

Synthesis of alkenylene-bridged macrocyclic silsesquioxanes by ruthenium or rhodium-catalyzed ring-closing reactions of bis(allyldimethylsilyl) groups†

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Received (in Cambridge, UK) 9th May 2001, Accepted 7th August 2001

First published as an Advance Article on the web 5th September 2001

Novel alkenylene-bridged oligosilsesquioxanes composed of half-caged structures with 16- or 17-membered rings as well as a titanium-containing molecule with a twisted 21-membered macrocycle have been synthesized by ruthenium or rhodium-catalyzed ring-closing reactions of silsesquioxanes with bis(allyldimethylsilyl) groups.

Recently, development of novel organic–inorganic hybrid materials, such as organic functionalized micro- and mesoporous materials, has attracted widespread attention because of the novel catalytic activities and physical properties of these substances.¹ Since silsesquioxanes and spherosilicates with cage-like core structures are expected to be candidates for building blocks of such materials, a number of silsesquioxanes with organic functional groups have been synthesized by various methods² including ruthenium or molybdenum-catalyzed cross-metathesis.³ Porous materials are reported to be obtained by the hydrosilylative polymerization of T₈ cubes.^{2d,4} Therefore, synthesis of oligosilsesquioxanes with novel core structures is of great importance. On the other hand, the synthesis of silacycloalkenes, which incorporate an alkenylene unit in the ring system, has attracted growing interest from the viewpoint of materials chemistry,⁵ and various methods⁶ for the synthesis of these compounds by catalytic ring-closing metathesis (RCM) reactions⁷ have been developed.

Here we report the synthesis of silsesquioxanes containing novel organic–inorganic hybrid half-caged core structures. The ring-closing reactions of bis(allyldimethylsilyl)-substituted silsesquioxanes in the presence of a catalytic amount of a ruthenium or rhodium complex successfully gave novel alkenylene-bridged oligosilsesquioxanes composed of 16-, 17- and 21-membered macrocycles in high yields.

A silsesquioxane with two allyldimethylsilyl groups **1a** was prepared by the stepwise silylation of silsesquioxane disilanol (*c*-C₅H₉)₇Si₇O₉(OSiMe₃)(OH)₂ (**2**) by allylchlorodimethylsilane.⁸ The RCM reaction of **1a** promoted by stepwise addition of 13 mol% of the ruthenium benzylidene complex, {(C₆H₁₁)₃P}₂Cl₂Ru=CHPh (**3**),⁷ at 65 °C for 54 h, followed by column chromatography and reprecipitation afforded the desired novel half-caged oligosilsesquioxane with a 17-membered ring **4a** in an isolated yield of 94% as a mixture of *cis* and *trans* isomers.‡ At present, the major isomer is assigned to be *cis* on the basis of IR and ¹³C NMR, and the ratio of *cis*:*trans* was estimated to be 4.9:1. The preliminary X-ray analysis of a single crystal of the major isomer established the structure illustrated in Scheme 1 with *cis* configuration of the butenylene bridge,§ although the complete solution of the structure was hampered by poor diffraction in the high angle region (2θ > 30°) and severe disorder at trimethylsilyl and cyclopentyl groups. According to the ¹H NMR spectrum, these single crystals were composed of the major isomer. The undesired intermolecular reaction was not observed. The ²⁹Si NMR

spectrum of *cis*-**4a** consists of one set of five peaks in a 1:1:2:2:1 ratio for seven silicon atoms in the silsesquioxane cage, which is in good accordance with the local C_s-symmetry of the siloxane framework. Note that the RCM reaction with a smaller amount of a ruthenium catalyst (reduced to 5 mol%) also gave **4a** in 85% yield (by ¹H NMR).

