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 $Cp_2M\{[(vinyl)Me_2Si](c\text{-}C_5H_9)_7Si_7O_{12}\}$ (Cp = cyclopentadienyl, M = Zr, Hf) were synthesized, as well as a derivative with a trimethylsilyl group $Cp_2Zr[(Me_3Si)(c\text{-}C_5H_9)_7Si_7O_{12}]$. 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 silsesquioxanes[2] 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 $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ **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, ^{13}C and ^{29}Si 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, $C_5Me_5Zr(c\text{-}C_6H_{11})_7Si_7O_{12}$ (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 ^{13}C 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 ^{29}Si-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 *Cs*-symmetry of their siloxane backbones.

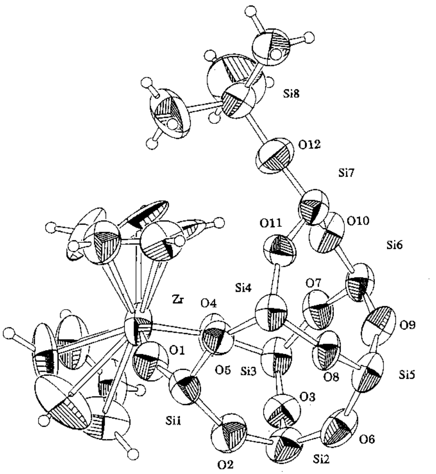
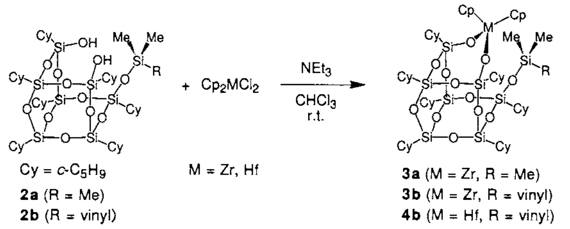


Figure 1. An ORTEP drawing of **3a** (30% probability thermal ellipsoids). Cyclopentyl rings have been omitted for clarity. Selected bond distances (Å) and angles (°): Zr-O(1) 1.96(2), Zr-O(4) 1.96(1), Si(1)-O(1) 1.59(1), Si(3)-O(4) 1.60(1), Si(7)-O(12) 1.58(2), Si(8)-O(12) 1.60(2), O(1)-Zr-O(4) 97.7(6),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



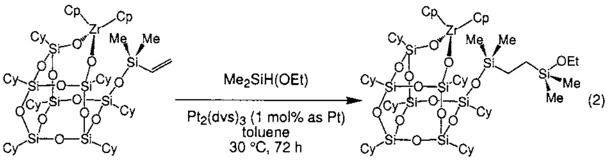
(1)

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, ^{13}C and ^{29}Si 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, $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$, 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 $Me_2SiH(OEt)$ in the presence of a $Pt_2(dvs)_3$ 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



3b (Cy = *c*-$\mathrm{C_5H_9}$) **5** (Cy = *c*-$\mathrm{C_5H_9}$) (2)

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 $\mathrm{m^2g^{-1}}$ 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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References and Notes

