Synthesis and Catalytic Activity of Group 4 Metallocene Containing Silsesquioxanes Bearing Functionalized Silyl Groups

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A series of metallocene-containing silsesquioxanes with alkenylsilyl and trimethylsilyl groups, $Cp'_2M[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2R)$ (**2b**−**d**, **3b**−**d**, **4d**, **5d**: Cp′ = Cp (cyclopentadienyl), Cp* (pentamethylcyclopentadienyl); M = Ti, Zr, Hf, R = methyl, vinyl, allyl), have been synthesized. The structures of the complexes $Cp_2M[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2CH_2CH{=}CH_2)$ (M = Zr (**3d**), Hf (**5d**)) have been unambiguously established by single-crystal X-ray diffraction analyses. Silylation or germylation of the zirconocene-containing silsesquioxane monosilanol $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OH)$ (**3a**) or its hafnocene derivative $Cp_2Hf[(c\text{-}C_5H_9)_7Si_7O_{11}](OH)$ (**5a**), which can be prepared by the careful reaction of the silsesquioxane trisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (**1a**) with zirconocene dichloride or hafnocene dichloride, yields the new series of metallocene-containing silsesquioxanes $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2H)$ (**3e**), $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OGeMe_3)$ (**3f**), and $Cp_2Hf[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2H)$ (**5e**). The reaction of **3e** with 2 equiv of hydrogen chloride results in the formation of the dimethylsilyl-containing silsesquioxane disilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2H)$ (**1e**), indicating the applicability of metallocene moieties as protecting groups of two adjacent silanol groups. Silsesquioxanes bearing alkenylsilyl groups can be easily converted to derivatives with ethoxysilyl groups, $Cp_2M[(c\text{-}C_5H_9)_7Si_7O_{11}][OSiMe_2(CH_2)_3SiMe_2(OEt)]$ (M = Ti (**2g**), Zr (**3g**)), by the hydrosilylative reaction. The preliminary examination of the catalytic activity of these metallocene-containing silsesquioxanes toward the epoxidation of cyclohexene by *tert*-butyl hydroperoxide revealed that titanocene-containing silsesquioxanes (**2b**−**d**) show modest catalytic activity. The presence of alkenylsilyl groups has been found to accelerate the reactions, especially in the case of titanium-bridged silsesquioxanes.

Introduction

Silica-supported transition-metal catalysts play significant roles in current chemical industries.[1] Supported group 4 metal containing catalysts are now widely used for a number of important reactions: i.e., oxidation,[2] alkene polymerization,[3] degradation of polyolefins,[4] and so on. For the preparation of active heterogeneous catalysts, a precise understanding of the nature of active sites and/or mechanisms of catalytic reactions is crucial. Despite the recent marked developments in surface science, difficulties still remain in the strict control of their active sites.

Recently, incompletely condensed oligosilsesquioxanes with silanol groups[5] and metal-containing silsesquioxanes[6] have attracted much attention from the viewpoint of discrete, well-defined soluble model compounds of the transition-metal-containing siliceous heterogeneous catalysts. Recent studies by us[7] and other research groups[6a,d,e,g,8,9] have revealed the utility of this class of compounds as homogeneous catalysts in organic synthesis. With regard to the group 4 transition metal

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containing silsesquioxanes the catalytic activities for the epoxidation of alkenes[6d,e,8] and polymerization of small alkenes[6a,g,9] have been reported. Several titanium,[9b,d,10] zirconium,[9b,c,10f,11] and hafnium-containing[10b,12] silsesquioxanes bearing cyclopentadienyl ligands have been prepared, and some of them have been revealed to be effective catalysts.[8a,9,10f,11c,d]

In addition to their utility as homogeneous catalysts, these silsesquioxanes have been found to be an excellent source of heterogeneous catalysts.[11b,13−16] For example, we have found that controlled calcination of metallasilsesquioxanes yields mixed oxides of well-dispersed metallic species and characteristic pore structures.[14] After the reports by us, several research groups reported the preparation of oxide catalysts from silsesquioxanes.[15] There are other methods for the preparation of heterogeneous catalysts utilizing metallasilsesquioxanes. For example, immobilization onto other materials, polymerization, or incorporation into sol−gel matrixes of metallasilsesquioxanes seem to be promising methods to prepare catalysts with well-defined structures of the active sites.[11b,13] For this purpose introduction of appropriate functional groups, i.e., alkenylsilyl or alkoxysilyl groups, is of importance. There are, however, only a limited number of metal-containing silsesquioxanes with other functional groups.[11b,13d,17]

In preliminary studies, we have prepared several group 4 metal containing molecular silsesquioxanes bearing alkenylsilyl groups.[11b] These silsesquioxanes have been further applied to the preparation of macrocyclic molecules[18] and polymeric materials.[19] In the present paper, we have extended the previous studies to the synthesis of a series of group 4 metallocene containing silsesquioxanes with functional silyl or germyl groups. The structures of two group 4 metal containing silsesquioxanes are established by X-ray crystallographic studies. Included in this report is the preparation of silsesquioxanes with vinylsilyl, allylsilyl, hydridosilyl, or trimethylgermyl groups via different pathways, as well as the introduction of alkoxysilyl groups. The catalytic activities of some of these metallocene-containing silsesquioxanes for the epoxidation of cyclohexene are also briefly discussed.

Results and Discussion

Synthesis of Group 4 Metallocene Containing Silsesquioxanes Bearing Functionalized Silyl Groups. A series of group 4 transition metal containing silsesquioxanes including alkenylsilyl groups were prepared by the reaction of the disilanols $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2R)$ (**1c**, R = vinyl; **1d**, R = allyl) with the corresponding metallocene dichlorides. Disilanols **1c**,**d** can be prepared easily by the direct, kinetically controlled monosilylation of a silsesquioxane triol, $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (**1a**), using 0.6 equiv of chlorodimethylvinylsilane or allylchlorodimethylsilane. On the other hand, the preparation of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2H)$ (**1e**) or $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OGeMe_3)$ (**1f**) cannot be achieved by the direct silylation or germylation of **1a**. Even the reaction of **1a** with 0.1 equiv of $ClSiMe_2H$ produces a mixture of mono-, di-, and trisilylated products together with a small amount of decomposed products. Complete isolation of **1e** from the reaction mixture has not been successful yet. Instead, $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_2H)_3$ was isolated by the recrystallization. Note that an alternative "indirect" method successfully produces **1e** (see below).

As reported previously,[11b] no attempts at the synthesis of titanocene-containing silsesquioxanes by the reaction of titanocene dichloride with **1b**−**d** in chloroform, dichloromethane, or 1,2-dichloroethane were successful. The reactions of titanocene dichloride with a thallium-containing silsesquioxane, $(c\text{-}C_5H_9)_7Si_7O_9(OTl)_2(OSiMe_3)$, also did not proceed. Our recent attempted reaction in toluene for 3 days in the presence of excess triethylamine cleanly produced the titanocene-containing silsesquioxanes **2b**−**d** in moderate yields (eq 1). The structures of these silsesquioxanes have been deduced on the basis of ^1H, ^{13}C, and ^{29}Si NMR and FAB-MS analyses. The ^{13}C NMR spectra indicate the presence of two nonequivalent Cp rings and five resonances in a

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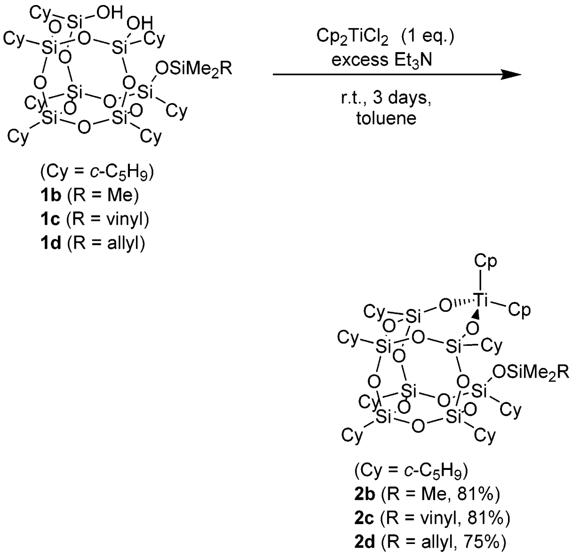
1:2:2:1:1 ratio for the ipso carbon atoms in the cyclopentyl rings. The ^{29}Si NMR spectra of these molecules consist of four peaks in a 1:3:1:2 ratio for the silicon atoms in the silsesquioxane cages, consistent with the local C_s symmetry of their siloxane backbone. Although the reaction of titanocene dichloride with silsesquioxane silanols has been examined for years by several researchers, the formation of bipodal tetravalent titanocene-containing silsesquioxanes such as **2b** has not been reported before. Instead, various more complicated titanium-containing silsesquioxanes were produced. For example, Edelmann et al. have reported the formation of a dimeric titanium-containing silsesquioxane, $\{(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OTiCp_2)\}_2(\mu\text{-}O)$, by the reaction of titanocene dichloride and a silsesquioxane disilanol with peripheral cyclohexyl groups, $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_2(OSiMe_3)$,[10f] under conditions almost identical with those of the present reactions. They also reported that the reactions were not straightforward and usually resulted in the formation of product mixtures.[10f] Although the exact reason for the different results is still not clear, this can be an interesting example of the selection of the products by changing the peripheral organic substitutent of the silsesquioxane cage. A silsesquioxane including a trivalent titanocene group has been synthesized recently.[10e]



