

Synthesis of Cooligomers of Titanium-Bridged Silsesquioxanes and Octakis(hydridosilsesquioxane)

Kenji Wada, Koichi Yamada, Daisuke Izuhara, Teruyuki Kondo, and Take-aki Mitsudo*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501

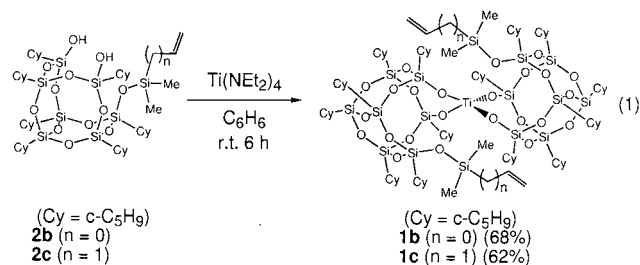
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New titanium-bridged silsesquioxanes having olefinic groups, $\text{Ti}[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}(\text{SiMe}_2\text{R})_2]$ ($\text{R} = \text{vinyl}$, allyl), react with octakis(hydridosilsesquioxane) under hydrosilylation reaction conditions to give oligomeric materials. The local structure around the titanium atoms of the starting silsesquioxanes is unchanged even in the oligomeric materials.

Metal-containing oligosilsesquioxanes have attracted attention from the viewpoint of their role as well-defined, homogeneous models for the active surface sites of the supported catalysts or metal-containing zeolites.¹ Among them, recent interest has been focused on the catalytic activities of titanium-containing silsesquioxanes² including $\text{Ti}[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}(\text{SiMe}_3)_2]$ (**1a**)^{2a,b} for epoxidation of olefins as a soluble analog of titanosilicates.³ On the other hand, silsesquioxanes and spherosilicates of cage-like core structures are expected to be candidates for building blocks of novel organic-inorganic hybrid materials, and porous or heat-resistant materials are produced by the hydrosilylation polymerization of T_8 cubes.^{4,5} Therefore, introduction of appropriate functional groups into metallasilsesquioxanes is of interest. We have recently reported the synthesis and functionalization of a series of metallocene-containing silsesquioxanes with a vinyl group.⁶ Note that there are reports on the catalytic activities of polymeric materials produced from a silsesquioxane diol and metallic species.^{2c,7}

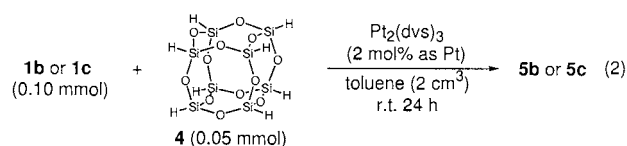
In the present communication, new titanium-bridged silsesquioxanes with olefinic moieties, $\text{Ti}[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}(\text{SiMe}_2\text{R})_2]$, $\text{R} = \text{vinyl}$ (**1b**) or allyl (**1c**), are synthesized, and the hydrosilylative oligomerization of these compounds with octakis(hydridosilsesquioxane) is reported.

The reaction of disilanols having an olefinic group ($(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{10}(\text{SiMe}_2\text{R})(\text{OH})_2$, $\text{R} = \text{vinyl}$ (**2b**),⁶ allyl (**2c**)⁸), which were prepared by the controlled silylation of a silsesquioxane triol $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ **3**,¹ with tetrakis(diethylamino)titanium in benzene at room temperature, produced titanium-bridged silsesquioxanes **1b** (68%)⁹ or **1c** (62%),¹⁰ respectively. The structures of **1b** and **1c** were deduced on the basis of ^1H -, ^{13}C -, ^{29}Si -NMR, and FAB mass analyses. The ^{29}Si -NMR spectrum of **1b** consists of eight peaks of almost the same intensity for sixteen silicon atoms, indicating apparent



local C_2 -symmetry of their siloxane frameworks.

The hydrosilylation of olefinic groups in titanium-bridged silsesquioxane **1b** or **1c** with 0.5 equiv of octakis(hydridosilsesquioxane) ($\text{H}_8\text{Si}_8\text{O}_{12}$, **4**)¹¹ in the presence of a $\text{Pt}_2(\text{dvs})_3$ catalyst (2 mol% as Pt, dvs = divinyltetramethyldisiloxane) in toluene at room temperature for 24 h afforded cooligomers, **5b** or **5c**, respectively (see eq 2). The produced cooligomers are



highly soluble in THF, toluene, and hexane.

The GPC analysis of crude **5b** showed the oligomer formation ($M_w = 45000$, $M_n = 9200$ based on polystyrene standards). The profile of **5b** consists of a large peak in a high M_w region ($M_w = 200000\text{--}10000$) together with several low M_w peaks ($M_w = 6000$). A very small shoulder was found at around $M_w = 2000$, indicating only a trace amount of unreacted **1b** remained in the crude mixture. In addition, there was no sign of unreacted **4**. Note that the reaction of **1b** with an equimolar amount of **4** only produced a low molecular weight species ($M_w = 9600$, $M_n = 2700$). The oligomer **5c** shows higher M_w of 63000, but the molecular weight distribution is broader ($M_n = 6600$).

