls into the octasilsesquioxane region. In fact, no other molecular ion of larger cages was clearly observed. We suggest that nucleophilicity of nitrogen atom in *o*-sulfobenzimide anion is significantly suppressed by the presence of more electron-delocalizing groups such as sulfonyl ($-SO_2R$). Likewise, decreased reactivity of the nucleophilic substitution reaction via S_N2 is also consistent with this proposition. Consequently,

Scheme 2. Synthesis of Octa *o*-Sulfobenzimide-Functionalized Silsesquioxane



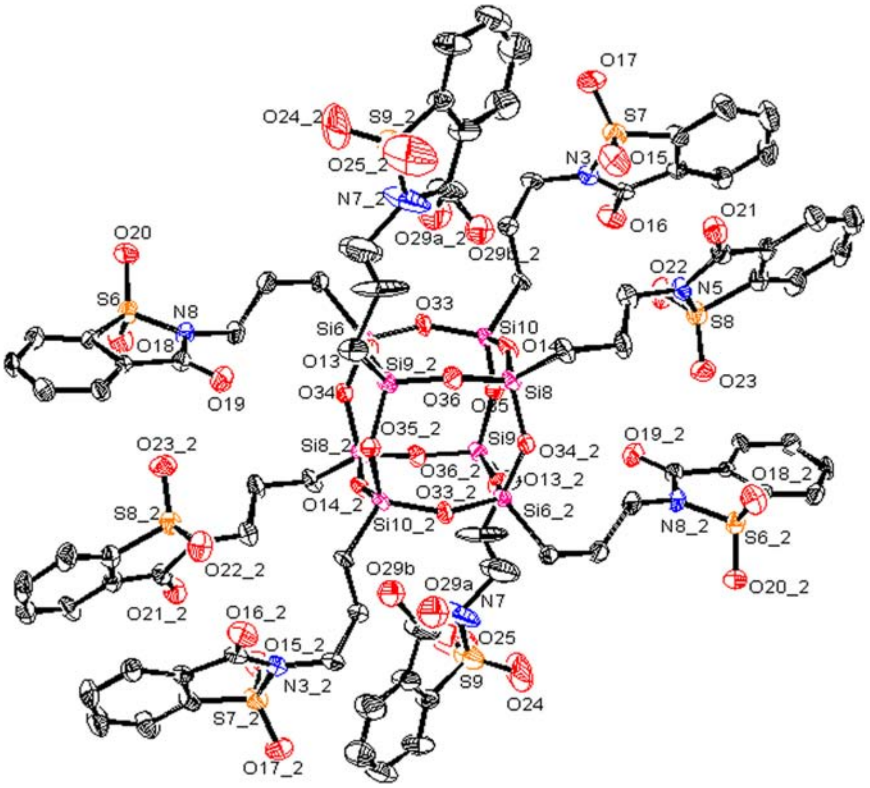


Figure 3. Thermal ellipsoids plot at 30% probability level of **5**; H atoms are omitted for clarity.