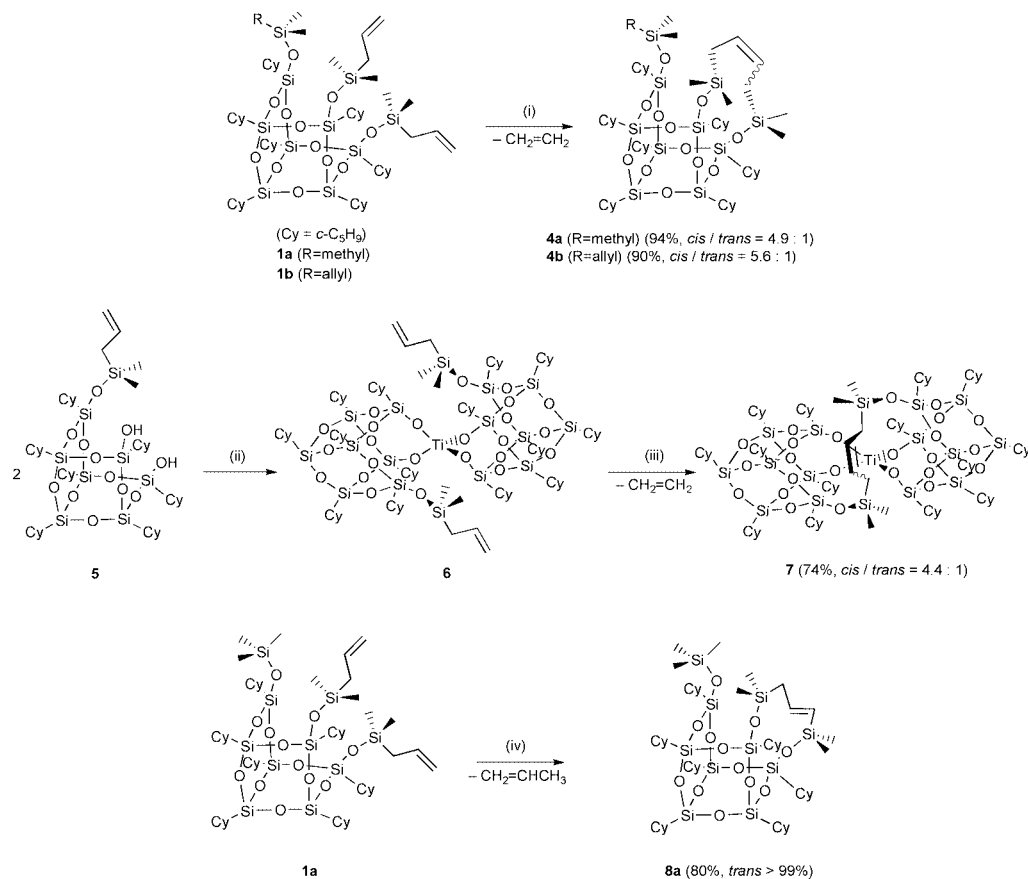
The treatment of **1b**, which has three allyldimethylsilyl groups, by stepwise addition of 10 mol% of **3** at 65 °C for 36 h afforded **4b**, a silsesquioxane containing both terminal and internal alkenyl groups, in 90% yield as a mixture of *cis* and *trans* isomers in a 5.6:1 ratio.

The synthesis of a titanium-containing silsesquioxane with a more extended alkenylene-bridged macrocycle by the RCM reaction was examined. The RCM reaction of a titanium-containing silsesquioxane having two allylic moieties **6**⁸ (prepared by the reaction of an allyldimethylsilyl-substituted silsesquioxane disilanol **5** with tetrakis(diethylamino)titanium) in the presence of 15 mol% of the ruthenium catalyst **3** at 65 °C for 54 h afforded the desired silsesquioxane **7** in 74% yield (*cis*:*trans* = 4.4:1). The product (**7**) which contains an organic–inorganic hybrid 21-membered macrocycle, was fully characterized by NMR, IR, FAB-MS, and elemental analysis. ¹H and ¹³C NMR measurements indicate the presence of one butenylene unit together with two half-caged silsesquioxane cores in **7**. The ²⁹Si NMR spectrum of *cis*-**7** consists of eight peaks of almost the same intensity for sixteen silicon atoms in the molecule, which indicates the apparent local C₂-symmetry of its siloxane framework.

