

Synthesis of Novel Group 4 Metallocene-Containing Silsesquioxanes with a Vinyl Group

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Novel zirconocene or hafnocene-containing silsesquioxanes with a vinyl group $\text{Cp}_2\text{M}[(\text{vinyl})\text{Me}_2\text{Si}(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]$ (Cp = cyclopentadienyl, M = Zr, Hf) were synthesized, as well as a derivative with a trimethylsilyl group $\text{Cp}_2\text{Zr}[(\text{Me}_3\text{Si})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]$. A derivative containing a dimethylethoxysilyl group was also synthesized.

Metal-containing oligosilsesquioxanes have attracted attention from a view point of well-defined, homogeneous models for the active surface sites of the supported catalysts or metal-containing zeolites.¹ Especially, recent interests are focused on the catalytic activities of titanium-containing silsesquioxanes² for epoxidation of olefins as soluble analog of titanosilicates.³ Several titanium or zirconium-containing silsesquioxanes were reported to be active catalysts for olefin polymerization.⁴ In addition, these metal-containing silsesquioxanes were found to be convenient precursors for porous M-Si-O materials with high surface areas and uniformly-controlled micropores.⁵ Therefore development of novel group 4 metal-containing silsesquioxanes is required. On the other hand, introduction of appropriate functional groups into these molecules is of great importance with regard to the development of novel organic-inorganic hybrid materials.⁶

In the present communication, we report the syntheses of novel zirconocene or hafnocene-containing silsesquioxanes with a vinyl group, **3b** and **4b**, as well as a derivative with a trimethylsilyl group, **3a**. The synthesis of a derivative containing a dimethylethoxysilyl anchor, **5**, from **3b** is reported. In addition, they are good precursors for microporous oxides.

The reaction of disilanols **2a**⁷ and **2b**,⁸ which were prepared by the kinetically-controlled silylation of a silsesquioxane triol ($c\text{-C}_5\text{H}_9$)₇Si₇O₉(OH)₃ **1**, with zirconocene dichloride in the presence of excess triethylamine in chloroform at room temperature produced zirconocene-containing silsesquioxanes **3a**⁹ and **3b**,¹⁰ respectively, in high yields. The structures of **3a** and **3b** were deduced on the basis of ¹H, ¹³C and ²⁹Si NMR, FAB-MASS, and exactly confirmed by X-ray analyses.^{11,12} Figure 1 shows the structure of **3a** together with selected bond distances and angles reported in the caption. The structure around the zirconium atom is represented by a pseudo-tetrahedron. The Zr-O bond distances are within the range observed for another zirconium-containing silsesquioxane with cubic core structure, C₅Me₅Zr($c\text{-C}_6\text{H}_{11}$)₇Si₇O₁₂ (1.958(6) Å).¹³ Note that the Si(7)-O(12)-Si(8) bond angle is very large, 173(1)°, probably due to the steric repulsion between the trimethylsilyl group and the cyclopentadienyl ring. Other bond distances and bond angles are within the range expected.^{13,14} The ¹³C NMR spectra of **3a** and **3b** indicate the presence of two unequivalent Cp rings, and five resonances in a 1 : 2 : 2 : 1 : 1 ratio for the *ipso*-carbon atoms in the cyclopentyl rings. The ²⁹Si-NMR spectra of both molecules also consist of five peaks in a 1 : 2 : 1 : 1 : 2 ratio for seven silicon atoms in the silsesquioxane cage, which are in good accordance with local C-

