

# Incompletely Condensed Silsesquioxanes: Versatile Tools in Developing Silica-Supported Olefin Polymerization Catalysts

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Robbert Duchateau (born 1966) grew up in Groningen, The Netherlands. After attending the University of Groningen, where he received his B.S. in chemistry in 1989, he joined the group of Prof. S. Gambarotta at the University of Ottawa (Canada) for one year, where he worked on low-valent titanium chemistry. He then returned to The Netherlands, where he did his Ph.D. on "Ancillary Ligand Effects in Organoyttrium Chemistry" in the group of Prof. J. H. Teuben at the University of Groningen. He continued his academic career by joining the group of Prof. M. Bochmann at the University of Leeds (U.K.) for one year as a postdoc working on zwitterionic olefin polymerization catalysts. In 1996 he went to the catalysis group of Prof. R. A. van Santen at the Eindhoven University of Technology to work as a research associate on immobilization of homogeneous olefin polymerization catalysts and silsesquioxane chemistry. Since July 2002, Duchateau has been an assistant professor in the polymer chemistry group of Prof. C. E. Koning at the Eindhoven University of Technology and is building his own research group, developing new catalytic routes to engineering plastics and resins from basic (renewable) feedstocks.

## I. Introduction

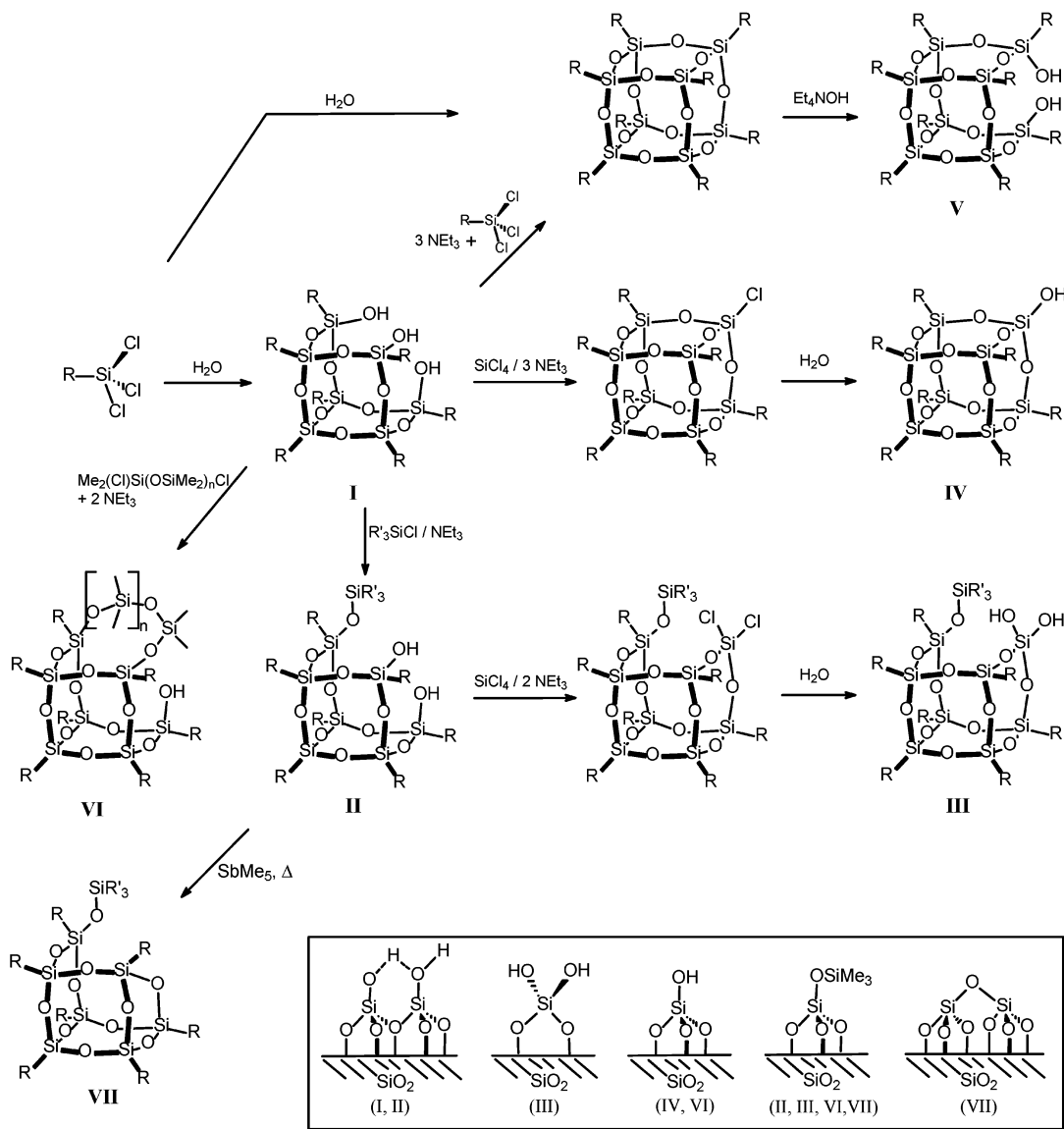
For 40 years, the industrial production of polyolefins has mainly been based on classical heterogeneous (Ziegler–Natta- and Phillips-type) catalysts. Only during the past decade have metallocene, constrained geometry, and related olefin polymerization catalysts been developed to a point that they can be commercialized.<sup>1–18</sup>

In the currently applied gas-phase and slurry processes,<sup>1–3</sup> solid catalyst particles of appropriate size and shape are required as these catalyst particles serve as templates for the growing polymer particles. If performed well, each single catalyst particle will grow into a polymer particle with the same morphology, and additionally this template function will suppress reactor fouling.<sup>13–16</sup> Hence, when homogeneous catalysts are to be applied in the existing processes, they will have to be immobilized onto a support to give catalyst particles with the required properties. Catalyst immobilization has become an important but difficult issue in modern olefin polymerization catalysis.<sup>13–16</sup> Catalyst leaching, resulting in bad polymer morphology and reactor fouling, and loss of activity are persistent problems.<sup>14–18</sup> Improvement of immobilization techniques remains therefore a topic of great importance.