On the other hand, treatment of **1a** with 10 mol% of the rhodium complex Cp*Rh(ethylene)₂ **9** produced a *trans*-propenylene-bridged silsesquioxane **8a** in an isolated yield of 90%, which has a 16-membered ring. There was no sign of the *cis* isomer in the crude reaction mixture. Note that the reaction in toluene instead of ethanol did not proceed at all, strongly suggesting that formation of a rhodium hydride species is crucial for the present reaction. Although the present untypical formation of (*E*)-propenylene-bridges has been reported in the RuHCl(CO)(PPh₃)₃ or RuCl₂(PPh₃)₃-catalyzed coupling or polycondensation of allylsilanes,^{9–11} the use of these ruthenium catalysts in toluene at 80 °C reduced the yield of **8a** drastically (less than 25% by ¹H NMR), where considerable isomerization of **1a** to 1-propenylsilyl-substituted silsesquioxanes occurred. These reactions previously had been explained in terms of isomerization of allylsilanes to 1-propenylsilanes followed by metathesis,⁹ but a mechanism including the formation of a silylmethyl species *via* the silyl group transfer is now generally accepted.^{11,12} Treatment of a titanium-containing silsesquioxane **6** under similar reaction conditions, however, did not give any desired propenylene-bridged product, and only the isomerization of allylic groups was observed.

In conclusion, a series of novel alkenylene-bridged silsesquioxanes with 16- to 21-membered rings were synthesized in high yields by ruthenium or rhodium complex-catalyzed reactions. These molecules are quite interesting as building blocks for new materials or a platform for novel macrocyclic

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b1/b104086n/>



Scheme 1 Reagents and conditions: i, **3** (13 mol% for **1a** or 10 mol% for **1b**) in (CH₂Cl)₂ at 65 °C, 54 h (for **1a**) or 36 h (for **1b**); ii, Ti(NEt₂)₄ (0.5 equiv.) in benzene at room temperature for 18 h; iii, **3** (15 mol%) in (CH₂Cl)₂ at 65 °C, 54 h; iv, **9** (10 mol%) under EtOH reflux for 18 h.

hosts. The present work also provides the potential for synthesis of new organic–inorganic hybrid cage-like molecules *via* the annulation of unsaturated substituents of silsesquioxanes.

The authors are grateful to Dr M. Shiro of Rigaku Corporation for his kind help in the X-ray crystallographic study.

Notes and references

‡ All new compounds gave satisfactory NMR spectra and microanalytical data. **4a** (*cis*:*trans* = 4.9:1); Mp 239.0–242.0 °C, Anal. Calc. for C₄₆H₉₀O₁₂Si₁₀ (1116.05): C, 49.50; H, 8.13. Found C, 49.28; H, 8.16%. NMR data for *cis*-**4a**: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 5.35 (t, ³J_{HH} = 5.6 Hz, 2H, SiCH₂CH=CHCH₂Si), 1.75–1.47 (br m, 60H, CH₂ of Cy and SiCH₂CH=CHCH₂Si), 0.99–0.89 (br m, 7H, CH of Cy), 0.14 (s, 6H, Si(CH₃)₂), 0.13 (s, 9H, Si(CH₃)₃), 0.10 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 122.97 (SiCH₂CH=CHCH₂Si), 27.63, 27.58, 27.53, 27.29, 27.10, 26.99, 26.95, 26.92 (CH₂ of Cy), 24.89, 24.21, 23.80, 23.51, 22.45 (1:2:2:1:1 for CH of Cy), 19.63 (SiCH₂CH=CHCH₂Si), 1.99 (Si(CH₃)₃), 0.23, 0.11 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.02 M Cr(acac)₃, 25 °C) δ 8.10 (Si(CH₃)₃), 5.57 (Si(CH₃)₂), –66.28, –67.68, –67.81, –67.98, –68.37 (1:1:2:2:1).

§ Colorless single crystals of **4a** which have monoclinic space group P2₁/c, were obtained by slow diffusion of acetonitrile into a mesitylene solution. The unit-cell constants were *a* = 20.7421(5); *b* = 13.942(1); *c* = 21.0128(5) Å; β = 90.8196(7)°; *V* = 6075.9(5) Å³. Data analysis revealed the structure depicted in Scheme 1 with a (*Z*)-butenylene bridge, although at present only silicon and oxygen atoms could be refined anisotropically because of poor diffraction in the high angle region of 2θ > 30°.

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