The IR and ^1H -NMR study revealed that about half of the SiH groups of **4** remained in both **5b** and **5c**. According to the ^{13}C -NMR (DEPT) spectra, the silylation cleanly occurred at the terminal carbon atoms of the olefinic groups with excellent regioselectivity. No other possible regioisomeric connection

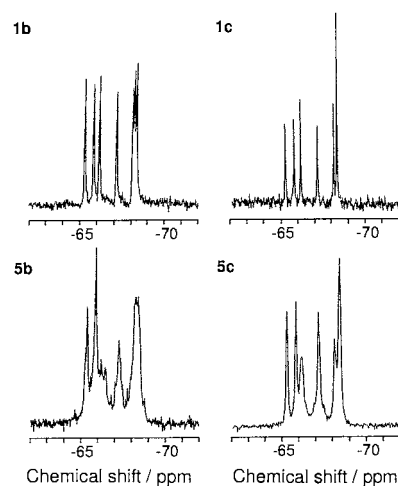


Figure 1. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the cooligomers in CDCl_3 solutions. 0.2 M $\text{Cr}(\text{acac})_3$, PD = 10 s.

was detected by NMR.

The materials in the present work include only a specific titanium species. The ^{29}Si -NMR peaks of **5b** and **5c** in the T-silicon region were very similar to those of **1b** and **1c**, respectively, although broadening was observed (Figure 1). In addition, no ^{29}Si -peaks were found in the region of -50 to -60 ppm¹ even after the treatment with methanol followed by the column chromatography to remove the Pt catalyst, indicating the absence of silanols formed by cleavage of the Ti–O–Si bonds. The UV spectra of **5b** and **5c** displayed a sharp absorption band at 210 nm, characteristic of a tetrahedrally coordinated, monomeric titanium species,^{2b} almost identical to the case with **1b** and **1c** ($\lambda_{\text{max}} = 210$ nm). Therefore, the local structure around the titanium atoms of **5b** or **5c** is estimated to be very similar to those of **1b** or **1c**. These results suggest the structures

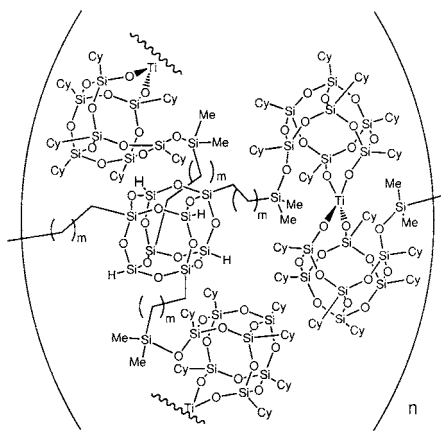


Figure 2. Possible structure of **5b** ($m = 1$) and **5c** ($m = 2$). Substitution positions of the 4-originated moieties are not determined.

of oligomers exemplified in Figure 2.

In conclusion, hydrosilylation between octakis(hydrido-silsesquioxane) and new titanium-bridged silsesquioxanes with olefinic groups afforded novel oligomeric materials. These oligomers are estimated to possess a titanium species very similar to that in **1b** or **1c**. They would be appropriate precursors of organic–inorganic hybrid materials for the catalysts with titanosilicate-like active sites,³ or porous oxides with uniformly controlled micropores.¹²