The nearly universal choice of support for heterogeneous olefin polymerization catalysts is amorphous silica gel,<sup>14,19</sup> it has a high surface area, good morphology and fragmentation properties, and silanol functionalities to anchor the catalyst. Molecular properties of silicas are strongly affected by the nature of their surface sites. The unsaturated surface valencies are satisfied by surface hydroxyl functionalities, which, depending on the calcination temperature, exist in more or less extent as *vicinal* (hydrogen-bonded silanols), *geminal* (two silanol groups attached to the same silicon atom), or *isolated* (no hydrogen bonds possible) silanol sites (Scheme 1).<sup>20,21</sup>

The molecular structure of the supported catalysts is a key step for the understanding of the rules governing the stability and reactivity of the system. However, detailed studies on porous silicious materials and zeolites as well as the supported catalysts thereof are considerably hampered by the heteroge-

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**Scheme 1. Synthesis of Various Silsesquioxanes and the Surface Silanol and Siloxide Sites They Represent**


neity of these systems. The molecular properties are best studied by a combination of physical and chemical methods such as IR, Raman, Mössbauer, and NMR spectroscopy as well as EXAFS, XANES, and XPS. However, these techniques are bulk measurements, and their sensitivity is often inadequate to obtain accurate data of the various sites that are present on the surface in low concentration.

To gain more insight at a molecular level into the interaction of catalyst precursors with the surface and the structure and reactivity of the heterogeneous catalyst, suitable model systems are of great importance. By using the surface organometallic chemistry (SOMC) approach, developed by Basset et al.,<sup>22–24</sup> the groups of Basset, Choplin, and Scott synthesized relatively well-defined active surface sites with a uniform distribution and rather high concentration,<sup>25–30</sup> which has greatly contributed to the understanding of several heterogeneous catalytic processes. A good example for the success of this approach forms a recent study on supported (half)-

metallocene catalysts by surface organometallic chemistry.<sup>27</sup>

Another approach, which forms the subject of this review, uses homogeneous model systems with a coordination sphere equivalent to that of surface sites. The major advantage of such homogeneous models is that different complexes that possibly represent different surface sites can be studied one at a time using a wide range of powerful techniques such as multinuclear solution NMR spectroscopy and single X-ray diffraction. Several silanols, silanediols, and silanetriols have been applied as homogeneous models for silica surface silanol sites.<sup>31–36</sup> Incompletely condensed silsesquioxanes are probably the most realistic homogeneous model systems known to date for surface silanols as found in dehydroxylated amorphous silicas, mesoporous silicas (MCM-41), and (dealuminated) zeolites.<sup>37–54</sup> Roughly 10 years ago silsesquioxane chemistry started as an art. In the meantime, it has developed into a versatile tool to clarify various issues of supported catalysts. Krijnen

et al. assigned the IR vibrations of zeolite defects by comparing these absorptions with those of several silsesquioxane silanols.<sup>55</sup> Basset et al. recently used tin, tantalum, and boron silsesquioxane complexes in a comparative study with the corresponding silica-grafted systems.<sup>26,56,57</sup> Various heterogeneous catalytic processes such as alkene epoxidation,<sup>58–65</sup> metathesis,<sup>66–68</sup> and polymerization<sup>69–82</sup> have also been mimicked using metallasilsesquioxane complexes. A good example of the success of homogeneous model systems for heterogeneous catalysis is formed by titanasilsesquioxane complexes  $[R_7Si_7O_9]TiX$  ( $R = c-C_5H_9$ ,  $c-C_6H_{11}$ ;  $X =$  alkyl, alkoxide, amido, cyclopentadienyl)<sup>58–65</sup> that are active olefin epoxidation catalysts that very well resemble titanium sites in heterogeneous epoxidation catalysts such as TS-1 and titanium grafted onto MCM-41.

In this review, the usefulness and drawbacks of silsesquioxanes as model supports in developing silica-supported olefin polymerization catalysts will be discussed. It will be shown that homogeneous models can contribute to improve immobilization strategies and provide useful suggestions about the stability and reactivity of supported catalysts. However, their homogeneous nature also forms a clear disadvantage as it allows these systems to undergo consecutive reactions affording thermodynamically stable products.