(1)

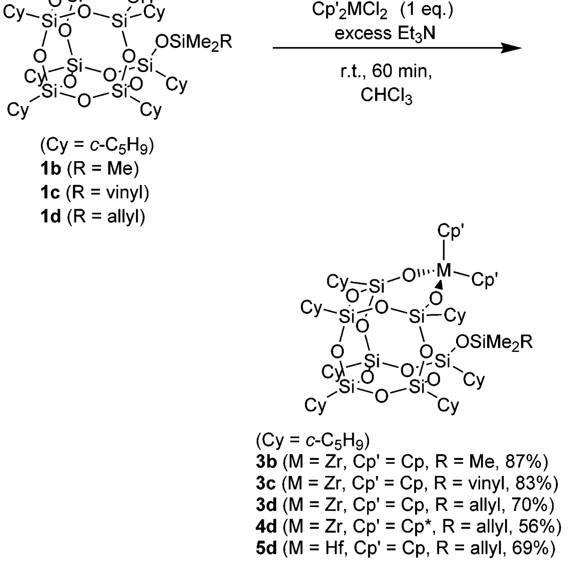
On the other hand, the reaction of zirconocene dichloride with **1c**,**d**, as well as the trimethylsilyl-substituted disilanol **1b**, proceeds more smoothly in the presence of excess triethylamine in chloroform at room temperature to produce the zirconocene-containing silsesquioxanes **3b**−**d** in high yields (eq 2). The reactions usually require less than 1 h for completion. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3b**−**d** are very close to those of **2b**−**d**, indicating their structural similarities. The reaction of the more sterically demanding $Cp^*{}_2ZrCl_2$ with a disilanol (**1d**) also proceeds smoothly to yield the corresponding $Cp^*{}_2Zr$-containing molecule (**4d**).

Colorless crystals of **3d** of sufficient quality for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile into a concentrated mesitylene solution at room temperature. Details of the data collection, structure solution, and refinement of **3d** crystallizing in the monoclinic space group $P2_1/c$ are provided in the Experimental Section and Tables 2−4. A thermal ellipsoid plot of **3d** is shown in Figure 1. An allyl group is located at the opposite side of the zirconium atom. Other parts of the structure are almost identical with the structures of previously reported $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_3)$ (**3b**)[11b] and its dimethylphenylsilyl derivative $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2Ph)$.[11c] The structure around the zirconium atom is represented by a pseudo-tetrahedron, and the centroids of Cp rings and the Zr, Si(2), Si(5), Si(7), and Si(8) atoms are located nearly on the same plane. The Zr−O bond distances (1.988(5) and 1.986(5) Å) are within the range observed for other silsesquioxanes with cubic core structures containing cyclopentadienylzirconium moieties, $Cp^*Zr(c\text{-}C_6H_{11})_7Si_7O_{12}$ (1.985(6) Å),[11a] $Zr[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2\cdot DME$ (2.00 Å average),[9a] $\{PhCH_2Zr[(c\text{-}C_5H_9)_7Si_7O_{12}]\}_2$ (1.96 Å average),[9a] **3b** (1.96(1) and 1.96(1) Å),[11b] and $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2Ph)$ (1.994(2) and 1.995(2) Å).[11c] Other bond distances and angles around the zirconium atom are also in the range observed for reported analogous molecules,[9a,11b,c] indicating the absence of significant steric distortion around the zirconocene moiety. Note that significantly shorter Zr−O bond distances and larger O−Zr−O angles are reported for $[(Me_3Si)_2C_5H_3]ZrCl(OSiPh_3)_2$ (1.921(4) and 1.929(5) Å, 102.17(19)°), in which the presence of strong

Table 1. Catalytic Activities of Group 4 Transition Metal Containing Silsesquioxanes for the Epoxidation of Cyclohexene[a]

catalyst	temp, °C	yield of epoxide, %
2b	50	22
2c	50	25
2d	50	28
3b	50	trace
7[b]	50	66
8b	50	15
8c	50	30
8d	50	33
7[b]	60	76
8d	60	64

[a] Conditions: catalyst 1.0 mol %, cyclohexene 3.3 mmol in toluene (1.5 cm^3), ^{t}BuOOH (3.3 mmol) in decane (0.6 cm^3), 4 h, under Ar. [b] The activity of a cyclohexyl analogue of **7** has been reported.[8a]



(2)

Table 2. Summary of Crystal Data, Collection Data, and Refinement Details for 3d and 5d

	3d	5d
	Crystal Data	
formula	$C_{50}H_{84}O_{12}Si_8Zr$	$C_{50}H_{84}O_{12}Si_8Hf$
formula wt	1193.11	1280.38
cryst color	colorless	colorless
habit	block	block
cryst size, mm	0.50 × 0.50 × 0.10	0.60 × 0.60 × 0.10
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	11.1457(2)	11.1065(3)
b, Å	22.0030(5)	22.0306(6)
c, Å	24.4973(6)	24.441(1)
β, deg	89.975(1)	90.111(1)
ς, Å^3	6007.7(2)	5980.4(3)
Z	4	4
D(calcd), g cm^{-3}	1.319	1.277
μ(Mo Kα), cm^{-1}	3.97	48.91
	Intensity Measurements	
diffractometer	Rigaku RAXIS−RAPID	
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)	
detector aperture, mm	270 × 256	270 × 256
data image	74 exposure	
ω oscillation range (κ = 45.0, Φ = 0.0), deg	130.0−190.0	
exposure rate, s deg^{-1}	60.0	
ω oscillation range (κ = 45.0, Φ = 180.0), deg	0.0−162.0	
exposure rate, s deg^{-1}	60.0	
detector position, mm	127.40	
pixel size, mm	0.100	
$2\theta_{\max}$, deg	55.0	54.8
no. of measd rflns		
total	45 746	47 836
unique	13 148	12 524
R_{int}	0.033	0.033
	Structure Solution and Refinement	
structure soln	direct methods (SIR92)	
no. of obsd rflns	11 016 ($I > 3.00\sigma(I)$)	10 619 ($I > 3.00\sigma(I)$)
no. of params refined	724	724
R^a	0.047 ($I > 3.00\sigma(I)$)	0.042 ($I > 3.00\sigma(I)$)
$R_w{}^a$	0.110 ($I > 3.00\sigma(I)$)	0.095 ($I > 3.00\sigma(I)$)
GOF	3.35	2.36
max shift/error	0.00	0.01
peak in final diff map		
max, e Å^{-3}	0.85	1.05
min, e Å^{-3}	−0.72	−1.14

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 3. Selected Bond Distances (Å) for 3d and 5d

	3d	5d
M(1)−O(1)	1.988(5)	1.97(1)
M(1)−O(4)	1.986(5)	1.98(1)
M(1)−Ct(C(36)−(40))	2.25	2.23
M(1)−Ct(C(41)−(45))	2.26	2.24
Si(1)−O(1)	1.601(5)	1.598(8)
Si(3)−O(4)	1.603(5)	1.602(8)
Si(7)−O(12)	1.607(5)	1.610(8)
Si(8)−O(12)	1.631(6)	1.619(8)

Table 4. Selected Bond Angles (deg) for 3d and 5d

	3d	5d
O(1)−M(1)−O(4)	97.9(2)	97.7(6)
O(1)−M(1)−Ct(C(36)−(40))	106.3	106.6
O(1)−M(1)−Ct(C(41)−(45))	103.2	105.6
O(4)−M(1)−Ct(C(36)−(40))	108.6	109.2
O(4)−M(1)−Ct(C(41)−(45))	106.3	106.4
Ct−M(1)−Ct	127.7	127.4
Si(7)−O(12)−Si(8)	153.5(4)	153.7(6)

oxygen pπ−dπ donation of the siloxy ligand to the zirconium center has been proposed.[9b] Such an effect is considered to be not included in the present system.

