Synthesis of Novel Organic–Inorganic Hybrid Cages via Cobalt-catalyzed Cyclotrimerization of Dimethylethynylsilyl Groups on a Silsesquioxane

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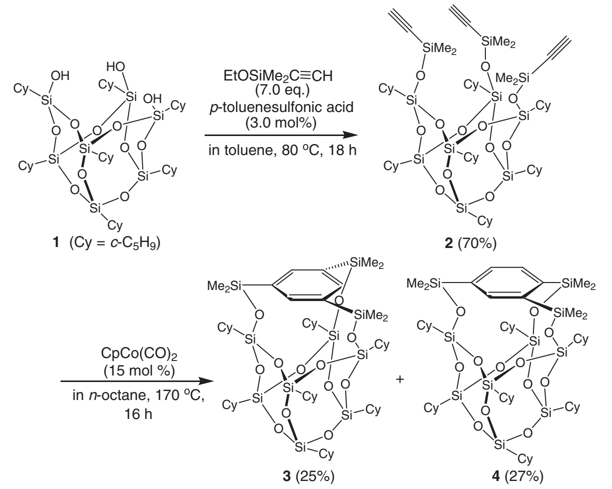
Novel organic–inorganic hybrid cages composed of a half-caged silsesquioxane skeleton and a benzene ring have been synthesized by cobalt-catalyzed intramolecular cyclotrimerization of a silsesquioxane bearing three dimethylethynylsilyl groups.

Development of novel organic–inorganic hybrid materials of ordered structures has attracted widespread attention because of the direct design of organic functional groups as well as their new catalytic activities and physical properties.[1] A number of silsesquioxanes of cage-like core structures with versatile organic functional groups[2] have been utilized as building blocks of various functionalized materials, such as porous hybrid materials[3] or heat-resistant polymers.[4] Therefore, the synthesis of novel cage oligosilsesquioxanes is of increasing practical interest. In addition, preparation of cage siloxane molecules which can accommodate a metallic species or a small molecule is of great interest. Previously, we reported the synthesis of alkenylene-bridged oligosilsesquioxanes containing macrocycles by the ruthenium or rhodium complex-catalyzed ring-closing reactions.[5]

Here we report preliminary results of our investigations on the synthesis of novel organic–inorganic hybrid cages utilizing a polyhedral oligosilsesquioxane. The intramolecular cyclotrimerization of a tris(dimethylethynylsilyl)-substituted silsesquioxane in the presence of a catalytic amount of a cobalt complex successfully gave oligosilsesquioxanes composed of a half-open caged siloxane framework and a benzene ring.

A silsesquixane with three ethynylsilyl groups (**2**) was prepared in 70% yield by the reaction of incompletely condensed silsesquixane trisilanol ($(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (**1**) with 7.0 equiv. of dimethylethoxyethynylsilane in the presence of 3.0 mol % of *p*-toluenesulfonic acid in toluene at 80 °C for 18 h, followed by column chromatography.[6] The product was fully characterized by NMR, FAB-MASS, and elemental analysis.



1 ($Cy = c\text{-}C_5H_9$) **2** (70%) **3** (25%) **4** (27%)

Scheme 1.

Table 1. Synthesis of cage silsesquioxanes by the interamolecular cyclotrimerization of **2** catalyzed by $CpCo(CO)_2$[a]

Run	Catalyst /mol%	Reaction Temp. /°C	Time /h	Yield/% **3**	**4**	Total
1[b]	15.0	reflux	24	9	8	17
2	15.0	140	16	16	19	35
3	15.0	150	16	16	22	38
4	15.0	160	16	24	25	49
5	15.0	170	16	25	27	52
6	7.5	170	16	23	24	47
7	3.8	170	16	5	7	12

[a]Reaction conditions: **2** (0.20 mmol), *n*-octane (10 mL) in the autoclave.
[b]Reaction by the use of the glass vessel with a reflux condensor.