## II. Incompletely Condensed Silsesquioxanes

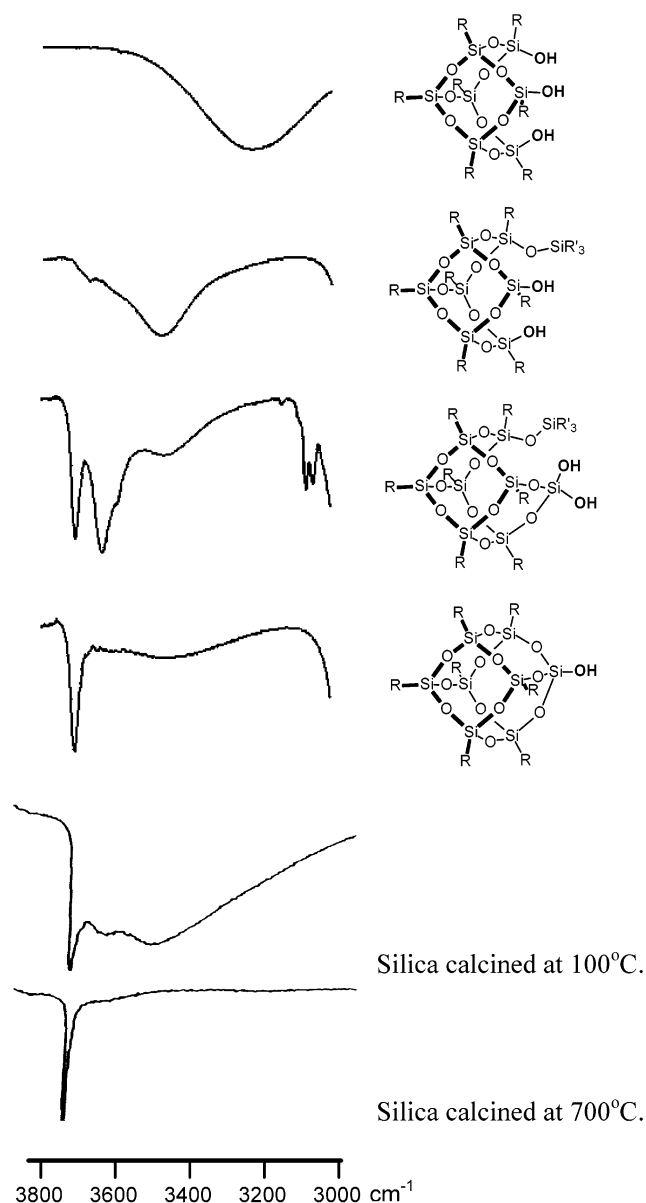
Silsesquioxanes is the general name for organosiloxide species with empirical formula  $(RSiO_{3/2})_n$  ( $R = H$ , hydrocarbon) and closely related compounds.<sup>83</sup> For these compounds irregular, ladder, and cage structures are known, of which the latter are the most familiar. These cage structures can be regarded as small three-dimensional pieces of silica as their oligomerization is sufficient to result in rigid structures that resemble, for example, crystalline forms of silica such as  $\beta$ -cristobalite or  $\beta$ -tridymite,<sup>39,84</sup> whereas their organic substituents allow solubility in the most common organic solvents.

Incompletely condensed silsesquioxanes have proven to be realistic homogeneous models for various surface silanol sites found in (partly dehydroxylated) amorphous and mesoporous silicas and (dealuminated) zeolites (Scheme 1).<sup>20,21,55</sup> The leading representative of these incompletely condensed silsesquioxanes is the trisilanol  $R_7Si_7O_9(OH)_3$  (**I**, Scheme 1). Although first reported by Brown et al.,<sup>37,38</sup> Feher and co-workers are synonymous for this silsesquioxane ligand.<sup>39–46,48–50</sup> Synthetic methodologies for silsesquioxane preparation are well-documented, and the general route consists of hydrolytic condensation of  $RSiCl_3$  precursors (Scheme 1). Feher and co-workers have carried out impressive work on both improving existing and developing new silsesquioxane syntheses. Recently, they reported an interesting route to incompletely condensed silsesquioxanes by either acid- or base-mediated splitting of one of the Si–O–Si edges of the fully condensed silsesquioxanes  $R_6Si_6O_9$  and  $R_8Si_8O_{12}$ .<sup>43–45,48–50</sup> In principle, incompletely condensed silsesquioxanes with a wide variety of organic substituents are available by this route. The ongoing research in silsesquioxane synthesis is

expected to result in a wide variety of incompletely condensed silsesquioxanes with various organic substituents.

As mentioned before, the leading representative of the incompletely condensed silsesquioxanes is the trisilanol  $R_7Si_7O_9(OH)_3$  (**I**, Scheme 1). It is a suitable model for vicinal silanol sites, abundantly present in hydroxylated amorphous and mesoporous silicas, and can be used to model, for example, silica-grafted species and the reaction of silica with silylating agents (e.g.,  $ClSiMe_3$ ,  $HN(SiMe_3)_2$ ),<sup>85,86</sup> other surface modifiers, and tethering groups (e.g.,  $XCH_2CH_2Si(OMe)_3$ ).<sup>87</sup> This trisilanol can be partially silylated to afford vicinal disilanol or isolated silanol (**II**, **VI**, Scheme 1),<sup>52–54</sup> similar to surface sites that are formed upon silylation of silica. In the search for simple yet realistic model compounds for isolated silanol functionalities as found in partially dehydroxylated silicas, the trisilanol  $R_7Si_7O_9(OH)_3$  was treated with  $SiCl_4$  in the presence of triethylamine to afford  $R_7Si_8O_{12}Cl$ , which was subsequently hydrolyzed to give the robust,  $C_3$ -symmetric silanol  $R_7Si_8O_{12}(OH)$  (**IV**, Scheme 1).<sup>47</sup> Geminal silsesquioxane siloxanediols  $R_7Si_7O_9(O_2Si(OH)_2)(OSiR'_3)$  (**III**, Scheme 1) could be obtained in a similar manner. Reacting the vicinal disilanol  $R_7Si_7O_9(OSiR'_3)(OH)_2$  (**II**, Scheme 1) with  $SiCl_4$  under basic conditions yielded the geminal siloxane dichlorides  $R_7Si_7O_9(O_2SiCl_2)(OSiR'_3)$ , which readily hydrolyze to form the geminal silsesquioxane siloxanediols.<sup>51</sup> Dependent on the dehydroxylation temperature applied, besides silanols, silica surfaces contain more or less siloxane functionalities,<sup>20,21</sup> which, when strained, can be quite reactive.<sup>26</sup> Strained siloxane functionalities in silsesquioxanes can also be obtained. Instead of heating, dehydroxylating agents (e.g.,  $SbMe_5$ ,  $O=PCl_3$ ,  $MoO_2Cl_2$ ) are often applied (**VII**, Scheme 1).<sup>35,39,53</sup>

