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Half-Sandwich Titanium Complexes Stabilized by a Novel Silsesquioxane Ligand: Soluble Model Systems for Silica-Grafted Olefin Polymerization Catalysts

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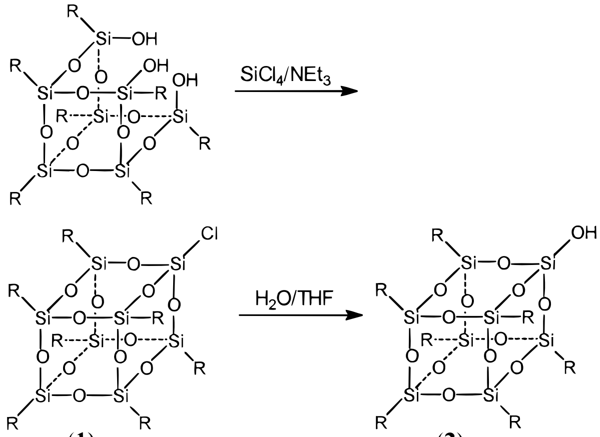
Summary: The cuboctameric silsesquioxane silanol (c-$C_5H_9)_7Si_8O_{12}(OH)$ has been applied as a model support for silica-grafted olefin polymerization catalysts. Complexes of the type $Cp''[(c\text{-}C_5H_9)_7Si_8O_{13}]TiX_2$ (Cp'' = 1,3-$C_5H_3(SiMe_3)_2$; X = Cl, CH_2Ph) form active α-olefin polymerization catalysts.

Heterogenization of well-defined homogeneous olefin polymerization catalysts gives the opportunity to combine the advantages of both supported and homogeneous catalysts such as morphology control and single active sites. The most common method to immobilize metallocene complexes consists of adsorption of the catalyst on a support that is pretreated with methylalumoxane (MAO) or other cocatalysts.[1] Alternatively, the catalyst can be tethered or directly grafted onto the oxidic support.[2,3] With regard to catalytic olefin polymerization, silica-grafted group 4 metal complexes of the type $[\equiv SiO]M(Cp)X_2$ (X = Cl, alkyl) are of interest. A major drawback, however, is that such heterogeneous metallasiliceous systems are very difficult to study.[4] The elegant work of Feher et al. has revealed that partially condensed silsesquioxanes can function as realistic model systems for silica supports,[5a] giving well-defined homogeneous metal complexes with reactivities that approach those of their silica-supported congeners.[5b]

We were looking for a simple yet realistic model for isolated silanol functionalities as found in partially dehydroxylated silica.[6,7] Here we report the synthesis and characterization of the cuboctameric silsesquioxane mono(silanol) (c-$C_5H_9)_7Si_8O_{12}(OH)$ and its use to model grafting of half-sandwich titanium complexes onto partially dehydroxylated silica. The titanasilsesquioxane complexes were subjected to olefin polymerization and leaching studies.

The reaction of (c-$C_5H_9)_7Si_7O_9(OH)_3$ with 1 equiv of $SiCl_4$ and 3 equiv of NEt_3 yields the chloro silsesquioxane (c-$C_5H_9)_7Si_8O_{12}Cl$ (**1**; eq 1),[8] which upon hydrolysis in a (2:1) THF/H_2O mixture (reflux, 48 h) provides the mono(silanol) (c-$C_5H_9)_7Si_8O_{12}(OH)$ (**2**; eq 1) in high yield.



(**1**) (**2**) (1)

Silanol **2** is an interesting model system to mimic isolated silanol sites in partially dehydroxylated silica. Its high (C_{3v}) symmetry reduces the formation of isomers and significantly facilitates NMR studies. Fur-

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[1] For example see: (a) Kaminsky, W. *Macromol. Symp.* **1995**, *89*, 203. (b) Soga, K.; Nozawa, A. H.; Uozumi, T. *Macromol. Symp.* **1995**, *97*, 53. (c) Collins, S.; Kelly, W. M.; Holden, D. A. *Macromolecules* **1993**, *26*, 4712. (d) Ko, Y. S.; Han, T. K.; Park, J. W.; Woo, S. I. *Macromol. Rapid Commun.* **1996**, *17*, 749. (e) Chien, J. C. W.; He, D. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1603.

