

# Homogeneous Models for Chemically Tethered Silica-Supported Olefin Polymerization Catalysts

John R. Severn,<sup>†</sup> Robbert Duchateau,<sup>\*,†</sup> Rutger A. van Santen,<sup>†</sup>  
Dianne D. Ellis,<sup>‡</sup> and Anthony L. Spek<sup>‡</sup>

*Dutch Polymer Institute/Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received April 27, 2001

**Summary:** The silsesquioxane-tethered fluorene ligand (*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>CH<sub>2</sub>-9-Flu(H) and zirconocene complexes thereof, C<sub>5</sub>H<sub>9</sub>(SiMe<sub>3</sub>)<sub>2</sub>[(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>CH<sub>2</sub>-9-Flu]ZrCl<sub>2</sub> and [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>CH<sub>2</sub>-9-Flu]<sub>2</sub>ZrCl<sub>2</sub>, have been used to optimize the synthetic strategies for the corresponding silica-tethered zirconocenes and to study their steric and electronic properties.

At present there is considerable academic and commercial interest in the immobilization of well-defined homogeneous olefin polymerization catalysts.<sup>1</sup> The goal is to marry the advantages of homogeneous catalysts with those of heterogeneous ones. Homogeneous catalysts are well defined, single-site catalysts that can be fine-tuned to produce tailor-made polymers.<sup>2</sup> Heterogeneous catalysts, however, have the technological advantages of good morphology control, high polymer bulk density, and no reactor fouling.<sup>3</sup> Since most of the existing polymerization plants run as slurry or gas-phase processes with heterogeneous catalysts, homogeneous catalysts must be heterogenized on a support for their application in these processes.

The most widely applied method to immobilize homogeneous olefin polymerization catalysts consists of anchoring metallocenes onto silicas that are pretreated with MAO. However, leaching remains one of the main problems in these systems.<sup>1,4</sup> Chemical tethering of organometallic compounds is, with respect to leaching, probably the best method to anchor a homogeneous catalyst to the support. Unfortunately, it is also the most laborious route. Nevertheless, tethering is a versatile method to anchor virtually any homogeneous catalyst

onto oxide<sup>5,6</sup> or polymer<sup>7</sup> supports and is gaining more and more attention in the recent literature. While several studies on tethering of olefin polymerization catalysts onto silicas have been reported, little information is available on the effectiveness of the applied immobilization method or the steric and electronic effects of the support on these immobilized catalysts. Suitable homogeneous model systems for silica surface silanol sites, such as (poly)siloxides<sup>8</sup> and silsesquioxanes,<sup>9</sup> could provide more insight.

In the past, (metalla)silsesquioxanes have proven to be suitable model systems to mimic the chemistry of silica silanols and silica-grafted olefin polymerization (co)catalysts.<sup>10</sup> We argued that these model supports could also be useful (i) to optimize the synthetic strategies to prepare chemically tethered systems, (ii) to assess the electronic and local steric effects of the support on the catalyst, and (iii) to understand the influence of different tethering units applied. We here

(5) For example see: (a) Lee, D.-H.; Yoon, K.-B. *Macromol. Rapid Commun.* **1997**, *18*, 427. (b) Iiskola, E. I.; Timonen, S.; Pakkanen, T. T.; Härkki, O.; Seppälä, J. V. *Appl. Surf. Sci.* **1997**, *121/122*, 372. (c) Vega, W. M.; Cañas, P. L.; Lafuente, A. M.-E.; Llinas, G. H.; Royo, J. S.; Llatas, L. M. U.S. Pat. Appl. 5,824,620, 1998. (d) Timonen, S.; Pakkanen, T. T.; Iiskola, E. I. *J. Organomet. Chem.* **1999**, *582*, 273. (e) Juvaste, H.; Pakkanen, T. T. *Organometallics* **2000**, *19*, 1729. (f) Uusitalo, A.-M.; Pakkanen, T. T.; Iiskola, E. I. *J. Mol. Catal. A: Chem.* **2000**, *156*, 181.