Not only do incompletely condensed silsesquioxanes structurally resemble various silica surface silanol sites, but their electronic properties also proved to be compatible with those of silicas.<sup>52,74,88</sup> For example, the IR vibration bands of the isolated and vicinal silsesquioxane silanols correspond very well with the vibration bands of isolated and hydrogen-bonded hydroxyl groups in silica.<sup>20,21,51,55</sup> Silsesquioxanes containing vicinal trisilanol are capable of poly-hydrogen-bonding ( $\nu_{OH} \leq 3200\text{ cm}^{-1}$ , Figure 1), while silsesquioxanes containing vicinal disilanol and geminal siloxanediols give considerably less effective hydrogen bridging ( $\nu_{OH} \approx 3450\text{--}3650\text{ cm}^{-1}$ , Figure 1). Interestingly, the geminal siloxanediol gives two distinct OH stretching vibration bands at 3625 and 3699  $\text{cm}^{-1}$ ; one hydroxyl is bridging, while the other is isolated (Figure 1). The monosilanol ( $c-C_5H_9$ ) $_7Si_8O_{12}(OH)$  (**IV**, Scheme 1) shows a stretching vibration at 3706  $\text{cm}^{-1}$ , characteristic of an isolated silanol which is in line with the calculated difference of the OH-stretching vibrations of isolated and poly-hydrogen-bonded silanols ( $\Delta\nu_{OH} = 300\text{ cm}^{-1}$ ) and agrees with the observed difference in acidity of isolated silanols and silanol nests in zeolitic materials.<sup>51,55,74</sup> Whereas the weak Brønsted acidity of silica surface silanols rarely affects catalytic reactions directly, a proper understanding of their chemical



**Figure 1.** IR stretching vibrations of various silanols in solution ( $\text{CCl}_4$ ).

nature is essential for the preparation of silica-supported catalysts. Acidity measurements<sup>89</sup> showed that the vicinal trisilanol ( $c\text{-C}_5\text{H}_9$ )<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> is up to 3 orders of magnitude more acidic than the vicinal disilanol ( $c\text{-C}_5\text{H}_9$ )<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OSiR<sub>3</sub>)(OH)<sub>2</sub> (SiR<sub>3</sub> = SiMe<sub>3</sub>, SiMePh<sub>2</sub>) and the isolated silanol ( $c\text{-C}_5\text{H}_9$ )<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>(OH) (Table 1).<sup>51,55,74</sup> This difference in acidity results from the more effective hydrogen bonding in the trisilanol that allows better stabilization of the conjugated base.<sup>42,52</sup> The difference in

acidity of the trisilanol ( $c\text{-C}_6\text{H}_{11}$ )<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> and the disilanol ( $c\text{-C}_6\text{H}_{11}$ )<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OSiMe<sub>3</sub>)(OH)<sub>2</sub> was nicely demonstrated by Feher and co-workers, who found that silylation of ( $c\text{-C}_6\text{H}_{11}$ )<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> is 4 orders of magnitude faster than that of ( $c\text{-C}_6\text{H}_{11}$ )<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OSiMe<sub>3</sub>)(OH)<sub>2</sub>.<sup>51,52</sup> Table 1 shows IR stretching vibrations and  $\text{p}K_{\text{ip}}^{\text{(THF)}}$  values of a selected number of silsesquioxane silanols.<sup>51</sup>

### III. Hetero- and Metallasilsesquioxanes

During the past decade a wide variety of hetero-silsesquioxanes and metallasilsesquioxanes have been prepared and described in detail in the literature and in recent review articles.<sup>31–54,58–82,90–155</sup> Figure 2 gives an overview of the elements that have been applied in silsesquioxane chemistry. Some interesting metallasilsesquioxanes have been reported that represent surface sites in metal-supported silicates, zeolites, or clays that play an important role as heterogeneous catalysts or catalyst supports.

For example, boron, aluminum, and gallium silsesquioxane complexes are interesting models for metal sites in zeolites.<sup>144–149</sup> Spectroscopic (IR and NMR) data and DFT calculations showed that the aluminosilsesquioxane  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)]_2\text{-Al}\}^-\text{H}^+$  contains a strong intramolecular hydrogen bond. This complex proved to be a fairly realistic structural model for a Brønsted acidic aluminosilicate site in zeolite HY (Figure 3).<sup>144,145,156–158</sup> The corresponding Brønsted acidic boron and gallium silsesquioxanes, representing boron and gallium zeolite sites, were isolated as either the lithium or ammonium salt  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMePh}_2)]_2\text{M}\}^-\{\text{X}\}^+$  (M = B, X<sup>+</sup> = Li<sup>+</sup>; M = Ga, X<sup>+</sup> = HNET<sub>3</sub><sup>+</sup>; Figure 3).<sup>145,149,159</sup>

Recently, silsesquioxane-based iron and titanium complexes have been prepared as models for silica-supported oxidation catalysts (Figure 4).<sup>58–65,117–118</sup> Whereas the titanasilsesquioxanes proved to be active olefin epoxidation catalysts, the iron silsesquioxanes showed no activity in benzene oxidation with N<sub>2</sub>O. This implies that the local structure or stability of the active center of the iron silicate differs from that in the iron silsesquioxane complex,<sup>117,160</sup> while the local structure of the active titanium center in, e.g., TS-1 resembles the coordination sphere of the titanium in the titanasilsesquioxanes.<sup>58–65</sup>