[2] For example see: (a) Arai, T.; Ban, H. T.; Uozumi, T.; Soga, K. *Macromol. Chem. Phys.* **1997**, *198*, 229. (b) Lee, D.-H.; Yoon, K.-B.; Noh, S.-K. *Macromol. Rapid Commun.* **1997**, *18*, 427. (c) Iiskola, E. I.; Timonen, S.; Pakkanen, T. T.; Härkki, O.; Lehmus, P.; Seppälä, J. V. *Macromolecules* **1997**, *30*, 2853.

[3] (a) Uozumi, T.; Toneri, T.; Soga, K. *Macromol. Rapid Commun.* **1997**, *18*, 9 and references therein. (b) Xu, J.; Zhao, J.; Fan, Z.; Feng, L. *Macromol. Rapid Commun.* **1997**, *18*, 875. (c) Quignard, F.; Lecuyer, C.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1153. (d) Dufaud, V.; Basset, J.-M. *Angew. Chem.* **1998**, *110*, 848.

[4] (a) Delannay, F., Ed. *Characterization of Heterogeneous Catalysts*; Marcel Dekker: New York, 1984. (b) Tamura, K., Ed. *Dynamic Heterogeneous Catalysis*: Academic Press: New York, 1978. (c) Delgass, W. N.; Haller, G. L.; Kellerman, R.; Lunford, J. H. *Spectroscopy in Heterogeneous Catalysis*; Academic Press: New York, 1979.

[5] (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (b) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239.

[6] Basset and co-workers have demonstrated that partially dehydroxylated silica is a well-suited supporting material for early-transition-metal alkyl and hydrido complexes. For example see: (a) Lecuyer, C.; Quignard, F.; Choplin, A.; Olivier, D.; Basset, J.-M. *Angew. Chem.* **1991**, *103*, 1692. (b) Quignard, F.; Lecuyer, C.; Bougault, C.; Lefebvre, F.; Choplin, A.; Olivier, D.; Basset, J.-M. *Inorg. Chem.* **1992**, *31*, 928. (c) Vidal, V.; Théolier, A.; Thiovolle-Cazat, J.; Basset, J.-M.; Corker, J. *J. Am. Chem. Soc.* **1996**, *118*, 4595. (d) Rosier, C.; Niccolai, G. P.; Basset, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 12408.

[7] A detailed study concerning the suitability of silanols Ph_3SiOH and (c-$C_5H_9)_3Si_8O_{12}(OH)$ (**2**) will be discussed elsewhere: Duchateau, R.; Cremer, U.; Harmsen, R.; Mohamud, S. I.; Abbenhuis, H. C. L.; van Santen, R. A.; Thiele, S. K.-H.; van Tol, M. F. H. Manuscript in preparation.

[8] The preparation of **1** is similar to that for the corresponding cyclohexyl-substituted [(c-$C_6H_{11})_7Si_8O_{12}(Cl)$]: Feher, F. J.; Weller, K. J.; Schwab, J. J. *Organometallics* **1995**, *14*, 2009.

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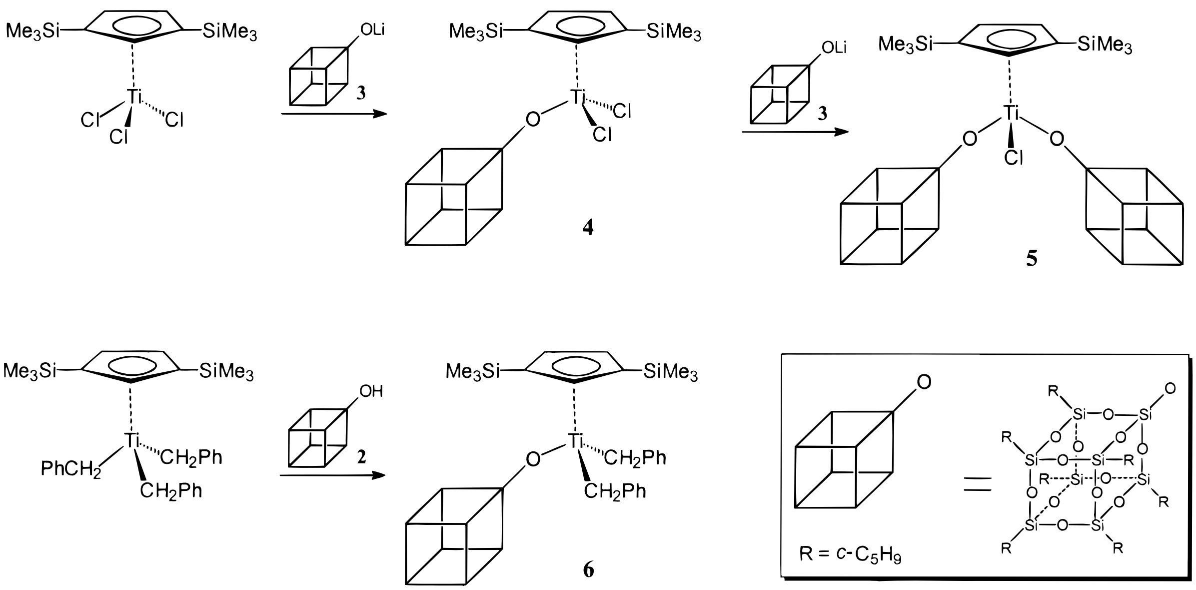
Scheme 1