(6) For example see: (a) Antberg, M.; Luker, H.; Böhm, L. U.S. Pat. Appl. 5,202,398, 1993. (b) Galan-Fereres, M.; Koch, T.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1999**, *580*, 145. (c) Alt, H. G.; Schertl, P.; Köppl, A. *J. Organomet. Chem.* **1998**, *568*, 263. (d) Lee, B. Y.; Oh, J. S. *Macromolecules* **2000**, *33*, 3194.

(7) For example see: (a) Kitagawa, T.; Uozumi, T.; Soga, K.; Takata, T. *Polymer* **1997**, *38*, 615. (b) Stork, M.; Koch, M.; Klapper, M.; Müllen, K.; Gregorius, H.; Rief, U. *Macromol. Rapid Commun.* **1999**, *20*, 210. (c) Chan, M. C. W.; Chew, K. C.; Dalby, C. I.; Gibson, V. C.; Kohlmann, A.; Little, I. R.; Reed, W. *Chem. Commun.* **1998**, 1673. (d) Barrett, A. G. M.; de Miguel, Y. R. *Chem. Commun.* **1998**, 2079. (e) Hong, S. C.; Teranishi, T.; Soga, K. *Polymer* **1998**, *39*, 7153.

(8) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205. (b) Noh, S. K.; Kim, S.; Kim, J.; Lee, D.-H.; Yoon, K.-B.; Lee, H.-B.; Lee, S. W.; Huh, W. S. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3717.

(9) (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (b) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931. (c) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *113*, 3859.

(10) (a) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614. (b) Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.* **1991**, *114*, 3618. (c) Liu, J.-C.; *J. Chem. Soc., Chem. Commun.* **1996**, 1109. (d) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K.-H.; van Tol, M. F. H. *Organometallics* **1998**, *17*, 5663. (e) Duchateau, R.; Cremer, U.; Harmsen, R. J.; Mohamad, S. I.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K.-H.; van Tol, M. F. H.; Kranenburg, M. *Organometallics* **1999**, *18*, 5447. (f) Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2000**, *19*, 809. (g) Skowronska-Ptasinska, M. D.; Duchateau, R.; van Santen, R. A. Yap, G. P. A. *Organometallics* **2001**, *20*, 3519.

\* To whom correspondence should be addressed. E-mail: R.Duchateau@tue.nl. Fax: +31 40 2455054. Tel: +31 40 2474918.

<sup>†</sup> Eindhoven University of Technology.

<sup>‡</sup> Utrecht University.

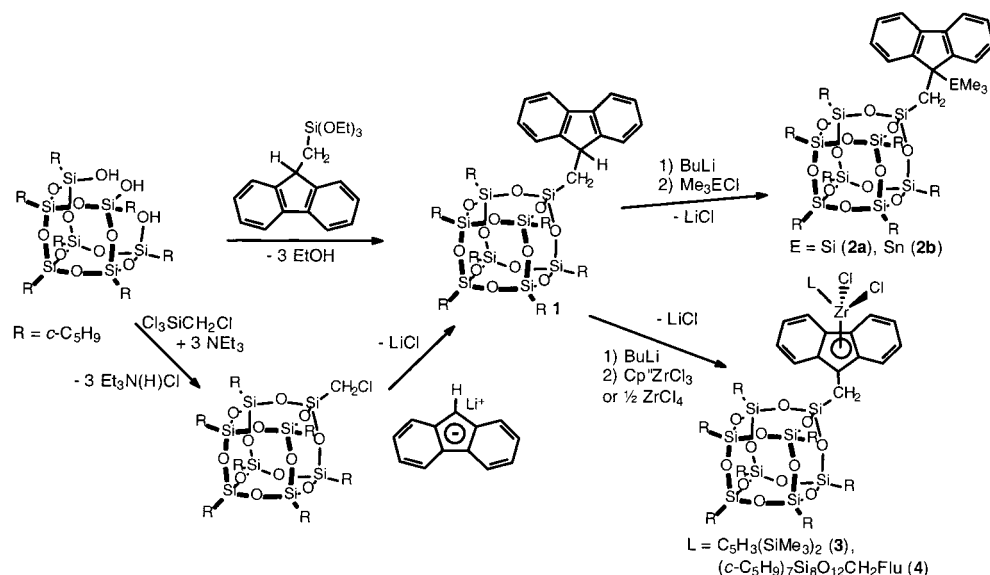
(1) (a) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243. (b) Chien, J. C. W. *Top. Catal.* **1999**, *7*, 23. (c) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.