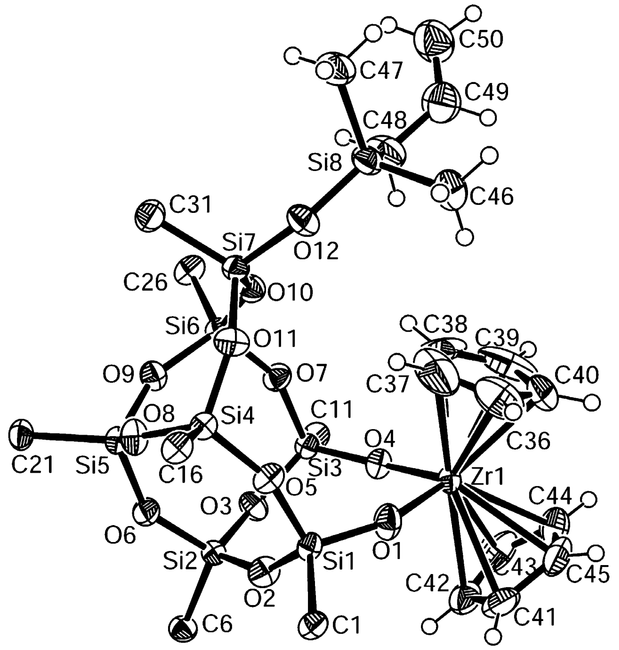


Figure 1. ORTEP drawing of **3d** (50% probability thermal ellipsoids). Cyclopentyl rings, except for ipso carbon atoms, are omitted for clarity.

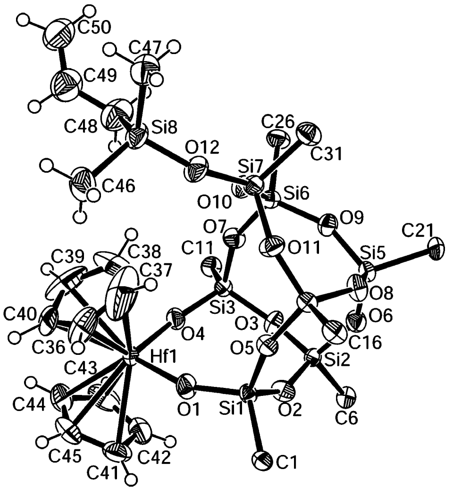


Figure 2. ORTEP drawing of **5d** (50% probability thermal ellipsoids). Cyclopentyl rings, except for ipso carbon atoms, are omitted for clarity.

The use of hafnocene dichloride in place of zirconocene dichloride resulted in the formation of the hafnocene-containing silsesquioxane **5d**. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra show its close structural resemblance to that of the zirconium-containing derivative. The solid-state structure of **5d** (Figure 2) is almost identical with that of **3d**. The hafnium−oxygen bond distances (1.97(1) and 1.98(1) Å) and O−Hf−O angle (97.7(6)°) are slightly longer and acute compared with those of other reported hafnium-containing silsesquioxanes and siloxanes, i.e., Cp*Hf(c-C_6H_{11})$_7$$Si_7O_{12}$ (1.949(4) Å, 102.7(2)°)[12] and $(Ph_3SiO)_2HfCl_2$·THF (1.929(2) Å, 99.80(13)°),[20] indicating the presence of slight distortion, probably due to the steric hindrance between the Cp groups and the allyldimethylsilyl group.

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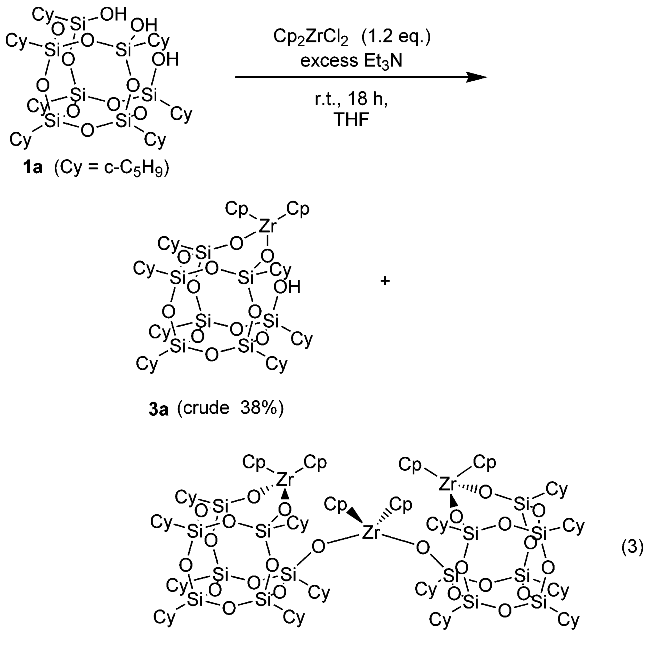
(20) Schweder, B.; Görls, H.; Walther, D. *Inorg. Chim. Acta* **1999**, *286*, 14.

As discussed above, direct monosilylation of the silsesquioxane trisilanol **1a** often results in poor selectivity for the desired products. Therefore, an alternative route for the synthesis of metallasilsesquoxanes bearing a functional silyl group has been explored. The synthesis of zirconocene-containing silsesquioxane monosilanol was examined. Reaction of silsesquioxane trisilanol (**1a**) and zirconocene dichloride in the presence of excess triethylamine in THF at room temperature produced a zirconocene-containing silsesquioxane monosilanol (**3a**) in 38% yield and a zirconocene-bridged silsesquioxane (**6**) as a byproduct in 24% yield (eq 3). The structure of **3a** was deduced from the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. Namely, the ^{29}Si NMR spectrum of **3a** consists of five peaks in a 1:1:2:1:2 ratio for seven silicon atoms in the silsesquioxane cage, which are in agreement with the local C_s symmetry of the siloxane framework, and one of the peaks in the ^{29}Si NMR spectrum was observed in the particular range for silanol silicons, δ −56.35 ppm. Unfortunately, **3a** is not stable enough for complete purification. According to the NMR spectra, **6** has been determined to be a dimeric, C_s-symmetric molecule. In the ^{1}H and ^{13}C NMR spectra there are three sets of resonances of the cyclopentadienyl rings. Two cyclopentadienyl rings are located on the bridging zirconium, two in exo positions with regard to the bridging zirconocene, and two in endo positions. A silsesquioxane monosilanol similar to **3a** has been suggested as an intermediate in the reaction of Cp[$Me_2(EtO)SiC_5Me_4$]$ZrCl_2$ with **1a**.[9c] However, such a compound has not been isolated and characterized, and the final product is an intractable polymeric species.[9c] Our present results also are in contrast to the work reported by Buys et al.[10b] In their work the reaction of a silsesquioxane triol, $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$, with zirconocene or hafnocene dichloride in the presence of excess bases resulted in the complete loss of both Cp ligands and produced an oligomeric species, i.e., $\{M_3[(c\text{-}C_6H_{11})_7Si_7O_{12}]_4Cl\}H$ (M = Zr, Hf).[10b] Again, this suggests that the reactions of metallocene dichlorides with silsesquioxane silanols are not straightforward and are easily affected by the slight changes in reaction conditions and organic substituents (see above).