thermore, the cubic silsesquioxane framework of **2** is less susceptible toward dehydration or cleavage/polymerization by nucleophilic reagents than the open structure of partially condensed silsesquioxanes $R_7Si_7O_9(OSiMe_3)_x(OH)_{3-x}$ (R = *c*-C_5H_9, *c*-C_6H_{11}; $x = 0-2$).[9] Whereas for $R_7Si_7O_9(OSiMe_3)_x(OH)_{3-x}$ only stable thallium and stibonium salts could be isolated,[9] deprotonation of **2** with an equimolar amount of *n*-BuLi (hexane, 25 °C) affords the stable silsesquioxane lithium salt [(*c*-$C_5H_9)_7Si_8O_{13}$]Li (**3**; eq 2).

$$\underset{(\mathbf{2})}{(C_5H_9)_7Si_8O_{12}(OH)} \xrightarrow[\text{Hexane}]{\text{BuLi}} \underset{(\mathbf{3})}{[(C_5H_9)_7Si_8O_{13}]Li} \qquad (2)$$

In $CDCl_3$, the cuboctameric silsesquioxane species (**1**–**3**) display simple yet particularly informative ^{13}C and ^{29}Si NMR spectra consistent with the C_{3v} symmetry of the silsesquioxane ligand: well-resolved sets of C*H* methine and silicon resonances are observed.[10] Not unexpectedly, the ^1H NMR spectra are much less informative, due to the large number of different CH_2 and C*H* protons present.

The room-temperature reaction of Cp″$TiCl_3$ (Cp″ = 1,3-$C_5H_3(SiMe_3)_2$) with an equimolar amount of [(*c*-$C_5H_9)_7Si_8O_{13}$]Li (**3**) in hexane affords Cp″[(*c*-$C_5H_9)_7Si_8O_{13}$]$TiCl_2$ (**4**; 51%) as a bright yellow microcrystalline material after repeated recrystallization from hexane (Scheme 1). Independent of the reaction temperature (−30 °C, reflux) and solvent (hexane, toluene, ether, THF) used, small amounts (^1H NMR, ~10%) of Cp″[(*c*-$C_5H_9)_7Si_8O_{13}]_2$TiCl (**5**) were also formed. Compound **5** could selectively be prepared by salt metathesis of Cp″$TiCl_3$ with 2 equiv of **3** in hexane at 25 °C (Scheme 1). Despite its high solubility, which prevented crystallization, the excellent selectivity of this reaction allows the isolation of analytically pure **5** as a bright yellow foam after evaporation of the hexane. For the mono(silsesquioxane) species **4**, the $^{13}C\{^1H\}$ NMR spectrum displays one resonance (δ 22.12 ppm) for all seven methine (*C*H) carbons. On the other hand, the bis(silsesquioxane) complex **5** shows a well-resolved set of methine *C*H resonances (δ 22.26, 22.21, 22.11 ppm; 1:3:3 ratio), in agreement with the C_{3v} symmetry of the silsesquioxane ligand. ^{29}Si NMR proves to be a very useful tool for the characterization of these silsesquioxane complexes, as the sensitivity is high enough to distinguish between very similar complexes (such as **4** and **5**) and integrated relative intensities are in good agreement with the expected stoichiometries. For compound **4**, the ^{29}Si NMR spectrum displays four resonances in a 2:3:4:1 ratio, whereas for **5** the ratio of the four signals observed is 1:3:4:1. The Cp–*Si*Me_3 resonances are found at −5.63 ppm for **4** and at −6.54 ppm for **5**. The alkyl-substituted silsesquioxane silicon atoms, $(\equiv O)_3Si(C_5H_9)$, show two resonances in a 3:4 ratio (**4**, −65.92, −66.66 ppm; **5**, −65.99, −66.54 ppm). Three of the seven silicon atoms, probably the ortho Si closest to the metal, are clearly distinct from the other four, resulting in two resonances with the observed relative intensities of 3:4. Finally, the resonances of the silicon atoms surrounded by four oxygen atoms have characteristic chemical shifts of −111.76 ppm (**4**) and −111.25 ppm (**5**), respectively.