(2) (a) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(3) For example see: (a) Hund, R. In *Ziegler Catalysts*; Fink, G., Mühlaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: New York, 1995; Chapter 20. (b) Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377.

(4) (a) Chien, J. C. W.; He, D. *J. Polym. Sci., A: Polym. Chem.* **1991**, *29*, 1603. (b) Collins, S.; Kelly, W. M.; Holden, D. A. *Macromolecules* **1992**, *25*, 1780. (c) Soga, K.; Kaminaka, M. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 221. (d) Soga, K.; Kaminaka, M. *Makromol. Chem.* **1993**, *194*, 1745. (e) Kaminsky, W.; Renner, F. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 239. (f) Janiak, C.; Rieger, B. *Angew. Makromol. Chem.* **1994**, *47*, 215. (g) Sacchi, M. C.; Zucchi, D.; Titto, I.; Locatelli, P.; Dall'Occo, T. *Macromol. Rapid Commun.* **1995**, *16*, 581. (h) Kamfjord, T.; Wester, T. S.; Rytter, E. *Macromol. Rapid Commun.* **1998**, *19*, 505.

**Scheme 1. Synthesis of  $(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{Flu}(\text{H})$  (**1**) and Formation of Trimethylsilyl (**2a**), Trimethylstannyl (**2b**) and Zirconocene Complexes (**3**, **4**)**



report the preliminary results of our study on silsesquioxane-tethered olefin polymerization catalysts as models for their silica-supported analogues.

There are two general routes applied to prepare chemically tethered catalyst systems onto silica: (i) building up both the ligand and metal complex at the surface<sup>5</sup> and (ii) immobilizing a presynthesized catalyst precursor containing an anchorable functionality.<sup>6</sup> Using silsesquioxane model supports, we tried to explore the advantages and drawbacks of the former approach: tethering the ancillary ligand to the silsesquioxane, followed by introduction of the metal precursor.

The most commonly applied method to tether organic substituents onto silica surfaces is by treating the silica with tris(alkoxy)silyl-functionalized substrates.<sup>5,11</sup> Likewise, treating the silsesquioxane trisilanol species  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$  with  $(\text{EtO})_3\text{SiCH}_2\text{-9-Flu}(\text{H})$  afforded the corner-capped silsesquioxane-containing fluorene  $(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{-9-Flu}(\text{H})$  (**1**; Scheme 1) in moderate yield (59%). Alternatively, **1** can also be prepared by reacting  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$  with (trichlorosilyl)methyl chloride ( $\text{Cl}_3\text{SiCH}_2\text{Cl}$ ) in the presence of an amine, yielding  $(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{Cl}$ , followed by reaction with fluorenyllithium (64% overall yield, Scheme 1). The selectivities of both routes are comparable. Whereas the second method is much faster, removal of the ammonium and lithium chlorides formed by this two-step method might be a major disadvantage when this synthetic route is applied to a solid support.

Once the ancillary ligand is attached to the silsesquioxane, it can be deprotonated and reacted with a metal precursor. Since Si–O bond breaking by nucleophiles such as *n*-BuLi is a well-known reaction for silsesquioxanes and silicas,<sup>12</sup> the deprotonation of **1** was carefully examined. Treatment of **1** with *n*-BuLi in THF at 0 °C gave a cherry red color, characteristic of the fluorenyl anion. Subsequent treatment with either trimethylsilyl chloride or trimethylstannyl chloride cleanly afforded the corresponding silyl- and stannyl-substituted products  $(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{-9-Flu}(\text{H})\text{E}(\text{SiMe}_3)$  (E = Si (**2a**), Sn (**2b**); Scheme 1), indicating that Si–O bond breaking does not occur under these conditions. React-

ing the lithium salt of **1** with  $\text{Cp}''\text{ZrCl}_3$  ( $\text{Cp}'' = 1,3\text{-C}_5\text{H}_3\text{(SiMe}_3)_2$ ) and  $\text{ZrCl}_4$  in toluene also proved to be a successful strategy to synthesize the zirconocene complexes  $\text{Cp}''[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{-9-Flu}]\text{ZrCl}_2$  (**3**) and  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{-9-Flu}]_2\text{ZrCl}_2$  (**4**), respectively.