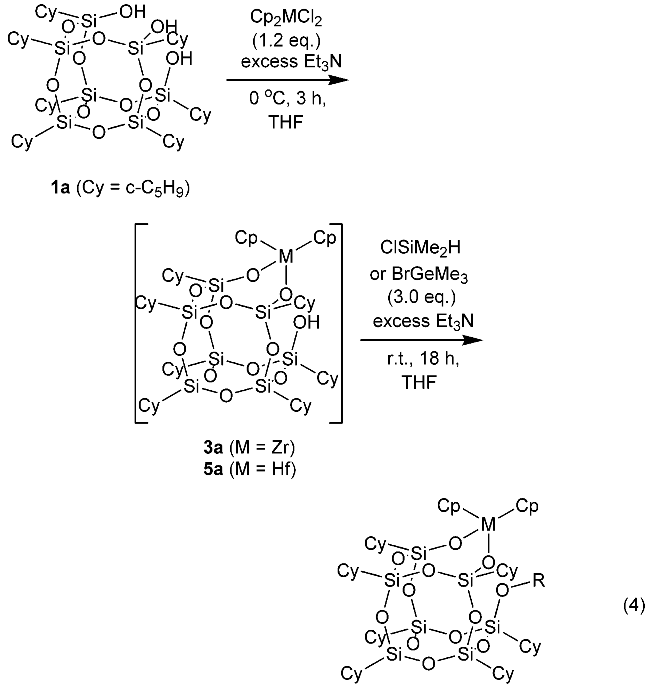


1a (Cy = c-C_5H_9)

3a (crude 38%)

6 (24%)

Further silylation or germylation of **3a** was examined. Because of the low stability of **3a**, the reaction with chlorodimethylsilane in the presence of amine was carried out successively just after the preparation of **3a**. The desired product **3e** was obtained in an isolated yield of up to 70% by the reaction of **1a** with zirconocene dichloride at 0 °C for 3 h in THF immediately followed by a reaction with chlorodimethylsilane at room temperature for 18 h (eq 4). A small amount of **6** was also produced as a byproduct. The characterization of **3e** revealed that it contains both a zirconocene group and a dimethylsilyl substituent. The ^{29}Si NMR spectrum comprises five peaks in a 1:1:2:1:2 ratio for seven silicon atoms in the silsesquioxane cage in the range of δ −64 to −68 ppm as well as a peak at δ −5.67 ppm, which is assigned to the silicon atom of the dimethylsilyl group. The synthesis of a silsesquioxane with a germyl group adjacent to the zirconocene moiety was examined, since it has been reported that the introduction of a germanium species onto the titanium−silica catalysts enhances their activities for the epoxidation of olefins.[21] By the successive in situ treatment of **3a** with trimethylgermanium bromide, a silsesquioxane including a trimethylgermanium group adjacent to the zirconocene moiety (**3f**) was obtained in 70% isolated yield. A silsesquioxane containing both hafnocene and dimethylsilyl groups, **5e**, was synthesized in a similar manner in 77% isolated yield. In this case, the hafnocene-containing silsesquioxane monosilanol **5a** would be formed as an intermediate, as suggested by the ^{1}H NMR observation of the reaction mixture.



1a (Cy = c-C_5H_9)

3a (M = Zr)
5a (M = Hf)

3e (M = Zr, R = Si(H)Me$_2$, 70%)
3f (M = Zr, R = GeMe$_3$, 70%)
5e (M = Hf, R = Si(H)Me$_2$, 77%)

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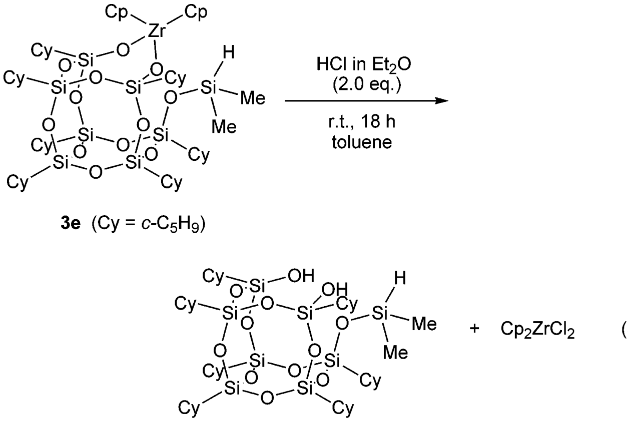
[21] (a) Oldroyd, R. D.; Thomas, J. M.; Sankar, G. *Chem. Commun.* **1997**, 2025. (b) Oldroyd, R. D.; Sankar, G.; Thomas, J. M.; Szkaya, D. *J. Phys. Chem. B* **1998**, *102*, 1849.

Treatment of the zirconocene-containing silsesquioxane **3e** with 2 equiv of hydrogen chloride in toluene almost quantitatively gives the dimethylsilyl group containing silsesquioxane disilanol **1e** and zirconocene dichloride (eq 5). The NMR spectra of **1e** indicate local C_s symmetry of the siloxane backbone and the presence of two silanol groups. In the ^{29}Si NMR spectrum, there is a peak in the particular range for silanol groups at −56.35 ppm. In the present case the zirconocene moiety acts as a protecting group for disilanols. This method provides an alternative route for functionalized disilanols, while the selective synthesis of **1e** via direct silylation of **1a** is very difficult (see above),

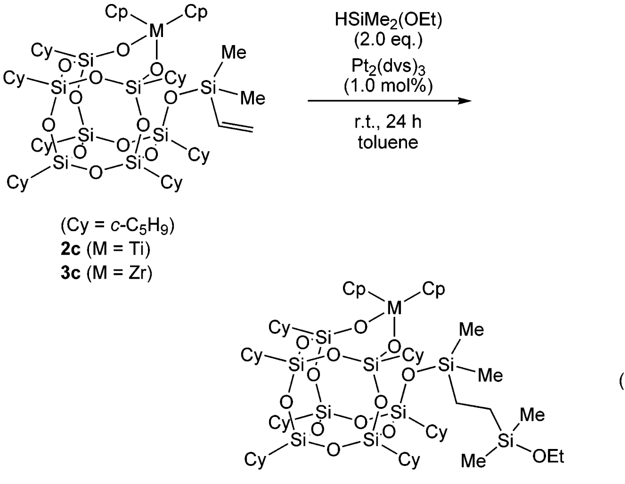


3e (Cy = *c*-C_5H_9)

1e (>95%)

(5)

The synthesis of silsesquioxanes including ethoxysilyl groups was examined by utilizing hydrosilylative reactions. Our initial attempts at the hydrosilylation of ethoxysilanes bearing olefinic groups by **1e**, **3e**, and **5e** using platinum catalysts were, however, unsuccessful. In all cases examined, only the starting materials were recovered. This is probably caused by the steric hindrance around the −Si(H)Me$_2$ groups. On the other hand, the reactions of **2c** and **3c** with an excess amount of HSiMe$_2$(OEt) in the presence of the Pt catalyst quantitatively yield the desired titanocene- and zirconocene-containing silsesquioxanes bearing an ethoxysilyl group, respectively. The main products from **2c** and **3c** were **2g** and **3g**,[11b] the products with linear −SiCH$_2$CH$_2$Si− connections, together with a trace amount of byproducts including branched −SiCH(CH$_3$)Si− connections (**2g′** and **3g′**). Attempts at the preparation of heterogeneous catalysts by immobilization of **2g** or **3g** onto other porous materials, such as mesoporous silicas, are now in progress, and the results will be reported in due course.



(Cy = *c*-C_5H_9)
2c (M = Ti)
3c (M = Zr)

(6)

(Cy = *c*-C_5H_9)
2g (M = Ti)
3g (M = Zr)

Catalytic Activity of Group 4 Metal Containing Silsesquioxanes toward the Epoxidation of Cyclohexene. The catalytic activities of titanium-containing oligosilsesquioxanes for the epoxidation of olefins have been examined from the viewpoint of a soluble analogue of titanosilicates.[6d,e,8] Crocker and Orpen have compared the catalytic activity of bipodal (with two Si−O−Ti bondings around the Ti atom), tripodal (with three Si−O−Ti bondings), and tetrapodal (with four Si−O−Ti bondings) titanium-containing silsesquioxanes toward the olefin epoxidation and reported that the tripodal molecule (c-C_5H_9)$_7$Si$_7$O$_{12}$Ti(O^{i}Pr) is far more reactive than the others by an order of magnitude.[8c] Now we have compared the catalytic activity of newly synthesized bipodal titanocene-containing silsesquioxanes for the epoxidation of cyclohexene with tripodal CpTi[(c-C_5H_9)$_7$Si$_7$O$_{12}$] (**7**),[8a] one of the most active silsesquioxane-based catalysts, and tetrapodal Ti[(c-C_5H_9)$_7$Si$_7$O$_{11}$(OSiMe$_3$)]$_2$ (**8b**).[8c] The results are shown in Table 1. The reaction using 1.0 mol % of **2b** at 50 °C for 4 h with ^{t}BuOOH as an oxidating reagent selectively gives cyclohexene oxide in 22% yields. As byproducts, trace amounts of cyclohexanone and cyclohexanol were also produced. When the reaction was longer than 4 h, the gradual formation of intractable high-molecular-weight species was observed, while the amounts of such products were very small within 4 h. Similar to the case reported by Crocker and Orpen, the catalytic activity decreased in the following order: tripodal **7** > bipodal **2b** > tetrapodal **8b**. Remarkably, silsesquioxanes with alkenylsilyl groups, **2c**,**d**, show higher activity than **2b**. Acceleration of the reaction by the presence of alkenylsilyl groups is much more remarkable with tetrapodal titanium silsesquioxanes. The yield of the epoxide in the presence of **8d** bearing two allyldimethylsilyl groups is almost double the yield with **8b**, and at 60 °C the yield increased to 64%. The exact reasons that the presence of alkenylsilyl groups enhances the catalytic activity are still unclear, and a more detailed study on the promotional effect of these substituents is now in progress.