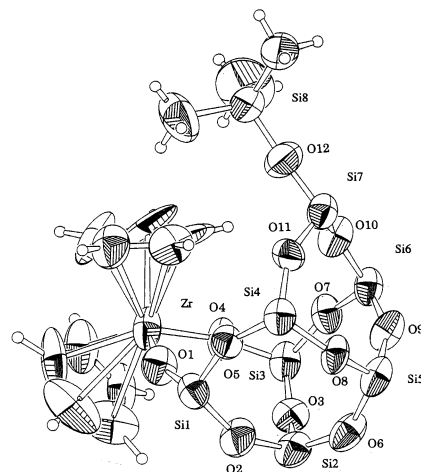
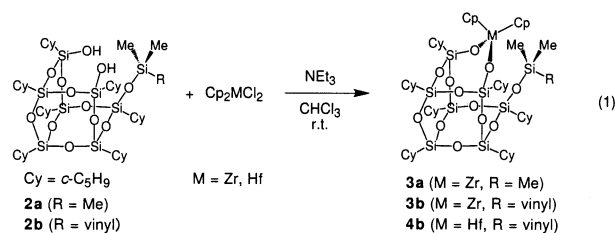


Figure 1. An ORTEP drawing of **3a** (30% probability thermal ellipsoids). Cyclopentyl rings have been omitted for clarity. Selected bond distances (Å) and angles (°): Zr-O(1) 1.96(2), Zr-O(4) 1.96(1), Si(1)-O(1) 1.59(1), Si(3)-O(4) 1.60(1), Si(7)-O(12) 1.58(2), Si(8)-O(12) 1.60(2), O(1)-Zr-O(4) 97.7(6), Zr-O(1)-Si(1) 157.6(9), Zr-O(4)-Si(3) 155.9(10), Si(7)-O(12)-Si(8) 173(1).



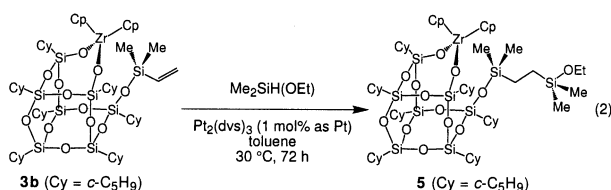
symmetry of their siloxane backbones.

The use of hafnocene dichloride in place of zirconocene dichloride resulted in the formation of a hafnocene-containing silsesquioxane **4b** (yield 73%).¹⁵ Analysis of **4b** on the basis of ¹H, ¹³C and ²⁹Si NMR clearly shows its structural resemblance to **3b**. On the other hand, the reaction of **2a** or **2b** with titanocene dichloride did not produce titanium-containing silsesquioxanes, and unreacted disilanols were recovered almost quantitatively.

The present result contrasts with the early result by Buys et al., in which the reaction of a silsesquioxane triol, ($c\text{-C}_6\text{H}_{11}$)₇Si₇O₉(OH)₃, with zirconocene or hafnocene dichloride resulted in the complete loss of both Cp ligands and produced oligomeric species.¹⁶ One of the reasons would be higher reactivities of silsesquioxane triols than those of disilanols.¹

The hydrosilylation of a vinyl group in **3b** with Me₂SiH(OEt) in the presence of a Pt₂(dvs)₃ catalyst (1 mol% as Pt, dvs = divinyltetramethyldisiloxane) in toluene at 30 °C for 72 h cleanly occurred with excellent regioselectivity to give **5**,¹⁷ a derivative containing a dimethylethoxysilyl group, which would be a good precursor for the immobilized heterogeneous catalysts. The other possible regioisomer was not observed even by NMR.

The present metallocene-containing silsesquioxanes are



also found to be precursors for microporous oxides.⁵ For example, the calcination of **3b** in air stream at 823 K for 2 h produced a Zr-Si-O material with a high BET surface area of 370 m²g⁻¹ and a Type I isotherm typical for microporous materials.

In conclusion, silsesquioxanes containing both metallocene moiety and olefinic functionality in their framework, **3b** and **4b**, were synthesized, as well as **3a**, for the first time. A derivative with an ethoxysilyl anchor was also synthesized. These molecules would be appropriate model compounds for the silica-supported metallocene catalysts,¹⁸ or precursors for novel immobilized catalysts or organic-inorganic hybrid materials.