The selectivity of both anchoring the fluorene ligand to the silsesquioxane support and introducing the zirconium is moderate. For silsesquioxanes this synthetic strategy is still convenient, only because the silsesquioxane-bonded ancillary ligand and the metal complexes thereof can be purified. More importantly, there are no adjacent silanol functionalities that can interfere with the intended reactions.<sup>13</sup> Using this multistep approach to form silica-tethered zirconocene systems is therefore likely to result in more than one type of surface metal site.

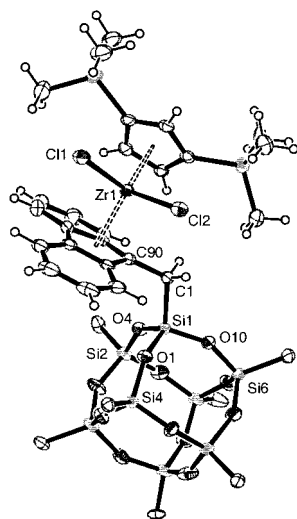
Earlier studies showed that silsesquioxanes are strongly electron-withdrawing substituents.<sup>10e,14</sup> To assess the actual electronic influence of the silsesquioxane substituent in **1**, a comparative acidity experiment was carried out using equimolar amounts of **1**, Me-9-Flu(H), and *n*-BuLi. The silsesquioxane containing fluorene **1** was found to be considerably more acidic than Me-9-Flu(H) ( $\Delta\text{p}K_a \geq 1.5$  by <sup>1</sup>H NMR). Despite the methylene unit, the silsesquioxane substituent has a significant electronic effect on the fluorene ligand and consequently on the metal center. Hence, longer isolating spacers are required to block the electronic influence of the (model) support.

(11) (a) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem.* **1986**, *98*, 237. (b) Price, P. M.; Clark, J. H.; Macquarrie, D. J. *J. Chem. Soc., Dalton Trans.* **2000**, 101.

(12) (a) Feher, F. J.; Rahimian, K.; Budzichowski, T. A.; Ziller, J. W. *Organometallics* **1995**, *14*, 3920. (c) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Milar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262.

(13) As will be discussed in detail elsewhere, adjacent silanols, as for example in  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_2\text{CH}_2\text{-9-Flu}(\text{H}))_2(\text{OH})_2$ , are more acidic than the fluorene. As a consequence, these silanols severely influence the metalation reactions, leading to various products: Severn, J. R.; Duchateau, R.; van Santen, R. A.; Ellis, D. D.; Spek, A. L.; Yap, G. P. A. Manuscript in preparation.

(14) (a) Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *379*, 33. (b) Feher, F. J.; Tajima, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 2145.



**Figure 1.** Molecular structure of  $\text{Cp}''[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{CH}_2\text{-9-Flu}]\text{ZrCl}_2$  (**3**). Solvent molecules are not shown. Only the methyne carbons of the cycloalkyl groups are shown for clarity. Displacement ellipsoids are shown at the 40% probability level.