Concluding Remarks

A series of new group 4 metallocene containing silsesquioxanes including functionalized silyl groups have been synthesized in excellent yields. The successful synthesis of titanocene-containing molecules, **2b**−**d**, will fill in the blanks in a series of titanosilsesquioxanes bearing cyclopentadienyl-type ligands. New zirconocene- or hafnocene-containing silsesquioxanes, which are expected to be appropriate model compounds for the mechanistic studies and as potential catalyst precursors of industrially important silica-supported metallocenes, have been synthesized. The present study also gives an alternative route for the synthesis of silsesquioxanes bearing functionalized silyl groups that cannot be prepared by direct silylation. It has been demonstrated that the zirconocene moiety can act as a protecting group for disilanols. The reaction of zirconocene-containing molecules with 2 equiv of hydrogen chloride resulted in the clean formation of functionalized disilanols. The thus-introduced functional silyl groups are useful for further transformation into other functional groups, such as an ethoxysilyl group, or for the preparation of polymeric materials and immobilized heterogeneous catalysts. As shown in the earlier reports, cyclopentadienyltitanium siloxane compounds can be excellent homogeneous catalysts for the epoxidation of alkenes.[8a] In the present study, titanocene-containing molecules (**2b**−**d**) are found to show moderate catalytic activities. An unexpected effect of alkenylsilyl groups of improving the catalytic activities has been found in the present study. This phenomenon is also recognized in the case of tetrapodal titanium silsesquioxanes **8b**−**d**, implying its generality. An extensive study on the exploration of the functionality and further transformation of these silsesquioxanes will be reported in due course.

Experimental Section

Materials and Methods. All reactions and subsequent manipulations were carried out under anaerobic and anhydrous conditions under either high vacuum or an atmosphere of argon using standard Schlenk techniques. Organic solvents and triethylamine were dried and distilled under argon with appropriate drying agents (sodium, calcium chloride, calcium hydride)[22] just before use. Dehydrated acetone and acetonitrile were purchased from Kanto Chemical Co. Inc. and used as received. Titanocene dichloride and zirconocene dichloride (Wako Pure Chemical Industries, Ltd.) and bis(pentamethylcyclopentadienyl)zirconium dichloride, hafnocene dichloride, chlorodimethylsilane, chlorotrimethylsilane, trimethylgermanium bromide, hydrogen chloride in diethyl ether solution (1.0 M), and 1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1^{5,11}]-heptasiloxane-*endo*-3,7,14-triol (**1a**) (Aldrich) were obtained commercially and used without further purification. $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2R)$ (**1b**, R = methyl;[23] **1c**, R = vinyl;[11b] **1d**, R = allyl[19]), $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_2R)]$ (**3b**, R = methyl; **3c**, R = vinyl),[11b] $CpTi[(c\text{-}C_5H_9)_7Si_7O_{12}]$ (**7**),[8a,14b] and $Ti[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_2R)]_2$ (**8b**, R = methyl;[8c] **8c**, R = vinyl;[19] **8d**, R = allyl[19]) were synthesized on the basis of the methods described in previous reports by us or other researchers.

Physical and Analytical Measurements. Solution-phase NMR spectra were recorded on JEOL JNM-AL-300 and JEOL JNM-EX-400 instruments. ^1H and ^{13}C spectra were referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for the ^{29}Si nuclei were referenced to the resonance of external $SiMe_4$. Fast atom bombardment (FAB) mass spectra were recorded using a JEOL SX-102A mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The oxidation products were analyzed by GC-MS (Shimadzu QP 5000, CBP10-S25-050 capillary column, i.d. 0.33 mm, length 25 m, o.d. 0.43 mm at 323∼473 K) and gas chromatography (SE-30, i.d. 3.0 mm, length 3.0 m at 323∼473 K).

Synthesis of $Cp_2Ti[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_3)$ (2b). In a typical experiment, to a solution of **1b** (947 mg, 1.0 mmol) and Cp_2TiCl_2 (249 mg, 1.0 mmol) in toluene (50 cm^3) was added triethylamine (0.3 cm^3, 2.17 mmol) dropwise at room temperature, and the mixture was stirred for 72 h. The solution turned yellow. After filtration, the clear filtrate was evaporated. Yellow microcrystals of the product **2b** were obtained from recrystallization by slow diffusion of acetonitrile into a toluene solution. Yield: 81%. Mp: 129 °C dec. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 6.29 (s, 5H), 6.03 (s, 5H), 1.98−1.54 (br m, 56 H), 1.24−1.19 (br m, 7H), 0.10 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 117.75, 116.97 (C_5H_5), 28.83, 28.68, 28.59, 28.40, 28.35, 28.32, 28.23, 27.96, 27.80, 27.72, 27.69, 27.65, 27.49 (CH_2), 25.53, 24.71, 24.26, 24.39, 23.46 (1:2:2:1:1 for CH), 2.26 ($Si(CH_3)_3$). $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C): δ 7.54, −64.47, −65.08, −66.05, −67.21 (1:1:3:1:2). MS (FAB): *m/z* 1057 $[M - C_5H_5]^+$, 988 $[M - C_5H_5 - C_5H_9]^+$. IR spectrum (KBr): 2954 (s), 2913 (sh), 2872 (s), 1636 (w), 1450 (m), 1255 (m), 1111 (vs), 1013 (sh), 946 (sh), 915 (m), 861 (m), 848 (m), 817 (w), 755 (m), 498 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{82}O_{12}Si_8Ti$ (1123.74): C, 51.30; H, 7.36. Found: C, 51.06; H, 7.17.

Synthesis of $Cp_2Ti[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2CH{=}CH_2)$ (2c). A method similar to that for **2b** was adopted by using **1c** (960 mg, 1.0 mmol) instead of **1b**. Yellow microcrystals. Yield: 81%. Mp: 172 °C dec. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 6.28 (s, 5H), 6.18 (dd $^3J_{HH}$(trans) = 20.2 Hz, $^3J_{HH}$(cis) = 14.9 Hz, 1H), 6.03 (s, 5H), 5.86 (dd, $^3J_{HH}$(cis) = 14.9 Hz, $^2J_{HH}$ = 3.7 Hz, 1H), 5.72 (dd, $^3J_{HH}$(trans) = 20.0 Hz, $^2J_{HH}$ = 3.9 Hz, 1H), 1.99−1.55 (br m, 56 H), 1.26−1.16 (br m, 7H), 0.15 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ 139.57 ($Si\text{-}CH{=}CH_2$), 131.80 ($SiCH{=}CH_2$), 117.80, 116.96 (C_5H_5), 28.85, 28.69, 28.56, 28.40, 28.34, 28.24, 27.98, 27.82, 27.73, 27.70, 27.67, 27.50 (CH_2), 25.48, 24.73, 24.26, 23.50, 23.47 (1:2:2:1:1 for CH), 0.65 ($Si(CH_3)_2$). $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C): δ −3.51, −64.47, −65.08, −65.88, −67.18 (1:1:3:1:2). MS (FAB): *m/z* 1069 $[M - C_5H_5]^+$, 1000 $[M - C_5H_5 - C_5H_9]^+$. IR spectrum (KBr): 3052 (vw), 2949 (s), 2913 (sh), 2867 (s), 1631 (w), 1451 (m), 1409 (w), 1250 (m), 1106 (vs), 1008 (sh), 951 (sh), 910 (m), 822 (m), 802 (m), 786 (m), 719 (m), 493 (m) cm^{-1}. Anal. Calcd for $C_{49}H_{82}O_{12}Si_8Ti$ (1135.75): C, 51.82; H, 7.28. Found: C, 51.48; H, 7.74.