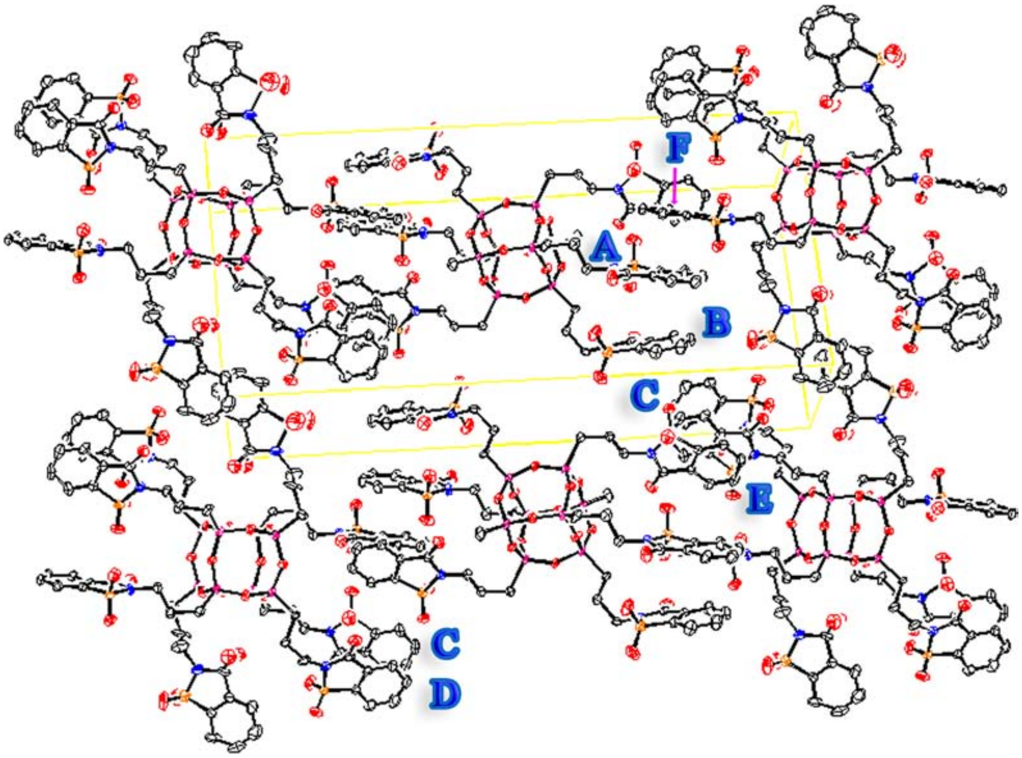


Figure 4. Packing diagram of **5** is presented by intra- and intermolecular $\pi-\pi$ interactions.

an *o*-sulfobenzimide nucleophile ineffectively interacts with silicon atoms and unfavorably induces cage-opening at the silsesquioxane core. Thus, the nitrogen atom of *o*-sulfobenzimide anion could not lead to a cage-rearrangement or yield a mixture of octa-, deca-, and dodecasilsesquioxanes cages, which were found in the reactions with azide and phthalimide anions.

Crystal Structure. To prove our assumption above, the crystallized product **5** was also analyzed by the single-crystal X-ray diffraction analysis. In Figure 3, the final refinement of structure reveals unambiguously that this compound is actually cubic T_8 octasilsesquioxane cage (Figure 3). This evidence could strongly support our previous characterizations by ^{29}Si-{^{1}H} NMR and mass spectrometry. The packing diagram of **5** in Figure 4 and the Supporting Information also shows the extended molecular structure by shorter distances of intermolecular $\pi-\pi$ stacking interactions between neighboring molecules of sulfobenzimide A (S1, N9, C1, C2, C3, C8, C9, C10, C11) and F (S6, N8, C34, C35, C36, C41, C42, C43, C44) rings and between C (S8, N5, C60, C61, C62, C63, C64, C65, C66) and E (S5, N1, C16, C17, C18, C19, C20, C21, C22) rings. The centroid-to-plane distances between A−F and C−E benzene rings are 1.410 and 1.379 Å, respectively, and the dihedral angles between these ring planes are 6.13° and 6.19°. In addition, it should be noted that there are two intramolecularly symmetry-unrelated weak slipping face to face $\pi-\pi$ stacking interactions between benzene rings on sulfobenzimide groups: A and B (S3, N10, C27, C28, C29, C30, C31, C32, C33) rings, and C and D (S10, N3, C45, C46, C47, C48, C49, C50, C51) rings. The centroid-to-plane distances between A−B and C−D benzene rings are 1.640(3) and 1.665(3) Å, respectively. Thus, the dihedral angles between these ring planes are 12.767° and 13.069°.

Influence of Nitrogen Nucleophiles toward the Selectivity of Cage-Rearrangement Phenomena. According to the experimental results, nitrogen atom in phthalimide anion leads to the formation of cage-rearrangement products, while sulfobenzimide anion does not, even at harsher conditions. We hypothesize that the electronic nature of nitrogen anions is the major factor in promoting cage-rearrangement reaction. The silicon structures of products (T_8, T_{10}, and T_{12}) obtained from the reaction of **1** with phthalimide anion are the same as azide anion in our previous report.[18] Because the cleavage of Si−O bond, and subsequent formation of nitrogen−silicon bonds occur within the core of cage-structure, azide and phthalimide anions must be able to get through to the inorganic core structure of silsesquioxane, sulfobenzimide anion, yet could not. In this model, the electron density of nitrogen atoms among these three nucleophiles is consistent with the degree of nucleophilicity in the substitution reaction. We conclude that the experimental rate of nucleophilicity-induced cage-rearrangement would be azide > phthalimide > sulfobenzimide anions.