Although the difference in acidities of **1** and Me-9-Flu(H) would have suggested otherwise, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts of the acidic  $\text{CH}$  in **1** ( $^1\text{H}$ , 4.13 ppm;  $^{13}\text{C}$ , 42.72 ppm) and the 9-substituted methylene group in **1** ( $^1\text{H}$ , 1.24 ppm;  $^{13}\text{C}$ , 17.56 ppm) are virtually identical with the resonances in Me-9-Flu(H) (acidic  $\text{CH}$ ,  $^1\text{H}$  3.98 ppm;  $^{13}\text{C}$  42.42 ppm;  $\text{CH}_2$ -9-Flu(H),  $^1\text{H}$  1.57 ppm;  $^{13}\text{C}$  18.20 ppm).<sup>15,16</sup> The  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra of **1–4** show the expected resonances for the  $\text{CH-C}_5\text{H}_9$  (1:3:3 ratio),  $(\equiv\text{O})_3\text{SiC}_5\text{H}_9$ , and  $(\equiv\text{O})_3\text{SiCH}_2$  (1:3:3:1 ratio) resonances of a  $\text{C}_3$ -symmetric silsesquioxane ligand, respectively.<sup>17</sup> The  $^{13}\text{C}$  NMR chemical shifts for the C(9) carbons (**3**, 101.50 ppm; **4**, 96.71 ppm) indicate that in solution the fluorenyl moieties in **3** and **4** adopt an  $\eta^5$ -bonding mode similar to that found for  $\text{Cp}[\text{Me-9-Flu}]\text{ZrCl}_2$  (99.0 ppm).<sup>15</sup>

The solid-state structure of **3** as derived from single-crystal X-ray diffraction study is illustrated in Figure 1.<sup>18</sup> The Si–O distances (1.607(5)–1.635(6) Å) and Si–O–Si bond angles (147.3(4)–152.0(4)°) in **3** are normal within the wide range of Si–O distances and Si–O–Si angles found for silsesquioxanes.<sup>9,10</sup> To reduce the steric hindrance between the fluorenyl group and silsesquioxane cyclopentyl substituents in **3**, the Si1–C1–C90 angle is slightly opened (116.4(3)°). The structure of **3** consists of a standard metallocene in which the tetrahedrally surrounded zirconium atom is  $\eta^5$ -bonded to both the cyclopentadienyl and fluorenyl ligands, while

(15) For acidities and chemical shifts of 9-substituted fluorenes see: (a) Bausch, M. J.; Gong, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5963. (b) Zhang, S.; Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1995**, *117*, 602.

(16) (a) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1996**, *525*, 15. (b) Severn, J. R.; Duchateau, R.; van Santen, R. A.; Ellis, D. D.; Spek, A. L. Manuscript in preparation.

(17) Full experimental and NMR data of **1–4** are given in the Supporting Information.

(18)  $T = 150$  K,  $\text{C}_{60}\text{H}_{94}\text{Cl}_2\text{O}_{12}\text{Si}_{10}\text{Zr} \cdot 2.5\text{CH}_2\text{Cl}_2$ ,  $M_w = 1662.71$ , triclinic,  $P\bar{1}$ ,  $a = 11.3551(4)$  Å,  $b = 18.1661(7)$  Å,  $c = 19.8473(8)$  Å,  $\alpha = 86.0297(17)^\circ$ ,  $\beta = 83.156(2)^\circ$ ,  $\gamma = 77.2346(18)^\circ$ ,  $V = 3960.5(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.394$  g cm<sup>-3</sup>,  $\mu = 0.580$  mm<sup>-1</sup>,  $F(000) = 1738$ , 13 918 reflections,  $\text{GOF} = 1.023$ ,  $R = 0.0537$ ,  $R_w = 0.1135$ . Data were collected on a Nonius Kappa CCD area detector with a graphite monochromator ( $\lambda = 0.710$  73 Å).