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8 **2b**: To a solution of **1** (3.06 g, 3.5 mmol) and triethylamine (5.0 $\mathrm{cm^3}$) in THF (50 $\mathrm{cm^3}$), chlorodimethylvinylsilane (0.253 g, 2.1 mmol) in THF (30 $\mathrm{cm^3}$) 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 $\mathrm{cm^3}$) 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; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 6.22 (dd, ^3J = 20.9 Hz, 14.9 Hz, 1H, $\mathrm{SiC}\mathit{H}\mathrm{{=}CH_2}$), 5.99 (dd, ^3J = 14.9 Hz, ^2J = 4.0 Hz, 1H, *cis*-$\mathrm{SiCH{=}C}\mathit{H}_2$), 5.82 (dd, ^3J = 20.9 Hz, ^2J = 4.0 Hz, 1H, *trans*-$\mathrm{SiCH{=}C}\mathit{H}_2$), 4.14 (s, 2H, $\mathrm{SiO}\mathit{H}$), 1.77–1.48 (br m, 56H, $\mathrm{C}\mathit{H}_2$ of Cy, Cy = *c*-$\mathrm{C_5H_9}$), 1.05–0.88 (br m, 7H, $\mathrm{C}\mathit{H}$ of Cy), 0.23 (s, 6H, $\mathrm{Si(C}\mathit{H}_3\mathrm{)_2}$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 139.24 ($\mathrm{Si}\mathit{C}\mathrm{H{=}CH_2}$), 132.67 ($\mathrm{SiCH{=}}\mathit{C}\mathrm{H_2}$), 27.52, 27.43, 27.40, 27.36, 27.27, 27.24, 27.10, 27.03, 27.01 ($\mathit{C}\mathrm{H_2}$), 23.64, 22.79, 22.44, 22.28, 22.20 (1 : 2 : 2 : 1 : 1 for CH), -0.01 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$); ^{29}Si{^{1}H} NMR (76 MHz, $\mathrm{CDCl_3}$, 0.02 M $\mathrm{Cr(acac)_3}$, 25 °C) δ -1.08, -56.70, -65.59, -66.40, -67.46 (1 : 2 : 2 : 1 : 2). Anal. Calcd for $\mathrm{C_{39}H_{74}O_{12}Si_8}$ (959.68): C, 48.81; H, 7.77%. Found C, 48.54; H, 7.55%.
9 **3a**: In a typical experiment, to a solution of **2a** (948 mg, 1.0 mmol) and $\mathrm{Cp_2ZrCl_2}$ (292 mg, 1.0 mmol) in $\mathrm{CHCl_3}$ (50 $\mathrm{cm^3}$), triethylamine (1.4 $\mathrm{cm^3}$, 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 $\mathrm{cm^3}$) 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 $\mathrm{CHCl_3}$ solution. Yield 87%. M.p. > 300 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 6.32 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 6.18 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 1.77–1.50 (br m, 56H, $\mathrm{C}\mathit{H}_2$ of Cy), 0.97–0.89 (br m, 7H, $\mathrm{C}\mathit{H}$ of Cy), -0.07 (s, 9H, $\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 113.95, 113.21 ($\mathit{C}_5\mathrm{H_5}$), 27.97, 27.81, 27.71, 27.59, 27.51, 27.46, 27.33, 27.20, 27.09, 27.06, 27.02, 26.90 ($\mathit{C}\mathrm{H_2}$), 24.94, 23.56, 23.50, 22.73, 22.67 (1 : 2 : 2 : 1 : 1 for CH), 1.82 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$); ^{29}Si{^{1}H} NMR (76 MHz, $\mathrm{CDCl_3}$, 0.02 M $\mathrm{Cr(acac)_3}$, 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 $[\mathrm{M + H}]^+$, 1099 $[\mathrm{M - C_5H_5}]^+$. Exact mass Found 1165.3068. Calcd for $\mathrm{C_{48}H_{83}O_{12}Si_8Zr}$ $[\mathrm{M + H}]^+$: 1165.3086.
10 **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; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 6.32 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 6.17 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 6.00 (dd, ^3J = 20.2 Hz, 14.8 Hz, 1H, $\mathrm{SiC}\mathit{H}\mathrm{{=}CH_2}$), 5.81 (dd, ^3J = 14.8 Hz, ^2J = 4.2 Hz, 1H, *cis*-$\mathrm{SiCH{=}C}\mathit{H}_2$), 5.61 (dd, ^3J = 20.2 Hz, ^2J = 4.2 Hz, 1H, *trans*-$\mathrm{SiCH{=}C}\mathit{H}_2$), 1.77–1.48 (br m, 56H, $\mathrm{C}\mathit{H}_2$ of Cy), 1.00–0.84 (br m, 7H, $\mathrm{C}\mathit{H}$ of Cy), -0.02 (s, 6H, $\mathrm{Si(C}\mathit{H}_3\mathrm{)_2}$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 139.42 ($\mathrm{Si}\mathit{C}\mathrm{H{=}CH_2}$), 131.36 ($\mathrm{SiCH{=}}\mathit{C}\mathrm{H_2}$), 113.98, 113.21 ($\mathit{C}_5\mathrm{H_5}$), 27.99, 27.82, 27.70, 27.60, 27.53, 27.48, 27.34, 27.20, 27.10, 27.07, 27.02, 26.91 ($\mathit{C}\mathrm{H_2}$), 24.86, 23.57, 23.53, 22.75, 22.69 (1 : 2 : 2 : 1 : 1 for CH), 0.13 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$); ^{29}Si{^{1}H} NMR (76 MHz, $\mathrm{CDCl_3}$, 0.02 M $\mathrm{Cr(acac)_3}$, 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 $[\mathrm{M + H}]^+$, 1111 $[\mathrm{M - C_5H_5}]^+$. Exact mass Found 1177.3070. Calcd for $\mathrm{C_{49}H_{83}O_{12}Si_8Zr}$ $[\mathrm{M + H}]^+$: 1177.3086.
11 Crystal data for **3a:** $\mathrm{C_{48}H_{82}O_{12}Si_8Zr}$ (FW = 1167.07), monoclinic, $P2_1/n$, a = 13.20(1), b = 20.01(1), c = 23.740(7) Å, β = 104.60(4)°, V = 6068(6) Å^3, 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)].
12 The compound **3b** crystallized in the monoclinic space group $P2_1/n$ with a cell volume of 6131(5) Å^3 (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 goup is located at the opposite side of the zirconium atom. Poor diffraction prevented a satisfactory solution of the structure.
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15 NMR data for **4b**: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 6.28 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 6.14 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 6.01 (dd, ^3J = 20.2 Hz, 14.8 Hz, 1H, $\mathrm{SiC}\mathit{H}\mathrm{{=}CH_2}$), 5.82 (dd, ^3J = 14.8 Hz, ^2J = 4.2 Hz, 1H, *cis*-$\mathrm{SiCH{=}C}\mathit{H}_2$), 5.63 (dd, ^3J = 20.2 Hz, ^2J = 4.2 Hz, 1H, *trans*-$\mathrm{SiCH{=}C}\mathit{H}_2$), 1.79–1.52 (br m, 56H, $\mathrm{C}\mathit{H}_2$ of Cy), 1.05–0.90 (br m, 7H, $\mathrm{C}\mathit{H}$ of Cy), -0.03 (s, 6H, $\mathrm{Si(C}\mathit{H}_3\mathrm{)_2}$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 139.39 ($\mathrm{Si}\mathit{C}\mathrm{H{=}CH_2}$), 131.32 ($\mathrm{SiCH{=}}\mathit{C}\mathrm{H_2}$), 112.72, 112.10 ($\mathit{C}_5\mathrm{H_5}$), 27.95, 27.80, 27.69, 27.58, 27.51, 27.47, 27.34, 27.21, 27.10, 27.06, 27.01, 26.90 ($\mathit{C}\mathrm{H_2}$), 24.83, 23.57, 23.55, 22.70, 22.67 (1 : 2 : 2 : 1 : 1 for CH), 0.10 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$); ^{29}Si{^{1}H} NMR (76 MHz, $\mathrm{CDCl_3}$, 0.02 M $\mathrm{Cr(acac)_3}$, 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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17 The reaction was quantitative judging from NMR. **5**: ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 6.37 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 6.15 (s, 5H, $\mathrm{C_5}\mathit{H}_5$), 3.62 (q, ^3J = 7.0 Hz, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 2.11-1.40 (br m, 56H, $\mathrm{C}\mathit{H}_2$ of Cy), 1.28–1.05 (br m, 7H, $\mathrm{C}\mathit{H}$ of Cy), 1.20 (t, ^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}\mathit{H}_3$), 0.61 (s, 4H, $\mathrm{Si(C}\mathit{H}_2\mathrm{)_2Si}$), 0.20 (s, 6H), 0.18 (s, 6H, both $\mathrm{Si(C}\mathit{H}_3\mathrm{)_2}$); ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ 114.43, 113.71 ($\mathit{C}_5\mathrm{H_5}$), 58.24 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 28.59, 28.53, 28.43, 28.30, 28.22, 28.11, 28.08, 27.82, 27.69, 27.54, 27.35 ($\mathit{C}\mathrm{H_2}$), 25.58, 24.17, 24.10, 23.29 (1 : 2 : 2 : 2 for CH), 18.94 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 9.86, 8.15 ($\mathrm{Si(}\mathit{C}\mathrm{H_2)_2Si}$), -0.22, -2.48 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$).
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