### IV. Silsesquioxane-Based Olefin Polymerization Catalysts

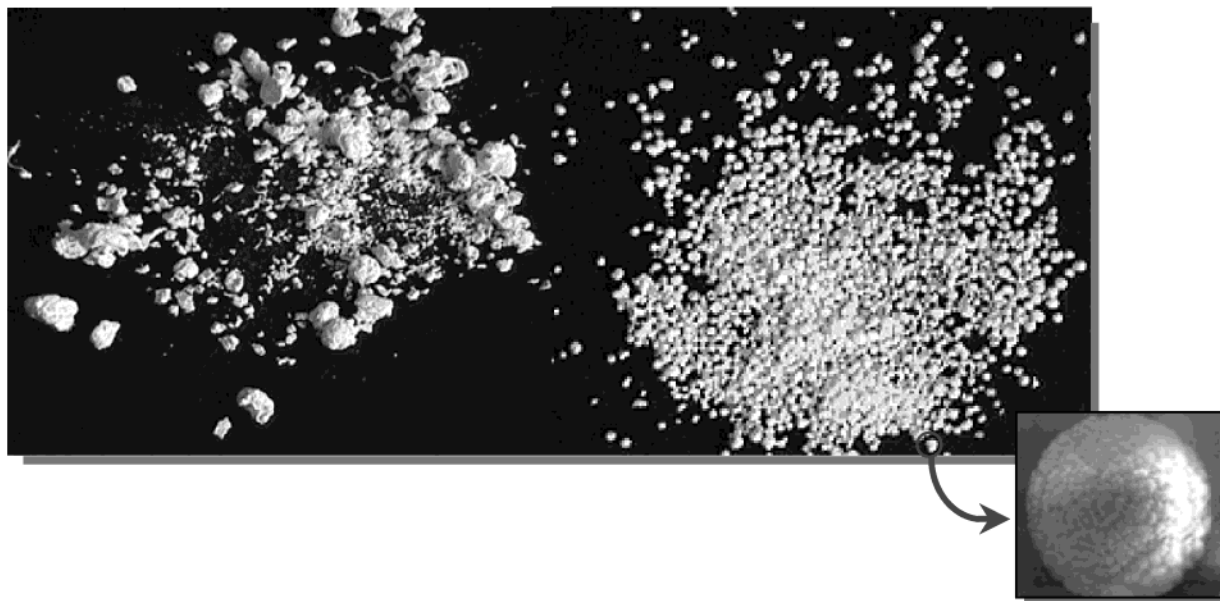
As already outlined in the Introduction, the existing slurry and gas-phase processes require heterogeneous olefin polymerization catalysts.<sup>1–18</sup> Morphol-

**Table 1.** Comparison of the Acidity of Vicinal, Geminal, and Isolated Silanol Groups

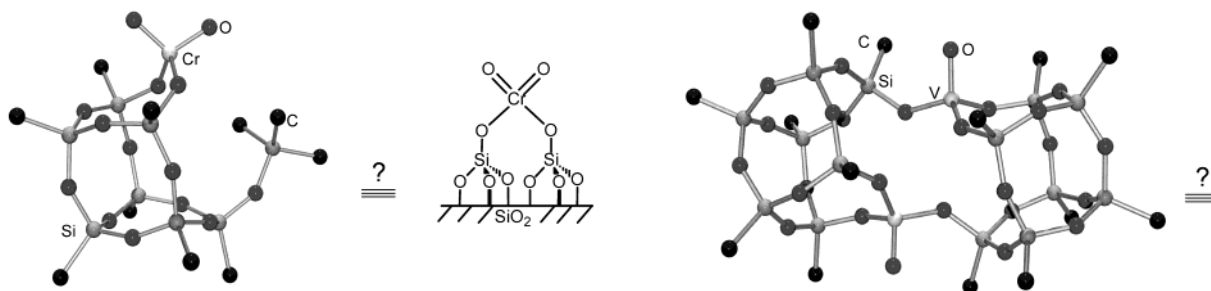
type of silanol	compound	$\text{p}K_{\text{ip}}^{\text{a}}$	IR (Nujol, $\text{cm}^{-1}$ ) $\nu_{\text{OH}}$	IR ( $\text{CCl}_4$ , $\text{cm}^{-1}$ ) $\nu_{\text{OH}}$
vicinal trisilanol	( $c\text{-C}_6\text{H}_{11}$ ) <sub>7</sub> Si <sub>7</sub> O <sub>9</sub> (OH) <sub>3</sub>	7.6 (±0.2)	3158	3217
vicinal disilanol	( $c\text{-C}_5\text{H}_9$ ) <sub>7</sub> Si <sub>7</sub> O <sub>9</sub> (OSiMe <sub>3</sub> )(OH) <sub>2</sub>	9.5 (±0.1)	3261	3471
geminal siloxanediol	( $c\text{-C}_5\text{H}_9$ ) <sub>7</sub> Si <sub>7</sub> O <sub>9</sub> (OSiMePh <sub>2</sub> ) <sub>2</sub> Si(OH) <sub>2</sub>	9.7 (±0.3)	3582, 3438	3699, 3625
isolated monosilanol	( $c\text{-C}_5\text{H}_9$ ) <sub>7</sub> Si <sub>8</sub> O <sub>12</sub> (OH)	8.9 (±0.4)	3706	3700

<sup>a</sup>  $\text{p}K_{\text{ip}}$  averages of two indicators, deviation in parentheses.





**Figure 5.** Polyethylene particle morphology prepared by (left) a homogeneous and (right) a supported metallocene catalyst.



**Figure 6.** Molecular structure of  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)]\text{-CrO}_2^{159}$  and a schematic presentation of a possible corresponding surface structure.

activity of the thus formed catalyst is sensitive to the amount of  $\text{AlMe}_3$  used to generate the active species and is the highest when 2 equiv of  $\text{AlMe}_3$  per silsesquioxane chromate is employed. The molecular weights of the polymer were in the range  $M_w = 61000\text{--}377000$  with  $M_w/M_n = 3.5\text{--}6.1$ , suggesting that more than one active catalyst is present in this system. No details about the molecular structure of the actual catalytically active site(s) in this homogeneous model system have been reported.<sup>69</sup> The silsesquioxane chromate seems to be a realistic model for a silica-supported chromate site. However, since the activation behaviors of the real Phillips catalyst and the silsesquioxane chromate are quite different, comparison of this homogeneous system with the actual active Phillips catalyst should be done with some reservations.