The intramolecular cyclotrimerization of alkynylsilyl substituents in **2** produces novel cage silsesquioxanes composed of a siloxane framework and a 1,3,5-substituted benzene ring (**3**) or a 1,2,4-substituted one (**4**) (Scheme 1).[7] Although the cyclotrimerization of alkynes is a very common reaction and usually proceeds smoothly in the presence of appropriate metallic promoters,[8,9] the present reactions require very severe conditions. Several catalysts reported to be effective for the cyclotrimerization of alkynes were employed. Among them, only $CpCo(CO)_2$[8] is effective, and the use of other catalysts, such as $RhCl(PPh_3)_3$ or $PdCl_2/CuCl_2$,[9] resulted in the stoichiometric recovery of **2**. Table 1 shows the effects of reaction conditions. The reaction does not proceed at all at under 100 °C. While under *n*-octane reflux the yields of **3** and **4** were low, the reactions at higher temperatures by the use of an autoclave proceeded catalytically. The desired products were obtained in a combined yield of 52 or 47% by the reaction at 170 °C for 16 h in the presence of 15.0 or 7.5 mol % of the cobalt catalyst, respectively. The conversion of **2** in run 5 is more than 95% together with intractable by-products, and prolonged reaction time did not improve the yields of the desired products.

Although the reactions yield a mixture of both isomers, the products can be separated by careful column chromatography. The FAB-MASS analyses of both isomers clearly show peaks at around m/z of 1122, $[M]^+$, and the isotope distribution pattern coincides with the composition of **3** and **4**. The ^1H NMR spectrum of **3** includes one singlet of the aromatic proton region and one singlet corresponding to the methyl groups. In addition, the ^{29}Si NMR spectrum of **3** consists of one set of three peaks in a 3:1:3 ratio for seven silicon atoms in the silsesquioxane cage, which is in good accordance with the local C_{3v}-symmetry of the molecule, clearly indicating that **3** is the 1,3,5-substituted isomer. On the other hand, three sets of peaks for aromatic protons and six peaks for methyl protons are shown in the ^{1}H NMR spectrum of **4**. Its ^{29}Si NMR spectrum consists of one set of seven equivalent peaks for seven silicon atoms in the silsesquioxane cage. On the basis of these spectroscopic results, the structure of **4** was determined to be the 1,2,4-substituted isomer, which has no symmetrical plane. For both isomers colourless single crystals were obtained, but their crystallographic analyses were hampered by the poor diffraction at high angle region of $2\theta > 30°$. The thermogravimetric analyses under Ar showed that gradual loss of their weight started at around 300 °C.

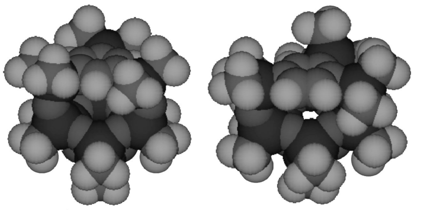


Figure 1. Optimized structure of **3**′ (left) and **4**′ (right) by DFT calculation (B3LYP/6-31G(d)).

Figure 1 shows the structures of model compounds, **3**′ and **4**′, in which cyclopentyl groups in **3** and **4** are replaced by methyl groups, optimized by DFT calculation (B3LYP/6-31G(d)). On the basis of electronic and zero-point energies (ΔE_0), the 1,2,4-substituted molecule (**4**′) is less stable than the 1,3,5-isomer (**3**′) by 10.7 kcal mol^{-1}. Since the reaction yields almost 1:1 mixture of **3** and **4**, the reaction is considered to be kinetically controlled. It is well established that the cobalt-catalyzed cyclotrimerization proceeds via the cobaltacyclopentadiene intermediates.[8] The predominant formation of α,α'-disubstituted metallacyclopentadiene has been often advocated in the reactions of silyl-substituted alkynes, from which only the 1,2,4-substituted isomer can be formed. This can be one reason for the formation of **4** in spite of its thermodynamic disadvantage. The DFT calculations also suggest the possibility of the presence of small inner spaces in these cage molecules. For example, the inclusion of F^{-} anion[9] in **3**′ is calculated to be thermally favorable by 9.9 kcal mol^{-1}. Attempts of inclusion of such small ions or molecules, however, have not been successful yet.

In conclusion, two novel cage oligosilsesquioxanes composed of half-caged siloxane skeletal and benzene rings have been synthesized by cobalt-catalyzed intramolecular cyclotrimerization of a silsesquioxane bearing three ethynyldimethylsilyl groups. These molecules are quite interesting as building blocks for new materials or as novel cage host molecules. Attempts direct towards enlargement of the inner spaces of these cage molecules, as well as the introduction of suitable functional groups for further polymerization into the molecules, are now proceeding.