Synthesis of $Cp_2Ti[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2CH_2CH{=}CH_2)$ (2d). A method similar to that for **2b** was adopted by using **1d** (974 mg, 1.0 mmol) instead of **1b**. Yellow microcrystals. Yield: 75%. Mp: 146 °C dec. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.27 (s, 5H), 6.02 (s, 5H), 5.83 (tdd, $^3J_{HH}$ = 8.0, 10.8, 16.4 Hz, 1H), 4.93 ($^3J_{HH}$ = 10.8 Hz, 1H), 4.92 (d, $^3J_{HH}$ = 16.4 Hz, 1H), 2.11−1.45 (br m, 56 H), 1.57 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 1.24−1.13 (br m, 7H), 0.11 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 134.63 ($SiCH_2CH{=}CH_2$), 117.73, 117.00 (C_5H_5), 113.69 ($SiCH_2CH{=}CH_2$), 28.84, 28.68, 28.59, 28.40, 28.32, 28.23, 27.98, 27.80, 27.72, 27.69, 27.66, 27.49 (CH_2), 26.61 ($SiCH_2CH{=}CH_2$), 25.47, 24.71, 24.26, 23.46 (1:2:2:2 for CH), 0.15 ($Si(CH_3)_2$). $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, 25 °C): δ 4.79, −64.49, −65.11, −66.12, −67.16 (1:1:3:1:2). MS (FAB): *m/z* 1083 $[M - C_5H_5]^+$, 1014 $[M - C_5H_5 - C_5H_9]^+$. IR spectrum (KBr): 3078 (vw), 2949 (s), 2913 (sh), 2867 (s), 1631 (w), 1451 (m), 1255 (m), 1106 (vs), 1008 (sh), 946 (m), 915 (m), 848 (m), 807 (m), 735 (m), 498 (m) cm^{-1}. Anal. Calcd for $C_{50}H_{84}O_{12}Si_8Ti$ (1149.77): C, 52.23; H, 7.36. Found: C, 51.93; H, 7.92.

Synthesis of $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}](OSiMe_2CH_2CH{=}CH_2)$ (3d). In a typical experiment, to a solution of **1d** (974 mg, 1.0 mmol) and Cp_2ZrCl_2 (292 mg, 1.0 mmol) in $CHCl_2$ (50 cm^3) was added triethylamine (1.4 cm^3, 10 mmol) dropwise and and the mixture was stirred at room temperature for 60 min. The solvent was then evaporated at room temperature to leave an off-white solid. This was extracted with hexane (60 cm^3) to give a clear filtrate and a white residue of triethylammonium chloride. The filtrate was evaporated, and the product **3d** was obtained from recrystallization by slow diffusion of acetone into a $CHCl_3$ solution. Yield: 70%. Mp: 170 °C dec. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.34 (s, 5H), 6.19 (s, 5H), 5.69 (m, 1H), 4.78 (m, 1H), 4.74 (m, 1H), 1.79−1.51 (br m, 56 H), 1.42 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 0.97−0.91 (br m, 7H), −0.05 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 134.63 ($SiCH_2CH{=}CH_2$), 113.95, 113.22 (C_5H_5), 113.03 ($SiCH_2CH{=}CH_2$), 27.99, 27.85,

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[22] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988.

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27.81, 27.68, 27.58, 27.51, 27.47, 27.33, 27.20, 27.09, 27.06, 26.90 (*C*H$_2$), 26.64 (Si*C*H$_2$CH=CH$_2$), 24.86, 23.57, 23.50, 22.72, 2268 (2:1:1:2:1 for *C*H), −0.37 (Si(*C*H$_3$)$_3$). ^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, 0.02 M Cr(acac)$_3$, 25 °C): δ 4.75, −65.22, −65.71, −66.23, −66.28, −67.66 (1:1:2:1:1:2). MS (FAB): *m/z* 1193 [M + H]$^+$, 1127 [M − C$_5$H$_5$]$^+$. IR spectrum (KBr): 3073 (vw), 2949 (s), 2913 (sh), 2862 (s), 1631 (w), 1451 (m), 1255 (m), 1100 (vs), 1008 (sh), 951 (m), 910 (m), 843 (m), 817 (sh), 802 (s), 488 (m) cm^{-1}. Anal. Calcd for $C_{50}H_{84}O_{12}Si_8Zr$ (1193.11): C, 50.33; H, 7.10. Found: C, 50.35; H, 6.89.

Synthesis of Cp*$_2$Zr[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OSiMe$_2$CH$_2$-CH=CH$_2$) (4d). A method similar to that for **3d** was adopted by using 433 mg (1.0 mol) of (pentamethylcyclopentadienyl)-zirconium dichloride in place of zirconocene dichloride. Yield: 56%. Mp: 110 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 5.77 (tdd, $^3J_{HH}$ = 8.2, 10.1, 15.8 Hz, 1H), 4.83 (m, 1H), 4.80 (m, 1H), 2.00 (s, 15H), 1.94 (s, 15H), 1.78−1.43 (br m, 56H), 1.57 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 1.03−0.83 (br m, 7H), 0.08 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ 134.54 (SiCH$_2$*C*H=CH$_2$), 121.16, 120.30 (C$_5$*Me*$_5$), 113.23 (SiCH$_2$CH=*C*H$_2$), 121.19 (*C*$_5$Me$_5$), 120.29 (*C*$_5$Me$_5$), 28.46, 28.37, 28.00, 27.71, 27.65, 27.56, 27.53, 27.20, 27.14, 27.11, 27.08, 26.98, 26.77 (*C*H$_2$), 26.30 (Si*C*H$_2$CH=CH$_2$), 26.98, 25.24, 23.67, 23.37, 22.81 (2:1:2:1:1 for *C*H), 11.98, 11.54 (C$_5$*Me*$_5$), −0.06 (Si(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, 0.02 M Cr(acac)$_3$, 25 °C): δ 3.74, −64.53, −65.59, −66.40, −66.70, −67.39 (1:1:2:1:1:2). IR spectrum (KBr): 3083 (vw), 2955 (s), 2913 (sh), 2867 (s), 1631 (w), 1451 (m), 1384 (w), 1255 (m), 1100 (vs), 997 (m), 945 (m), 503 (m) cm^{-1}. Anal. Calcd for $C_{60}H_{104}O_{12}Si_8Zr$ (1333.39): C, 54.05; H, 7.86. Found: C, 53.93; H, 7.86.

Synthesis of Cp$_2$Hf[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OSiMe$_2$CH$_2$-CH=CH$_2$) (5d). A method similar to that for **3d** was adopted by using 380 mg (1.0 mol) of hafnocene dichloride in place of zirconocene dichloride. Yield: 69%. Mp: 168−169 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 6.29 (s, 5H), 6.14 (s, 5H), 5.70 (tdd, $^3J_{HH}$ = 8.0, 10.0, 15.6 Hz, 1H), 4.76 ($^3J_{HH}$ = 10.0 Hz, 1H), 4.86 (d, $^3J_{HH}$ = 15.6 Hz, 1H), 1.79−1.39 (br m, 56H), 1.41 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 1.05−0.90 (br m, 7H), −0.06 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ 134.61 (SiCH$_2$*C*H=CH$_2$), 113.01 (SiCH$_2$CH=*C*H$_2$), 112.72, 112.13 (*C*$_5$H$_5$), 27.95, 27.84, 27.80, 27.68, 27.58, 27.50, 27.47, 27.34, 27.21, 27.09, 27.06, 27.02, 26.89 (*C*H$_2$), 26.03 (Si*C*H$_2$CH=CH$_2$), 24.84, 23.55, 22.67 (1:4:2 for *C*H), −0.39 (Si(*C*H$_3$)$_3$). ^{29}Si{^{1}H} NMR (76 MHz, CDCl$_3$, 0.02 M Cr(acac)$_3$, 25 °C): δ 4.73, −64.09, −65.10, −66.13, −66.33, −67.66 (1:2:1:1:1:2). IR spectrum (KBr): 3073 (vw), 2944 (s), 2908 (sh), 2862 (s), 1631 (w), 1456 (m), 1255 (m), 1106 (vs), 1023 (sh), 967 (m), 910 (m), 848 (m), 822 (m), 802 (s), 493 (m) cm^{-1}. Anal. Calcd for $C_{50}H_{84}O_{12}Si_8Hf$ (1280.38): C, 46.90; H, 6.61. Found: C, 46.30; H, 6.58.