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- 2b**: To a solution of **1** (3.06 g, 3.5 mmol) and triethylamine (5.0 cm³) in THF (50 cm³), chlorodimethylvinylsilane (0.253 g, 2.1 mmol) in THF (30 cm³) was added dropwise, and the mixture was stirred at room temperature for 20 h. After filtration, resulting clear solution was evaporated at room temperature to give a white solid. This was extracted with hexane (60 cm³) to give a clear filtrate and white solid. From hexane-insoluble solid, 1.4 mmol of unreacted **1** was recovered. The filtrate was evaporated, and the product was obtained by the recrystallization by slow diffusion of acetonitrile into a benzene solution. Yield 70% (based on chlorodimethylvinylsilane). M.p. 162.1–163.0 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 6.22 (dd, ³J = 20.9 Hz, ⁴J = 14.9 Hz, 1H, SiCH=CH₂), 5.99 (dd, ³J = 14.9 Hz, ²J = 4.0 Hz, 1H, *cis*-SiCH=CH₂), 5.82 (dd, ³J = 20.9 Hz, ²J = 4.0 Hz, 1H, *trans*-SiCH=CH₂), 4.14 (s, 2H, SiOH), 1.77–1.48 (br m, 56H, CH₂ of Cy, Cy = *n*-C₅H₉), 1.05–0.88 (br m, 7H, CH of Cy), 0.23 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 139.24 (SiCH=CH₂), 132.67 (SiCH=CH₂), 27.52, 27.43, 27.40, 27.36, 27.27, 27.24, 27.10, 27.03, 27.01 (CH₂), 23.64, 22.79, 22.44, 22.28, 22.20 (1 : 2 : 2 : 1 : 1 for CH), -0.01 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.02 M Cr(acac)₃, 25 °C) δ -1.08, -56.70, -65.59, -66.40, -67.46 (1 : 2 : 2 : 1 : 2). Anal. Calcd for C₃₉H₇₄O₁₂Si₈ (959.68): C, 48.81; H, 7.77%. Found C, 48.54; H, 7.55%.
- 3a**: In a typical experiment, to a solution of **2a** (948 mg, 1.0 mmol) and Cp₂ZrCl₂ (292 mg, 1.0 mmol) in CHCl₃ (50 cm³), triethylamine (1.4 cm³, 10 mmol) was added dropwise, and the mixture was stirred at room temperature for 30 min. The solvent was then evaporated at room temperature to give an off-white solid. This was extracted with hexane (60 cm³) to give a clear filtrate and a white residue of triethylammonium chloride. The filtrate was evaporated, and white microcrystals of **3a** were obtained by the recrystallization by slow diffusion of acetonitrile into a CHCl₃ solution. Yield 87%. M.p. > 300 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 6.32 (s, 5H, C₅H₅), 6.18 (s, 5H, C₅H₅), 1.77–1.50 (br m, 56H, CH₂ of Cy), 0.97–0.89 (br m, 7H, CH of Cy), -0.07 (s, 9H, Si(CH₃)₃); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 113.95, 113.21 (C₅H₅), 27.97, 27.81, 27.71, 27.59, 27.51, 27.46, 27.33, 27.20, 27.09, 27.06, 27.02, 26.90 (CH₂), 24.94, 23.56, 23.50, 22.73, 22.67 (1 : 2 : 2 : 1 : 1 for CH), 1.82 (Si(CH₃)₃); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.02 M Cr(acac)₃, 25 °C) δ 7.66, -65.29, -65.84, -66.26, -66.33, -67.83 (1 : 1 : 2 : 1 : 1 : 2). MS (FAB) *m/z* 1165 [M + H]⁺, 1099 [M - C₅H₅]⁺. Exact mass Found 1165.3068. Calcd for C₄₈H₈₃O₁₂Si₈Zr [M + H]⁺: 1165.3086.