■ CONCLUSION

Four highly functionalized T_n silsesquioxanes (n = 8, 10, and 12) have been successfully synthesized as novel precursors for Gabriel synthesis. Despite the dissimilar nitrogen nucleophiles, substitution reaction with the phthalimide anion surprisingly yields a mixture of octa-, deca-, and dodecasilsesquioxanes cages, whereas reaction with sulfobenzimide anion produces only the octasilsesquioxane cage. Thus, the influence of the electronic nature of nitrogen anions induced cage-rearrangement silsesquioxane was experimentally reported for the first time. The theoretically mechanistic study of these reactions is currently under investigation. We believe that these cage-liked silsesquioxanes are promising materials for further functionalization and preparation of other reactive nitrogen-based silsesquioxanes, especially for future generation of unreported amino-functionalized deca- and dodecasilsesquioxanes.

■ EXPERIMENTAL SECTION

Materials. 3-Chloropropyltrimethoxysilane (purity; >95.0%), potassium phthalimide (purity; >98.0%), and sodium saccharin (purity; >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. and used without additional purification. Anhydrous *N*,*N*-dimethylformamide was purchased from Sigma Aldrich, while the commercial grade of ethyl acetate, methylene chloride, and hexane was further distilled. Precoated silica gel 60 F_{254} plates and silica gel (no. 60) used for chromatography were purchased from Merck & Co., Inc.

Physical Measurement and Instrumentation. Fourier transform nuclear magnetic resonance spectra were obtained by using a Bruker-DPX 300 high-resolution nuclear magnetic resonance spectrometer for ^{1}H nuclei (300 and 500 MHz) and a Bruker-AV 500 high-resolution magnetic resonance spectrometer for ^{13}C{^{1}H} (125 MHz) and ^{29}Si{^{1}H} (99 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane, and residual solvents peaks were used as a reference. High-resolution mass spectrometry was performed with a VQ-TOF 2 Micromass spectrometer.

Synthesis of Cage-Rearrangement Silsesquioxanes. *Octakis-(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), Decakis-(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), and Dodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)dodecasilsesquioxane (**4**).* Octakis(3-chloropropyl) octasilsesquioxanes (**1**) was prepared following established procedures.[23] A mixture of **1** (0.80 g, 0.77 mmol) and potassium phthalimide (1.94 g, 10.47 mmol) was added into a dried two-necked flask. The solid mixture was further dried over vacuum at room temperature for an additional hour. Anhydrous DMF (20.00 mL) was added into the flask via a transfer syringe, and the solution mixture was connected to the condenser under dried nitrogen. After being heated at 60 °C for 3 days, the reaction solution was cooled and worked up by pouring into a slurry of deionized-water/ice. A white precipitate containing the crude product (1.56 g) was immediately formed, filtered, and dried in air. The composition of the crude product was further analyzed by TLC method with a solvent mixture of ethyl acetate:hexane (4.0:1.0) to obtain three major fractions at R_f values at 0.45, 0.33, and 0.23, identified as octakis(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), decakis(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), and dodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)dodecasilsesquioxane (**4**), respectively. Subsequently, 1.00 g of crude product was separated by silica gel column chromatography to give **2** (0.19 g, 0.098 mmol, 18.84% as a white powder solid), to give **3** (0.33 g, 0.14 mmol, 33.64% as a white powder solid), and to give **4** (0.16 g, 0.055 mmol, 15.86% as a transparent film). **2**, ^{1}H NMR (CDCl$_3$): δ 0.64 (t, 16H, $^3J_{H-H}$ = 8.10 Hz), 1.74 (quintet, 16H, $^3J_{H-H}$ = 7.80 Hz), 3.58 (t, 16H, $^3J_{H-H}$ = 6.0 Hz), 7.59 (multiplet, 16H), 7.66 (multiplet, 16H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.48, 21.81, 40.11, 122.94, 132.19, 133.43, 168.14 ppm. ^{29}Si{^{1}H} NMR (CDCl$_3$) δ −67.11 ppm. HRMS (ESI): [M + Na]$^+$ calcd for [$C_{88}H_{80}N_8NaO_{28}Si_8$]$^+$, m/z 1943.3128; found, m/z 1943.3844. **3**, ^{1}H NMR (CDCl$_3$): δ 0.63 (t, 20H, $^3J_{H-H}$ = 8.15 Hz), 1.73 (quintet, 20H), 3.61 (t, 20H, $^3J_{H-H}$ = 7.47 Hz), 7.58 (multiplet, 20H), and 7.65 (multiplet, 20H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.54, 21.97, 40.22, 122.96, 132.26, 133.41, 168.14 ppm. ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −68.95 ppm. HRMS (ESI): [M + Na]$^+$ calcd for [$C_{110}H_{100}N_{10}NaO_{35}Si_{10}$]$^+$, m/z 2425.4010; found, m/z 2425.4967. **4**, ^{1}H NMR (CDCl$_3$): δ 0.55 (t, 24H, $^3J_{H-H}$ = 8.01 Hz), 1.64 (quintet, 24H), 3.53 (t, 24H, $^3J_{H-H}$ = 7.30 Hz), 7.50 (multiplet, 24H), and 7.58 (multiplet, 24H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.55, 10.11, 22.01, 22.08, 40.12, 40.31, 122.92, 132.27, 133.33, 168.06, 168.07 ppm. ^{29}Si{^{1}H} NMR (CDCl$_3$) δ −68.74, −71.46 ppm. HRMS (ESI): [M + Na]$^+$ calcd for [$C_{132}H_{120}N_{12}NaO_{42}Si_{12}$]$^+$, m/z 2905.4819; found, m/z 2905.5907.