Synthesis of Cp$_2$Zr[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OH) (3a). To a solution of silsesquioxane trisilanol (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ (**1a**; 438 mg, 0.50 mmol) and zirconocene dichloride (176 mg, 0.60 mmol) in THF (70 cm^3) was added triethylamine (1.0 cm^3, 7.2 mmol) in THF (15 cm^3) dropwise, and the mixture was stirred at room temperature for 18 h. The triethylammonium chloride that deposited was filtered off, and the filtrate was evaporated in vacuo to give a white solid. Hexane was added, the mixture was stirred, and an insoluble white precipitate was recovered by filtration. Reprecipitation by diffusion of acetone into benzene solution gave a white powder of Cp$_2$Zr[Cp$_2$Zr(c-C$_5$H$_9$)$_7$-Si$_7$O$_{12}$]$_2$ (**6**) in a yield of 24%. The supernatant was evaporated under reduced pressure and gave a white powder of **3a**. Yield: 38% (crude).

3a: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ 6.37 (s, 5H), 6.20 (s, 5H), 1.89−1.34 (br m, 56H), 1.07−0.84 (br m, 7H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ 113.88, 113.33 (*C*$_5$H$_5$), 27.93, 27.82, 27.64, 27.53, 27.50, 27.36, 27.25, 27.16, 27.12, 27.10, 27.03, 27.00, 26.95 (*C*H$_2$ of Cy), 23.52, 23.37, 23.20, 22.74, 22.46 (2:1:2:1:1 for *ipso*-*C*H of Cy); ^{29}Si NMR (76 MHz, CDCl$_3$, 0.02 M Cr(acac)$_3$, 25 °C) δ −56.35, −65.12, −65.54, −66.43, −67.56 (1:1:2:1:2).

6: mp >300 °C; ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) δ 6.41 (s, 10H), 6.25 (s, 10H), 6.20 (s, 10H) 2.36−1.50 (br m, 112H), 1.50−1.11 (br m, 14H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ 114.26, 113.89, 113.83 (*C*$_5$H$_5$), 31.92, 30.19, 29.30, 28.64, 28.41, 28.29, 28.20, 28.11, 27.85, 27.68, 27.55, 27.35, 26.93 (*C*H$_2$ of Cy), 27.17, 24.19, 24.02, 23.48, 23.29 (1:2:2:1:1 for *ipso*-*C*H of Cy); ^{29}Si NMR (76 MHz, CDCl$_3$, 0.02 M Cr(acac)$_3$, 25 °C) δ −63.47, −65.07, −65.44, −65.93, −67.12 (1:1:2:1:2); IR spectrum (KBr) 3109 (w), 2949 (s), 2862 (s), 1631 (w), 1451 (m), 1245 (m), 1121 (vs), 1095 (sh), 1018 (s), 967 (s), 807 (m), 730 (m), 663 (w), 488 (m) cm^{-1}. Anal. Calcd for $C_{100}H_{156}O_{24}Si_{14}Zr_3$ (2409.19): C, 49.86; H, 6.53. Found: C, 50.06; H, 6.77.

Synthesis of Cp$_2$Zr[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OSiMe$_2$H) (3e) via 3a. Triethylamine (1.0 cm^3, 7.2 mmol) in THF (15 cm^3) was added dropwise to a solution of the silsesquioxane trisilanol (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ (**1a**; 876 mg, 1.0 mmol) and zirconocene dichloride (351 mg, 1.2 mmol) in THF (80 cm^3), and the mixture was stirred at 0 °C for 3 h. To this reaction mixture was added chlorodimethylsilane (0.34 cm^3, 3.0 mmol) in THF (15 cm^3) dropwise and the mixture was stirred at room temperature for 18 h. After filtration, the resulting clear solution was evaporated in vacuo to give a pale yellow solid. The solid was extracted with benzene (20 cm^3) to give a clear filtrate. To the filtrate was added acetone (50 cm^3), and the precipitate that formed was filtered off. The resulting clear solution was evaporated, and benzene (15 cm^3) was added. The product was obtained by slow diffusion of acetonitrile into a benzene solution. Yield: 70%. Mp: 297−298 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 6.36 (s, 5H), 6.15 (s, 5H), 5.22 (sept, $^3J_{HH}$ = 2.9 Hz, 1H), 2.18∼1.47 (br m, 56H), 1.32∼1.10 (br m, 7H), 0.46 (d, $^3J_{HH}$ = 2.9 Hz, 6H). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ 114.42, 113.69 (*C*$_5$H$_5$), 28.59, 28.44, 28.33, 28.23, 28.13, 28.04, 27.85, 27.80, 27.68, 27.52, 27.43, 27.34 (*C*H$_2$ of Cy), 25.11, 24.12, 24.03, 23.32, 23.21 (1:2:2:1:1 for *ipso*-*C*H of Cy), 1.05 (Si(*C*H$_3$)$_2$H). ^{29}Si NMR (76 MHz, C$_6$D$_6$, 0.02 M Cr(acac)$_3$, 25 °C): δ −5.67, −64.85, −65.39, −65.52, −66.01, −67.51 (1:1:1:2:1:2). IR spectrum (KBr): 2949 (s), 2862 (s), 2130 (w), 1724 (sh), 1585 (m), 1456 (m), 1255 (m), 1106 (vs), 946 (m), 848 (m), 802 (m), 740 (m), 493 (m) cm^{-1}. MS (FAB): *m/z* 1151 [M − H]$^+$, 1085 [M − H − C$_5$H$_5$]$^+$. Anal. Calcd for $C_{47}H_{80}O_{12}Si_8Zr$ (1153.05): C, 48.96; H, 6.99. Found: C, 48.95; H, 7.24.

Synthesis of Cp$_2$Zr[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OGeMe$_3$) (3f) via 3a. A method similar to that for **3e** was adopted by using trimethylgermanium bromide (0.51 cm^3, 4.0 mmol) in THF (10 cm^3) in place of chlorodimethylsilane. Yield: 70%. Mp: 197−198 °C. ^{1}H NMR (300 MHz, C$_6$D$_5$CD$_3$, 25 °C): δ 6.33 (s, 5H), 6.12 (s, 5H), 2.34−1.36 (br m, 56H), 1.29−1.11 (br m,7H), 0.30 (s, 9H). ^{13}C NMR (75 MHz, C$_6$D$_5$CD$_3$, 25 °C): δ 114.48, 113.67 (*C*$_5$H$_5$), 28.79, 28.66, 28.47, 28.39, 28.30, 28.16, 28.11, 27.85, 27.71, 27.62, 27.59, 27.41 (*C*H$_2$ of Cy), 26.13, 24.35, 24.22, 23.38, 23.35 (1:2:2:1:1 for *ipso*-*C*H of Cy), 2.98 (Ge(*C*H$_3$)$_3$). ^{29}Si NMR (76 MHz, C$_6$D$_5$CD$_3$, 0.02 M Cr(acac)$_3$, 25 °C): δ −63.94, −64.95, −65.64, −66.01, −67.95 (1:1:2:1:2). IR spectrum (KBr): 3119 (vw), 2954 (s), 2862 (s), 1450 (m), 1265 (sh), 1244 (m), 1105 (vs), 1017 (sh), 956 (sh), 801 (s), 616 (m), 492 (m) cm^{-1}. MS (FAB): *m/z* 1145 [M − C$_5$H$_5$]$^+$. Anal. Calcd for $C_{48}H_{82}O_{12}Si_7GeZr$ (1211.60): C, 47.58; H, 6.82. Found: C, 47.74; H, 6.55.