- 3b**: Similar method for **3a** was adopted by using 960 mg (1.0 mmol) of **2b** in place of **2a**. Yield 83%. M.p. > 300 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 6.32 (s, 5H, C₅H₅), 6.17 (s, 5H, C₅H₅), 6.00 (dd, ³J = 20.2 Hz, 14.8 Hz, 1H, SiCH=CH₂), 5.81 (dd, ³J = 14.8 Hz, ²J = 4.2 Hz, 1H, *cis*-SiCH=CH₂), 5.61 (dd, ³J = 20.2 Hz, ²J = 4.2 Hz, 1H, *trans*-SiCH=CH₂), 1.77–1.48 (br m, 56H, CH₂ of Cy), 1.00–0.84 (br m, 7H, CH of Cy), -0.02 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 139.42 (SiCH=CH₂), 131.36 (SiCH=CH₂), 113.98, 113.21 (C₅H₅), 27.99, 27.82, 27.70, 27.60, 27.53, 27.48, 27.34, 27.20, 27.10, 27.07, 27.02, 26.91 (CH₂), 24.86, 23.57, 23.53, 22.75, 22.69 (1 : 2 : 2 : 1 : 1 for CH), 0.13 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.02 M Cr(acac)₃, 25 °C) δ -3.55, -65.25, -65.76, -66.03, -66.28, -67.76 (1 : 1 : 2 : 1 : 1 : 2). MS (FAB) *m/z* 1177 [M + H]⁺, 1111 [M - C₅H₅]⁺. Exact mass Found 1177.3070. Calcd for C₄₉H₈₃O₁₂Si₈Zr [M + H]⁺: 1177.3086.
- Crystal data for **3a**: C₄₈H₈₂O₁₂Si₈Zr (FW = 1167.07), monoclinic, *P*₂/n, *a* = 13.20(1), *b* = 20.01(1), *c* = 23.740(7) Å, β = 104.60(4)°, *V* = 6068(6) Å³, *T* = 23 °C, *Z* = 4, *D*_{calcd} = 1.277 g·cm⁻³, *R* = 0.057 (*R*_w = 0.059), GOF = 0.68 for 1971 observed reflections [*I* > 3σ(*I*)].
- The compound **3b** crystallized in the monoclinic space group *P*₂/n with a cell volume of 6131(5) Å³ (*a* = 13.336(5), *b* = 19.83(1), *c* = 23.98(2) Å, β = 104.71(4)°). The structure of **3b** is quite similar to that of **3a**, and a vinyl group is located at the opposite side of the zirconium atom. Poor diffraction prevented a satisfactory solution of the structure.
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- NMR data for **4b**: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 6.28 (s, 5H, C₅H₅), 6.14 (s, 5H, C₅H₅), 6.01 (dd, ³J = 20.2 Hz, 14.8 Hz, 1H, SiCH=CH₂), 5.82 (dd, ³J = 14.8 Hz, ²J = 4.2 Hz, 1H, *cis*-SiCH=CH₂), 5.63 (dd, ³J = 20.2 Hz, ²J = 4.2 Hz, 1H, *trans*-SiCH=CH₂), 1.79–1.52 (br m, 56H, CH₂ of Cy), 1.05–0.90 (br m, 7H, CH of Cy), -0.03 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C) δ 139.39 (SiCH=CH₂), 131.32 (SiCH=CH₂), 112.72, 112.10 (C₅H₅), 27.95, 27.80, 27.69, 27.58, 27.51, 27.47, 27.34, 27.21, 27.10, 27.06, 27.01, 26.90 (CH₂), 24.83, 23.57, 23.55, 22.70, 22.67 (1 : 2 : 2 : 1 : 1 for CH), 0.10 (Si(CH₃)₂); ²⁹Si{¹H} NMR (76 MHz, CDCl₃, 0.02 M Cr(acac)₃, 25 °C) δ -3.55, -64.16, -65.22, -66.08, -66.16, -67.73 (1 : 2 : 1 : 1 : 1 : 2).
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