Another olefin polymerization precatalyst that is related to the silsesquioxane chromate is the vanadyl silsesquioxane complex  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{V}=\text{O}\}_n$  ( $n = 1, 2$ ; Figure 7), which exists in both monomeric and dimeric form.<sup>70–72</sup> After activation with 1–5 equiv of  $\text{AlMe}_3$ , ethylene (1 atm) is polymerized to yield polyethylene with an  $M_w$  of 48000 and a narrow molecular weight dispersity  $M_w/M_n$  of 2.3, indicating that this is a truly single-sited catalyst system.<sup>72</sup> Different olefins could also be polymerized or copolymerized. The activity for propene was rather low



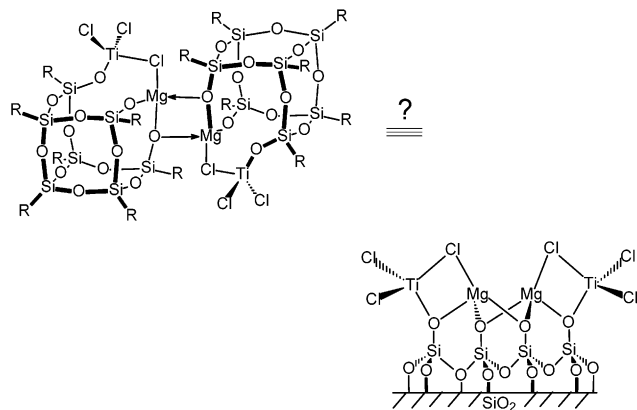
**Figure 7.** Molecular structure of  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{V}=\text{O}\}_2^{159}$  and a schematic presentation of a possible corresponding surface structure.

(25 °C, 3 bar, 3 h) and gave low molecular weight atactic polypropene ( $M_w < 10^4$ ). Copolymerization of propene (neat) and ethylene (1%) gave small amounts of polymer containing 5–10% propene units. On the other hand, 1,3-butadiene was readily polymerized to mainly *trans*-polybutadiene. Similar to that of the silsesquioxane chromate, the activity of the vanadium catalyst is sensitive to the amount of  $\text{AlMe}_3$  used, and the highest activity was observed when 3 equiv of  $\text{AlMe}_3$  was used as cocatalyst. Elegant mechanistic studies on the interaction of  $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$  with the vanadyl silsesquioxane indicated a stepwise alkylation of the vanadium by the aluminum alkyl that leads to the active aluminum–vanadium–silsesquioxane species, the first well-defined silsesquioxane-based olefin polymerization catalyst.<sup>72</sup>

In contrast to the activity exhibited by the silsesquioxane chromate and vanadyl complexes, simple siloxy analogues such as  $(\text{Ph}_3\text{SiO})_2\text{CrO}_2$ ,  $\{[\text{O}(\text{OSiPh}_2)_2]_2\text{Cr}(\text{=O})_2\}_2$ , and  $(\text{Ph}_3\text{SiO})_3\text{V}=\text{O}$  show little or no activity toward olefins in the presence

of  $\text{AlMe}_3$ .<sup>161,162</sup> Although the interaction of  $(\text{Ph}_3\text{SiO})_n$ - $(\text{Me}_3\text{SiCH}_2)_{3-n}\text{V}=\text{O}$  with  $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$  was found to be very similar to that of  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{V}=\text{O}$ , none of the aluminum alkyl-activated triphenylsiloxy complexes gave particularly active catalysts, and rapid deactivation was observed as well. This clearly indicates the difference between silsesquioxanes and simple (di)silanol.

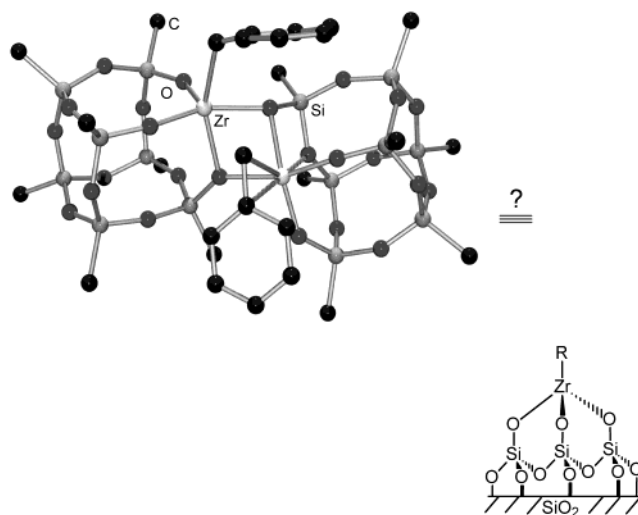
Recently, a silsesquioxane-based catalyst system was reported that could be regarded as a homogeneous model for a Ziegler–Natta-type catalyst.<sup>73</sup> Like the heterogeneous system it serves as a model for, the precatalyst  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{MgTiCl}_3]_n$  ( $n = 1, 2$ ; Figure 8) can be activated with  $\text{AlEt}_3$  to give an active



**Figure 8.** Proposed structure of  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{MgTiCl}_3]_2$  and a schematic presentation of a possible corresponding surface structure.

ethylene polymerization catalyst. This system was reported to be more active in ethylene polymerization than its heterogeneous congener, which makes it an interesting catalytic system. The high molecular weight dispersity of the polyethylene ( $M_w = 140000$ ,  $M_w/M_n = 5.5$ ) indicates the presence of multiple active sites. No further study on the nature of the catalytically active species was reported.<sup>73</sup> The bimetallic magnesium/titanium silsesquioxane complex reported by Liu is possibly a good model for a Ziegler–Natta-type precatalytic site. However, the fact that upon activation this single homogeneous complex yields multiple active sites raises some questions about how closely the active site in this homogeneous system resembles the actual active Ziegler–Natta catalyst.