Synthesis of Cp$_2$Hf[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OSiMe$_2$H) (5e) via Cp$_2$Hf[(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$](OH) (5a). A method similar to that for **3e** was adopted by using hafnocene dichloride (457 mg, 1.2 mmol) in THF (70 cm^3) in place of zirconocene dichloride. The intermediate **5a** has not been isolated. Yield: 77%. Mp: 243−244 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 6.32 (s, 5H), 6.11 (s, 5H), 5.05 (sept., $^3J_{HH}$ = 2.9 Hz, 1H), 2.18∼1.46 (br m, 56H),1.32∼1.11 (br m, 7H), 0.20 (d, $^3J_{HH}$ = 2.9 Hz, 6H). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ 113.19, 112.58 (*C*$_5$H$_5$), 28.56, 28.42, 28.33, 28.23, 28.17, 28.04, 27.82, 27.68, 27.55, 27.51, 27.35 (*C*H$_2$ of Cy), 25.10, 24.19, 24.03, 23.29, 23.21 (1:2:2:1:1 for *ipso*-*C*H of Cy), 0.81 (Si(*C*H$_3$)$_2$H). ^{29}Si NMR (76 MHz, C$_6$D$_6$, 0.02 M Cr(acac)$_3$, 25 °C): δ −5.71, −63.82, −64.80, −65.39,

−65.84, −67.46 (1:2:1:1:1:2). IR spectrum (KBr): 2939 (s), 2867 (s), 2130 (w), 1718 (sh), 1605 (m), 1445 (m), 1250 (m), 1095 (vs), 977 (m), 848 (m), 797 (m), 730 (m), 493 (m) cm^{-1}. MS (FAB): *m/z* 1239 [M − H]$^+$, 1175 [M − C_5H_5]$^+$. Anal. Calcd for $C_{47}H_{80}O_{12}Si_8Hf$ (1240.32): C, 45.51; H, 6.50. Found: C, 45.26; H, 6.24.

Synthesis of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2H)$ (1e) via 3e. Hydrogen chloride solution (1 M in Et_2O, 1.0 cm^3, 1.0 mmol) was added to a solution of **3e** (576 mg, 0.50 mmol) in toluene (15 cm^3), and the mixture was stirred at room temperature for 18 h. After the solvent was evaporated, the resulting white solid was extracted with hexane (20 cm^3). An almost quantitative yield of zirconocene dichloride (>95%) was obtained as a hexane-insoluble solid. The filtrate was evaporated, and the product was obtained almost quantitatively (>95%). The isolated product **1e** is unstable for the microanalysis. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 5.09 (sept, ^3J = 2.8 Hz, 1H), 4.55 (br s, 2H), 2.12−1.46 (br m, 56H), 1.32−1.10 (br m,7H), 0.39 (d, ^3J = 2.8 Hz, 6H). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 27.99, 27.95, 27.90, 27.86, 27.81, 27.49, 27.46, 27.43 ($\mathit{C}H_2$ of Cy), 23.88, 23.28, 23.05, 22.84, 22.72 (1:2:2:1:1 for *ipso*-$\mathit{C}H$ of Cy), 0.57 ($Si(\mathit{C}H_3)_2H$). ^{29}Si NMR (76 MHz, C_6D_6, 0.02 M $Cr(acac)_3$, 25 °C): δ −2.34, −56.35, −65.10, −65.27, −67.04 (1:2:1:2:2).

Synthesis of $Cp_2Ti[(c\text{-}C_5H_9)_7Si_7O_{11}][OSiMe_2(CH_2)_2SiMe_2(OEt)]$ (2g). An excess of freshly distilled $HSiMe_2(OEt)$ (1.0 mmol) was added dropwise to a toluene solution (5.0 cm^3) of **2c** (0.5 mmol) and $Pt(dvs)_2$ catalyst (1 mol %, dvs = divinyltetramethyldisiloxane), and the mixture was stirred at room temperature for 24 h. After short column chromatography on alumina and solvent evaporation, a viscous yellow solid of **2g** was obtained almost quantitatively. The ^{13}C NMR spectra (DEPT) shows that the product is **2g**, bearing a linear $-SiCH_2CH_2Si-$ group, together with a trace amount of the byproduct **2g′**, with branched $-SiCH(CH_3)Si-$ bonding. Because of the high reactivity of the ethoxysilyl group, complete purification has not been achieved. **2g**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 6.30 (s, 5H, $C_5\mathit{H}_5$), 6.03 (s, 5H, $C_5\mathit{H}_5$), 3.58 (q, ^3J = 7.2 Hz, 2H, $OC\mathit{H}_2CH_3$), 2.10−1.55 (br m, 56H, $C\mathit{H}_2$ of Cy), 1.24−1.14 (br m, 7H, $C\mathit{H}$ of Cy), 1.16 (t, ^3J = 7.2 Hz, 3H, $OCH_2C\mathit{H}_3$), 0.55 (s, 2H), 0.54 (s, 2H, both $Si(C\mathit{H}_2)_2Si$), 0.14 (s, 6H), 0.13 (s, 6H, both $Si(C\mathit{H}_3)_2$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C) δ 117.74, 116.96 (C_5H_5), 58.10 ($O\mathit{C}H_2CH_3$), 28.82−27.47 (m, $\mathit{C}H_2$), 25.57, 24.71, 24.23, 23.48, 23.45 (1:2:2:1:1 for $\mathit{C}H$), 19.06 ($OCH_2\mathit{C}H_3$), 10.00, 8.29 ($Si(\mathit{C}H_2)_2Si$), −0.10, −2.30 ($Si(\mathit{C}H_3)_2$); IR spectrum (KBr) 2949 (s), 2872 (s), 1450 (m), 1254 (m), 1110 (vs), 919 (s), 801 (s), 729 (m), 497 (m) cm^{-1}.

Synthesis of $Cp_2Zr[(c\text{-}C_5H_9)_7Si_7O_{11}][OSiMe_2(CH_2)_2SiMe_2(OEt)]$ (3g). A method similar to that for **2g** was adopted by using **3c** in place of **2c**. Again, **3g** with a linear $-SiCH_2CH_2Si-$ connection was obtained together with a trace amount of the byproduct **3g′**, with a branched connection. **3g**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 6.37 (s, 5H, $C_5\mathit{H}_5$), 6.15 (s, 5H, $C_5\mathit{H}_5$), 3.62 (q, ^3J = 7.0 Hz, 2H, $OC\mathit{H}_2CH_3$), 2.11−1.40 (br m, 56H, $C\mathit{H}_2$ of Cy), 1.28−1.05 (br m, 7H, $C\mathit{H}$ of Cy), 1.20 (t, ^3J = 7.0 Hz, 3H, $OCH_2C\mathit{H}_3$), 0.61 (s, 4H, $Si(C\mathit{H}_2)_2Si$), 0.20 (s, 6H), 0.18 (s, 6H, both $Si(C\mathit{H}_3)_2$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C) δ 114.43, 113.71 (C_5H_5), 58.24 ($O\mathit{C}H_2CH_3$), 28.59, 28.53, 28.43, 28.30, 28.22, 28.11, 28.08, 27.82, 27.69, 27.54, 27.35 ($\mathit{C}H_2$), 25.58, 24.17, 24.10, 23.29 (1:2:2:2 for $\mathit{C}H$), 18.94 ($OCH_2\mathit{C}H_3$), 9.86, 8.15 ($Si(\mathit{C}H_2)_2Si$), −0.22, −2.48 ($Si(\mathit{C}H_3)_2$); IR spectrum (KBr) 2949 (s), 2867 (s), 1455 (m), 1259 (m), 1104 (vs), 1007 (sh), 956 (m), 907 (sh), 791 (s), 729 (sh), 491 (m) cm^{-1}.

Catalytic Epoxidation of Cyclohexene. All the reactions were performed by the use of hot stirrers equipped with cooling blocks for refluxing the solution. The appropriate catalyst (0.033 mmol as M) and cyclohexene (3.3 mmol) in toluene solution (1.5 cm^3) were taken into a glass Schlenk tube under an Ar atmosphere. The reaction mixture was heated by the heating block and allowed to equilibrate at 50 or 60 °C for 10 min. ^{t}BuOOH (3.3 mmol) in decane solution (5.5 M, 0.6 cm^3) was then added by the use of a plastic pipet. The mixture was stirred for 4 h and then cooled rapidly in an ice bath. The products were identified by the use of GC-MS and quantified by GC analyses using biphenyl as an internal standard.

X-ray Crystallographic Study of 3d and 5d. Colorless single crystals of **3d** and **5d** suitable for analysis by X-ray diffraction were provided from recrystallization by slow diffusion of acetonitrile into mesitylene solutions. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). All calculations were performed using the Crystal Structure crystallographic software package. The structures were solved by direct methods using SIR97[24] and expanded using Fourier techniques, DIRDIF94.[25] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations, and hydrogen atoms were placed at their geometrically calculated positions and refined isotropically. Selected crystallographic parameters and bond distances and angles are given in Tables 2−4. The detailed final atomic parameters are given in the Supporting Information.

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Supporting Information Available: Tables giving full details of the crystal structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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