Synthesis of Cubic Octasilsesquioxane. *Octakis(3-(1,2-benzisothiazole-3-(2H)-one-1,1′-dioxydyl)propyl)octasilsesquioxane (**5**).* Initially, *o*-sulfobenzimide sodium salt dihydrate (4.85 g, 23.64 mmol) was dried over a vacuum at 60 °C for 6 h in a dried two-necked flask. After being cooled to room temperature, **1** (1.03 g, 0.99 mmol) was added into the reaction portion, and the solid mixture was further dried over vacuum at room temperature for an additional hour.

Anhydrous DMF (20.00 mL) was added into the flask via a transfer syringe, and the solution mixture was connected to the condenser under dried nitrogen. After being heated at 140 °C for 3 days, the reaction solution was cooled and worked up by pouring into slurry of deionized-water/ice. A white precipitate containing the crude product (3.19 g) was immediately formed, filtrated, and then dried over air. The composition of the crude product was further analyzed by TLC method with a solvent mixture of ethyl acetate:hexane (19.0:1.0) to reveal one major fraction at R_f value = 0.23, corresponding to octakis(3-(1,2-benzisothiazole-3-(2*H*)-one-1,1′-dioxydyl)propyl)-octasilsesquioxane (**5**), while other fractions were assigned to byproducts. Subsequently, 1.00 g of crude product was separated by silica gel column chromatography to obtain **5** (0.42 g). Recrystallization in CH_2Cl_2/hexane mixed-solvent yielded a colorless needle-like crystal (0.31 g, 0.14 mmol, 45% yield). Note that repeated recrystallization may be required to obtain purified compound. ^1H NMR ($CDCl_3$): δ 0.77 (t, 16H, $^3J_{H-H}$ = 8.10 Hz), 1.97 (quintet, 16H, $^3J_{H-H}$ = 7.50 Hz), 3.76 (t, 16H, $^3J_{H-H}$ = 6.00, 7.50 Hz), 7.75 (multiplet, 24H), and 7.95 (d, 8H, $^3J_{H-H}$ = 3.30 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.86, 21.93, 41.37, 102.69, 125.00, 127.56, 133.87, 134.22, 137.72, and 158.72 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −67.12 ppm. HRMS (ESI): $[M + K]^+$ calcd for $[C_{80}H_{80}KN_8O_{36}S_8Si_8]^+$, *m*/*z* 2247.0232; found, *m*/*z* 2247.1077.

X-ray Structural Determination. Crystalline **5** suitable for X-ray structural analysis was obtained by recrystallization in CH_2Cl_2/hexane. X-ray data were collected by Bruker SMART APEX II CCD area-detector diffractometer, with Mo Kα radiation source (λ = 0.7107 Å) at 296 K. The crystal structures were solved by the directed method with SHELXS-97.[24] The full matrix least-squares procedures using SHELXL-97 on F^2 anisotropic for all non-hydrogen atom was used to refine the crystal structures. Hydrogen atoms were placed in their calculated positions and refined following the riding model. The crystal data and structural refinement parameters are summarized in Table 1 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H, ^{13}C, ^{29}Si NMR, and ESI−MS spectra giving characterization data for new compounds **2**−**5** and crystallographic data in a CIF file of **5** (CCDC 891141). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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