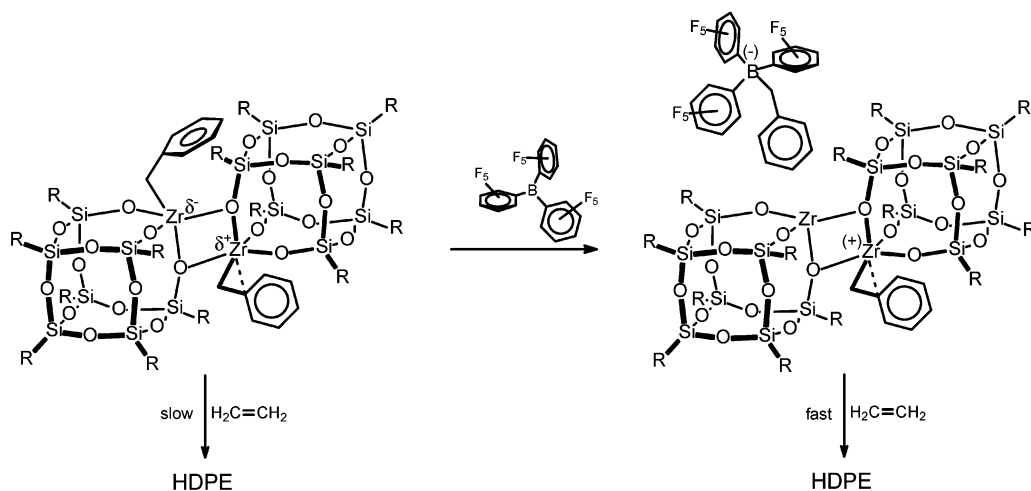
Oxide-supported zirconium alkyl and hydride species such as the  $\text{ZrR}_4/\text{SiO}_2$  system prepared by Basset et al.<sup>22–26,28,163–166</sup> and the  $\text{ZrR}_4/\text{Al}_2\text{O}_3$  system developed by Ittel et al.<sup>167,168</sup> proved to be interesting olefin polymerization catalysts. Thorough studies on the molecular structure of the silica-supported zirconium system revealed that the active site consists of a zirconium hydride bonded to three siloxy functionalities. Attempts to mimic this surface species by reacting the cyclopentyl-substituted trisilanol  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$  with an equimolar amount of  $\text{Zr}(\text{CH}_2\text{Ph})_4$  resulted in a dimeric zirconium benzyl complex,  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{ZrCH}_2\text{Ph}\}_2$  (Figure 9).<sup>75</sup> NMR spectroscopy demonstrated that the complex is also dimeric in solution. The formation of such a



**Figure 9.** Molecular structure of  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{ZrCH}_2\text{Ph}\}_2$ <sup>159</sup> and a schematic presentation of the surface structure it should represent.

dimeric structure is a typical example of consecutive aggregation homogeneous systems can undergo to form a thermodynamically stable structure. Consequently, comparing these dimeric models with silica-grafted zirconium hydride species should be met with great care. Nevertheless, like the silica-grafted zirconium hydride system, this dimeric zirconium complex is an active olefin polymerization catalyst, even without the need of additional cocatalyst! The activity of this neutral complex was explained by the peculiar dimeric structure of this zirconium silsesquioxane complex, in which one of the zirconium atoms acts as an adjacent Lewis acid activating the other zirconium. This compares well with the fact that zirconium hydride supported on silica doped with Lewis acidic aluminum sites showed enhanced activity compared to the all-silica system.<sup>165</sup>

The proposed synergic effect of the two zirconium centers in the dimeric structure is intensified when one of the benzyl groups of the dimer is abstracted by a strongly Lewis acidic borane,  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 2).<sup>75</sup> For the thus formed cationic monobenzyl dimer, an increase in ethylene polymerization activity of over 2 orders of magnitude was observed (2400 g of PE/mmol·h) compared to that of the neutral dimer (10 g of PE/mmol·h). With such activity, this complex is not only a model for oxide-supported zirconium species, but also an interesting catalyst itself. The  $M_w/M_n$  of 2.3 ( $M_w = 6600$ ) indicates that the catalyst is truly single-sited. The analogous hafnium complex  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{HfCH}_2\text{Ph}\}_2$  showed a very similar behavior. Whereas the complex itself is a poorly active ethylene polymerization catalyst (<10 g of PE/mmol·h), addition of  $\text{B}(\text{C}_6\text{F}_5)_3$  as cocatalyst resulted in an impressive increase in catalyst activity (4800 g of PE/mmol·h). Both complexes showed no activity toward higher olefins. The corresponding titanium silsesquioxane compound  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{TiCH}_2\text{Ph}$  proved to be monomeric in solution, and its structure resembles more the above-mentioned silica-supported zirconium hydride system; however, it showed no ethylene polymerization activity.

**Scheme 2. Accelerating Effect on Ethylene Polymerization by  $B(C_6F_5)_3$ -Induced Benzyl Abstraction**

**B. Supported Homogeneous Single-Site Catalysts**

Although metallocenes are among the most versatile olefin polymerization catalysts known to date, their commercial use is limited by their homogeneous nature.<sup>1–18</sup> To improve the polymer particle morphology and to solve the reactor-fouling problem, heterogenization of such well-defined homogeneous olefin polymerization catalysts is crucial for industrial applications.<sup>6–18,169–183</sup> Here we will discuss the three most commonly used methods to immobilize homogeneous olefin polymerization catalysts, being grafting and tethering of the catalyst precursor and immobilization of the catalyst by electrostatic interaction with the supported cocatalyst.