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6 **Synthesis of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_2C{\equiv}CH)_3$ (2).** To a solution of **1** (3.5 g, 4.0 mmol) and *p*-toluenesulfonic acid (0.12 mmol) in toluene (50 cm^{3}), $EtOMe_2SiC{\equiv}CH$ (4.1 cm^{3}, 28 mmol) was added dropwise and stirred at 80 °C for 18 h. The product was then chromatographed on alumina. Elutioned with pentane, the resulting clear solution was then evaporated at room temperature to leave a white solid. Yield 70%. mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.37 (3H, $C{\equiv}CH$), 1.76–1.48 (br m, 56H, CH_2 of Cy), 0.97–0.92 (br m, 7H, CH of Cy), 0.33 (18H, $Si(CH_3)_2C{\equiv}CH$); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 91.97 ($C{\equiv}CH$), 89.38 ($C{\equiv}CH$), 27.58, 27.52, 27.27, 27.04, 26.96 (CH_2 of Cy), 24.24, 23.59, 22.40 (3:3:1 for CH of Cy), 2.306 ($Si(CH_3)_2$); $^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C) δ −17.73 ($Si(CH_3)_2$), −66.18, −67.22, −67.63 (1:3:3). Anal. Found C, 50.43; H, 7.78% Calcd for $C_{47}H_{84}O_{12}Si_{10}$ (1122.03): C, 50.31; H, 7.55%. MS (FAB) m/z : 1096 $[M - HC{\equiv}CH]^{+}$, 1052 $[M - C_5H_{10}]^{+}$.

7 **Synthesis of $(c\text{-}C_5H_9)_7Si_7O_9[1,3,5\text{-}(OSiMe_2)_3C_6H_3]$ (3) and $(c\text{-}C_5H_9)_7Si_7O_9[1,2,4\text{-}(OSiMe_2)_3C_6H_3]$ (4).** In an autoclave equipped with a glass liner, a solution of **2** (0.224 g, 0.2 mmol) and $CpCo(CO)_2$ (15 mol %) in *n*-octane (10 cm^{3}) was stirred at 170 °C for 16 h. The products were isolated by column chromatography (silica gel) eluted with pentane, followed by vacuum evaporation at room temperature. **3**: Yield 25%, mp 216–218 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.90 (s, 3H,$C_6H_3Si_3$), 1.75–1.47 (br m, 56H, CH_2 of Cy), 0.91–0.88 (br m, 7H, CH of Cy), 0.45 (s, 18H, $Si(CH_3)_2$); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 139.48, 136.31 (for CH of $C_6H_3Si_3$), 27.57, 27.54, 27.23, 26.97, 26.91, 26.83 (CH_2 of Cy), 24.25, 23.93, 22.83 (3:3:1 for CH of Cy), −1.07 ($Si(CH_3)_2$); $^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C) δ0.94 ($Si(CH_3)_2$), −65.78, −66.54, −67.80 (3:1:3). MS (FAB) m/z : 1122 $[M]^{+}$, 1052 $[M - C_5H_{10}]^{+}$. **4**: Yield 27%, mp 206–207 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ8.10 (s, 1H, $C_6H_3Si_3$), 7.69 (d, $^{3}J_{HH} = 7.51$ Hz, 1H, $C_6H_3Si_3$), 7.53 (d, $^{3}J_{HH} = 7.51$ Hz, 1H, $C_6H_3Si_3$), 1.75–1.47 (br m, 56H, CH_2 of Cy), 0.97–0.70 (br m, 7H, CH of Cy), 0.61, 0.56, 0.47, 0.44, 0.42, 0.40 (1:1:1:1:1:1, s, 18H, $Si(CH_3)_2$); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 146.00, 142.97, 139.79, 138.27, 134.26, 132.04 (for CH of $C_6H_3Si_3$), 26.82–27.81 (CH_2 of Cy), 24.34, 24.05, 23.88, 23.76, 23.44, 22.83, 22.45 (1:1:1:1:1:1:1 for CH of Cy), 2.00 ($Si(CH_3)_3$), 3.11, 2.79, 2.36, 2.27, −1.15, −1.84 ($Si(CH_3)_2$); $^{29}Si\{^{1}H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C) δ0.45, −0.12, −1.40 (1:1:1 for $Si(CH_3)_2$), −64.71, −65.75, −66.02, −66.93, −67.01, −67.43, −68.07 (1:1:1:1:1:1:1). MS (FAB) m/z : 1122 $[M]^{+}$, 1052 $[M - C_5H_{10}]^{+}$. For the 1:1.1 mixure of **3** and **4**; Anal. Found C, 50.15; H, 7.66% Calcd for $C_{47}H_{84}O_{12}Si_{10}$ (1122.03): C, 50.31; H, 7.55%.

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