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- 8 **2c**: A disilanol ($c\text{-C}_6\text{H}_{11}$)₇Si₇O₁₀(SiMePhCH=CH₂)(OH)₂ has been prepared from [PPh₃Me]⁺[($c\text{-C}_6\text{H}_{11}$)₇Si₇O₁₂H₂][−] (F. J. Feher and S. H. Phillips, *J. Organomet. Chem.*, **521**, 401 (1996)). Alternatively, to a solution of **3** (10.5 g, 12.0 mmol) and triethylamine (5.0 cm³, 36 mmol) in THF (70 cm³), allylchlorodimethylsilane (1.1 cm³, 7.2 mmol) in THF (30 cm³) was dropwise added and stirred at room temperature for 18 h. Filtration followed by evaporation leave a white solid. This was extracted with pentane (100 cm³) to give a clear filtrate and a white solid. From the pentane-insoluble solid, 4.8 mmol of unreacted **3** was recovered, and from the filtrate the solvent was evaporated. The product was obtained by recrystallization by slow diffusion of acetonitrile into a benzene solution. Yield 98%. mp 166.0–168.0 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 5.83 (ddt, ³J = 17.1, 9.7, 8.1 Hz, 1H, SiCH₂CH=CH₂), 4.91 (d, ³J = 17.1 Hz, 1H, *trans*-CH₂CH=CH₂), 4.87 (d, ³J = 9.7 Hz, 1H, *cis*-CH₂CH=CH₂), 4.01 (br, 2H, SiOH), 1.75–1.50 (br m, 58H, CH₂ of Cy and SiCH₂CH=CH₂), 1.06–0.92 (br m, 7H, CH of Cy), 0.16 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 134.35 (SiCH₂CH=CH₂), 113.71 (SiCH₂CH=CH₂), 27.57, 27.45, 27.40, 27.34, 27.26, 27.24, 27.09, 27.02, 27.00, 26.88, 26.84 (CH₂ of Cy), 25.89 (SiCH₂CH=CH₂), 23.69, 22.82, 22.46, 22.27, 22.20 (1:2:2:1:1 for CH of Cy), −0.50 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.2 M Cr(acac)₃, 25 °C) δ 7.73, −56.62, −65.57, −66.43, −67.36 (1:2:2:1:2). Anal. Calcd for C₄₀H₇₆O₁₂Si₈ (973.73): C, 49.34; H, 7.87%. Found C, 49.36; H, 7.64%.
- 9 **1b**: To a solution of **2b** (768 mg, 0.8 mmol) in dry benzene (30 cm³), tetrakis(diethylamino)titanium (135 mg, 0.4 mmol) in dry benzene (15 cm³) was dropwise added and stirred at room temperature for 6 h. After the solvent was evaporated, the resulting off-white solid was extracted with hexane (30 cm³). Filtration by using a 0.45 μm PTFE filter gave a clear solution. After evaporation, **1b** was obtained by recrystallization by slow diffusion of acetone into a benzene solution. Yield 68%. mp 267.5–268.0 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 6.16 (dd, ³J = 20.2, 14.9 Hz, 2H, SiCH=CH₂), 5.93 (dd, ³J = 14.9 Hz, ²J = 4.0 Hz, 2H, *cis*-SiCH=CH₂), 5.74 (dd, ³J = 20.2 Hz, ²J = 4.0 Hz, 2H, *trans*-SiCH=CH₂), 1.89–1.43 (br m, 112 H, CH₂ of Cy), 1.02–0.85 (br m, 14 H, CH of Cy), 0.24 (s, 6H, Si(CH₃)₂), 0.23 (s, 6 H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 139.37 (SiCH=CH₂), 131.58 (SiCH=CH₂), 27.76, 27.61, 27.50, 27.36, 27.33, 27.16, 27.11, 27.06, 26.96, 26.93 (CH₂ of Cy), 24.30, 23.46, 23.12, 23.08, 23.00, 22.44, 22.33 (1:1:1:1:1:1 for CH of Cy), 0.45, 0.36 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.2 M Cr(acac)₃, 25 °C) δ −2.12, −65.24, −65.76, −66.11, −67.12, −68.05, −68.15, −68.28 (1:1:1:1:1:1:1). MS (FAB⁺) m/z 1892 (7) [M − C₅H₁₀]⁺, 861 (100). Anal. Calcd for C₇₈H₁₄₄O₂₄Si₁₆Ti (1963.25): C, 47.72; H, 7.39%. Found C, 47.28; H, 7.76%.
- 10 **1c**: Yield 62%. mp 288.0–289.0 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 5.80 (ddt, ³J = 17.1, 9.7, 8.1 Hz, 2H, SiCH₂CH=CH₂), 4.85 (d, ³J = 17.1 Hz, 2H, *trans*-SiCH₂CH=CH₂), 4.81 (d, ³J = 9.7 Hz, 2H, *cis*-SiCH₂CH=CH₂), 1.86–1.49 (br m, 116H, CH₂ of Cy and SiCH₂CH=CH₂), 0.96–0.90 (br m, 14H, CH of Cy), 0.18 (s, 6H, Si(CH₃)₂), 0.17 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 134.69 (SiCH₂CH=CH₂), 113.04 (SiCH₂CH=CH₂), 27.78, 27.72, 27.59, 27.48, 27.48, 27.38, 27.34, 27.30, 27.17, 27.09, 27.04, 26.94, 26.90, 26.87 (CH₂ of Cy), 26.11 (SiCH₂CH=CH₂), 24.26, 23.44, 23.14, 23.05, 23.01, 22.40, 22.29 (1:1:1:1:1:1:1 for CH of Cy), −0.21 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.2 M Cr(acac)₃, 25 °C) δ 6.53, −65.25, −65.76, −66.16, −67.14, −68.08, −68.27 (1:1:1:1:1:1:2). MS (FAB⁺) m/z 1948 (12) [M − C₅H₆]⁺, 1919 (13), 861 (100). Anal. Calcd for C₈₀H₁₄₈O₂₄Si₁₆Ti (1991.30): C, 48.25; H, 7.49%. Found C, 47.44; H, 7.39%.
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