two additional chlorides fill the coordination sphere. The Zr–Cp''<sub>centroid</sub> and Zr–Flu<sub>centroid</sub> distances in **3** (Zr–Cp'', 2.217 Å; Zr–Flu, 2.269 Å) are comparable to the bond distances found, for example, in  $\text{Cp}''_2\text{ZrCl}_2$  (2.20 Å),<sup>19a</sup>  $\text{Cp}'[\text{Cp}']\text{ZrCl}_2$  (Cp' =  $\text{C}_5\text{H}_4\text{SiMe}_3$ ; 2.219 Å),<sup>19b</sup> and 9-substituted fluorenylmetallocenes,  $\text{Cp}[\text{R-9-Flu}]\text{ZrCl}_2$  (R = *i*-Pr, 2.294 Å; R = *c*-C<sub>6</sub>H<sub>11</sub> = 2.253 Å; R = *t*-Bu, 2.278 Å).<sup>15</sup> The Cl–Zr–Cl bond angle of 96.00(4)° and Cp''<sub>centroid</sub>–Zr–Flu<sub>centroid</sub> angle of 128.8(1)° are virtually identical with those in  $\text{Cp}[i\text{-Pr-9-Flu}]\text{ZrCl}_2$  (Cl–Zr–Cl, 97.23(5)°; Cp–Zr–Flu, 129.8(5)°),  $\text{Cp}[c\text{-C}_6\text{H}_{11}\text{-9-Flu}]\text{ZrCl}_2$  (Cl–Zr–Cl, 96.3(1)°; Cp–Zr–Flu, 129.8(2)°), and  $\text{Cp}[t\text{-Bu-9-Flu}]\text{ZrCl}_2$  (Cl–Zr–Cl, 95.5(1)°; Cp–Zr–Flu, 129.7(2)°).<sup>15</sup> This suggests that, although the silsesquioxane is a very large substituent, the effective steric bulk of the methylene silsesquioxane substituent is not excessive.

Preliminary olefin polymerization experiments were carried out using silsesquioxane-substituted zirconocene dichlorides **3** and **4**. When they are activated with MAO, both complexes generated active ethylene polymerization catalysts. The polymerization activities of **3** ( $3.7 \times 10^6$  g of PE/(mol h bar)) and **4** ( $2.5 \times 10^6$  g of PE/(mol h bar)) are somewhat lower than of the corresponding non-silsesquioxane complexes  $\text{Cp}''[\text{Me-9-Flu}]\text{ZrCl}_2$  ( $5.0 \times 10^6$  g of PE/(mol h bar)) and  $[\text{Me-9-Flu}]_2\text{ZrCl}_2$  ( $3.8 \times 10^6$  g of PE/(mol h bar)), respectively. Alt and co-workers found that electron-withdrawing substituents in the 9-position of the fluorenyl ligand in  $\text{Cp}[\text{R-9-Flu}]\text{ZrCl}_2$  give rise to lower activities than electron-donating ones,<sup>15</sup> while steric effects influenced the activity much less. A methylene spacer proved to be sufficient to avoid close contact between the metal site and the silsesquioxane but insufficient to block the electron-withdrawing effect of the silsesquioxane moiety. Therefore, the lower activities of **3** and **4** compared to those of their nonsilsesquioxane analogues is probably due to electronic rather than steric influence of the model support. While the molecular weight of the polyethylenes formed by  $[\text{Me-9-Flu}]_2\text{ZrCl}_2$  ( $M_w = 12$  000;  $M_w/M_n = 2.5$ ) and **4** ( $M_w = 7000$ ;  $M_w/M_n = 2.2$ ) are similarly low, the molecular weight of the polyethylene formed by **3** ( $M_w = 409$  000;  $M_w/M_n = 4.9$ ) is considerably higher than that of  $\text{Cp}''[\text{Me-9-Flu}]\text{ZrCl}_2$  ( $M_w = 122$  000;  $M_w/M_n = 2.9$ ). Whether this is due to steric or electronic reasons is not clear at this point. A full account of our efforts to mimic silica-tethered systems using early-transition-metal silsesquioxane complexes will be reported in due course.<sup>13</sup>

**Acknowledgment.** This work was financed by DSM Research BV and the Dutch Polymer Institute (R.D., J.R.S.). D.D.E. and A.L.S. thank the Council for Chemical Sciences and The Netherlands Organization for Scientific Research for a financial contribution.

**Supporting Information Available:** Text giving full experimental details and tables giving atomic coordinates, thermal displacement parameters, and bond lengths and bond angles for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM010344D

(19) (a) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Oliver, H.; Ryan, E. J. *J. Chem. Soc., Chem. Commun.* **1992**, 474. (b) Thiele, K.-H.; Böhme, U.; Peters, K.; Peters, E.-M.; Walz, L.; von Schnering, H. *G. Z. Anorg. Allg. Chem.* **1993**, *619*, 771.