Despite several attempts, we were not able to cleanly replace the chlorides in complexes **4** and **5** with alkyl substituents. None of the alkylating agents used (MeLi, MeMgCl, Me_2Zn, $PhCH_2MgCl$) gave well-defined products. However, titanasilsesquioxane alkyl complexes could conveniently be prepared by protolysis reactions. For example, the reaction of Cp″$Ti(CH_2Ph)_3$ with silanol **2** (hexane, 0 °C) resulted in selective substitution of one of the benzyl groups, affording the mono(silsesquioxane) complex Cp″[(*c*-$C_5H_9)_7Si_8O_{13}$]$Ti(CH_2Ph)_2$ (**6**; Scheme 1) in moderate yield. Introduction of a second silsesquioxane ligand failed. Heating, necessary for the reaction between **6** and (*c*-$C_5H_9)_7Si_8O_{12}$(OH) (**2**) to proceed, resulted exclusively in thermolysis. This is in

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[9] (a) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3859. (b) Feher, F. J.; Rahimian, K.; Budzichowski, T. A.; Ziller, J. W. *Organometallics* **1995**, *14*, 3920.

[10] ^{13}C NMR (ppm): **1**, 27.23, 27.18, 26.99, 26.90 (*C*H_2 C_5H_9), 22.12, 22.05, 21.85 (*C*H C_5H_9, 1:3:3 ratio); **2**, 27.25, 26.98, 26.92 (*C*H_2 C_5H_9), 22.17, 22.12, 22.05 (*C*H C_5H_9, 1:3:3 ratio); **3**, 27.37, 27.29, 27.01 (*C*H_2 C_5H_9), 22.26, 22.21, 22.09 (*C*H C_5H_9, 1:3:3 ratio). ^{29}Si NMR (ppm): **1**, −66.28, −66.85, −66.98, −90.20 (3:3:1:1 ratio); **2**, −63.48, −64.18, −97.75 (4:3:1 ratio).

contrast with the reaction between Cp″$TiCl_3$ and 2 equiv of **3**, which quantitatively yields the bis(silsesquioxane) complex Cp″$[(c\text{-}C_5H_9)_7Si_8O_{13}]_2TiCl$ (**5**). The NMR (^1H and ^{13}C, benzene-d_6; ^{29}Si, toluene) spectra of **6** show roughly the same features as observed for the corresponding dichloro compound **4**. For example, only one resonance (22.78 ppm) is observed for all seven methine *C*H carbon atoms of the silsesquioxane ligand and the ^{29}Si NMR spectrum of **6** displays four resonances in the expected 2:3:4:1 ratio (Cp−*Si*Me_3, −7.98; $(\equiv O)_3SiC_5H_9$, −66.22, −6.70; $(\equiv O)_4Si$, −111.53 ppm). The methylene protons (TiC*HH′*) in **6** are diastereotopic, giving an AB spin system (3.48, 2.16 ppm, $^2J_{H-H} = 10$ Hz) in the ^1H NMR spectrum. The methylene (Ti*C*H_2) carbon appears as a triplet at 86.82 ppm ($^1J_{C-H} = 127$ Hz), virtually identical with the Ti*C*H_2 resonance (86.15 ppm) in Cp″$[Ph_3SiO]Ti(CH_2Ph)_2$[7] and very similar to the Ti*C*H_2 resonance (83.85 ppm) in (TCP)$Ti(CH_2Ph)_2$ (TCP = 2-(tetramethylcyclopentadienyl)-4-methylphenoxo).[11] The normal chemical shift and $^1J_{C-H}$ value of the Ti*C*H_2 group, in combination with the absence of a high-field shift of benzyl ortho phenyl protons, excludes significant η^2-bonding of the benzyl groups in **6**.[12]

Preliminary olefin polymerization experiments of the described titanasilsesquioxane complexes have been carried out. In combination with methylalumoxane (MAO), a toluene solution of Cp″$[(c\text{-}C_5H_9)_7Si_8O_{13}]TiCl_2$ (**4**) generates an active ethylene polymerization catalyst which continues until gelation of the solution prevents further uptake of ethylene.[13] The observation that a toluene solution of Cp″$[(c\text{-}C_5H_9)_7Si_8O_{13}]_2TiCl$ (**5**) and MAO[13] produces a comparably active ethylene polymerization catalyst (5.7 kg PE/(mmol of Ti h) clearly demonstrates the poor stability of titanium siloxy bonds toward aluminum alkyls.[14] The facile activation of **5** gives rise to some doubt about the stability of reported metallasilsesquioxanes[15] and corresponding silica-grafted systems[1,3] that are used as olefin polymerization catalysts in combination with aluminum alkyls. This assumption is supported by a study of Feher et al., who demonstrated that V−O bonds in the vanadasilsesquioxane $[(c\text{-}C_6H_{11})_7Si_7O_{12}]V{=}O$ are effectively split by aluminum alkyls.[15b]

The high affinity of aluminum alkyls for the silsesquioxane oxofunctionalities makes them unsuitable as cocatalysts/scavangers for silsesquioxane complexes and corresponding silica-grafted olefin polymerization catalysts. Alternatives for aluminum alkyls as cocatalyst are cation-generating boron reagents such as $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ in combination with the transition-metal bis(alkyl) precursors. Treatment of the bis(benzyl) complex **6** with $B(C_6F_5)_3$ (2 equiv) in toluene results in an active olefin polymerization catalyst. Ethylene was polymerized rapidly (7.3 kg PE/(mmol of Ti h)), and over a period of several hours 1-hexene was transformed into atactic poly-1-hexene ($M_w = 2900$, $M_w/M_n = 2.0$).[16] To test whether $B(C_6F_5)_3$ is capable of substituting silsesquioxane ligands, ^{19}F NMR studies were carried out on solutions of **5** and **6** with $B(C_6F_5)_3$. As expected, the ^{19}F NMR spectrum of **5** + $B(C_6F_5)_3$ (4 equiv) exclusively showed unreacted $B(C_6F_5)_3$, whereas the ^{19}F NMR spectrum of **6** + $B(C_6F_5)_3$ (4 equiv) showed $[PhCH_2B(C_6F_5)_3]^-$ [17] as the only boron species besides unreacted $B(C_6F_5)_3$. Hence, unlike MAO, $B(C_6F_5)_3$ does not abstract silsesquioxane ligands, which gives rise to promising perspectives for silica-supported analogues of **6** when they are activated with boron-based cocatalysts. A full account of our efforts to mimic silica-grafted systems, using early-transition-metal siloxy and silsesquioxane complexes, will be reported in due course.

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Supporting Information Available: Text giving experimental details for the preparation of **1**−**6** and for the ethylene and 1-hexene polymerization experiments and a table giving ^1H, $^{13}C\{^1H\}$, and ^{29}Si NMR data (6 pages). Ordering information is given on any current masthead page.

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(11) Chen, Y.-X.; Fu, P.-F.; Stern, C.; Marks, T. J. *Organometallics* **1997**, *16*, 5958.

(12) For example see: (a) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (b) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (c) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235 and references therein.

(13) Conditions for the polymerization experiments: catalyst, 20 μmol; MAO, 30 mmol; ethylene, 5 atm; $V = 75$ mL of toluene; $T = 25$ °C; time, 5 min.

(14) This is not very surprising, since $CpTi(OBu)_3$/MAO is a known styrene polymerization catalyst: Chien, J. C. W.; Salajka, Z. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1253.

(15) (a) Liu, J.-C. *J. Chem. Soc., Chem. Commun.* **1996**, 1109. (b) Feher, F. J.; Blanski, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 5886. (c) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614.

(16) As expected, without cocatalyst ($B(C_6F_5)_3$) **6** is inactive in olefin polymerization.

(17) The large $\Delta\delta(F_m-F_p)$ value of 4.0 ppm indicates that the $[PhCH_2B(C_6F_5)_3]^-$ anion is coordinated to the titanium cation: (a) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (b) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.