**1. Grafting of Catalyst Precursors**

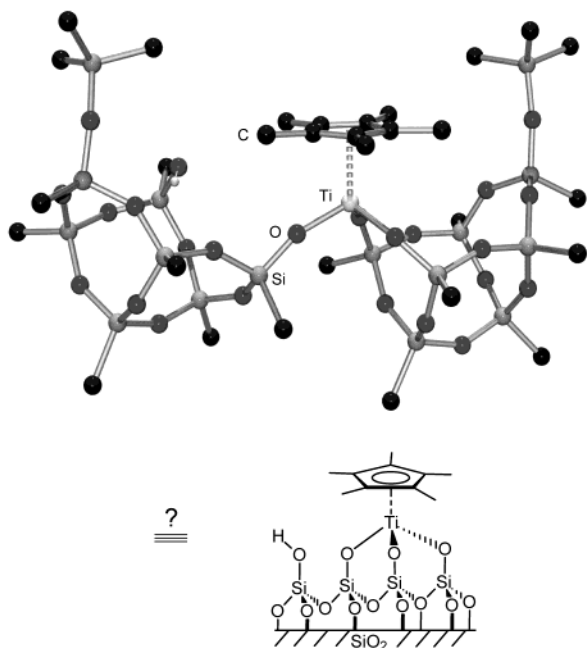
The earliest immobilization methods consisted of grafting metallocenes and half-sandwich complexes onto partly dehydroxylated silica. To activate these systems, they were subsequently treated with MAO solutions. Activities were low, and leaching proved to be a serious problem. In view of this immobilization technique, the interaction of silica surface silanols with metallocenes and half-sandwich compounds is of great importance, and silica-grafted species of the type  $[SiO_2]-O-M(Cp)X_2$  ( $X = \text{chloride, alkyl}$ ), containing two chloride or alkyl substituents, are of interest. Recently Basset et al. used surface organometallic chemistry to study the synthesis, characterization, and olefin polymerization activity of (half)metallocenes grafted onto oxidic supports.<sup>27</sup> Studies on the synthesis, characteristics, and reactivity of the corresponding homogeneous model complexes have also been carried out to contribute to the better understanding of such heterogeneous catalysts.

Maschmeyer and co-workers investigated the interaction of the silsesquioxane trisilanol  $(c-C_6H_{11})_7Si_7O_9(OH)_3$  with the group 4 metal complexes  $Cp_2MCl_2$  and  $CpMCl_3$  ( $M = Ti, Zr, Hf$ ) under basic conditions.<sup>102</sup> For titanium, two chlorides and one of the cyclopentadienyls are protonolyzed, yielding both monomeric and dimeric complexes with general formula  $\{[(c-C_6H_{11})_7Si_7O_{12}]TiCp\}_n$  ( $n = 1, 2$ ). For the heavier congeners Zr and Hf, both cyclopentadienyl groups are substituted and complicated structures

containing  $[(c-C_6H_{11})_7Si_7O_{12})_4M_3Cl]^-$  fragments have been proposed. Clearly, not only the chloride but also the cyclopentadienyl substituents were readily protonolyzed by the silsesquioxane silanols. Edelmann recently reported that the reaction of  $Cp_2TiCl_2$  and  $Cp^*TiCl_2$  with  $(c-C_6H_{11})_7Si_7O_9(OH)_2OSiMe_3$  in the presence of a base resulted in partial loss of cyclopentadienyl ligands and formation of  $\mu$ -oxo complexes of the types  $(\mu-O)[(c-C_6H_{11})_7Si_7O_{11}(OSiMe_3)TiCp]_2$  and  $Cp^*Ti_3O_3[(c-C_6H_{11})_7Si_7O_{11}(OSiMe_3)]_2$ .<sup>78</sup> The formation of  $\mu$ -oxo functionalities suggests that during the course of the reaction some kind of dehydroxylation process takes place. Protonolysis of the cyclopentadienyl ancillary ligand upon grafting metallocenes has also been reported in the absence of an amine.<sup>76,78,169</sup> Whereas protonolysis of the trivalent titanium fulvene complex  $(\eta^5-C_5Me_5)(\eta^5, \eta^1-C_5Me_4-CH_2)Ti^{III}$  with  $(c-C_6H_{11})_7Si_7O_9(OH)(OSiMe_3)_2$  yielded the trivalent species  $[(c-C_6H_{11})_7Si_7O_{10}(OSiMe_3)_2]Ti^{III}-Cp^*$ , reaction with the disilanol  $(c-C_6H_{11})_7Si_7O_9(OH)_2OSiMe_3$  resulted in loss of one pentamethylcyclopentadiene and oxidation to the tetravalent titanium complex  $[(c-C_6H_{11})_7Si_7O_{11}OSiMe_3][(c-C_6H_{11})_7Si_7O_{10}(OH)OSiMe_3]TiCp^*$  (Figure 10).<sup>76,78</sup> These reactions clearly demonstrate the reactivity of surface silanols and show that even the robust pentamethylcyclopentadienyl ligands can be displaced by silanols, although it has to be stated that most of these reactions were performed in the presence of an amine to scavenge the hydrogen chloride. How this will compare with the acidic conditions when silicas are treated with metallocene precursors is not clear.

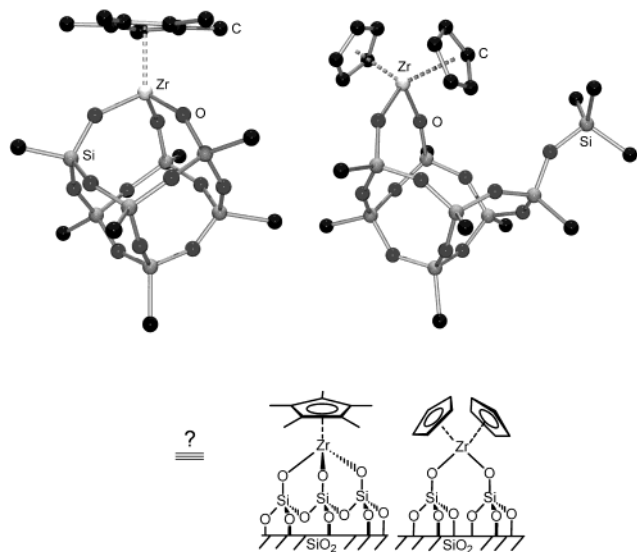
An important criterion for silica-grafted olefin polymerization catalysts forms the stability of the metal–oxygen bonds. Early-transition-metal–oxygen bonds are strong and therefore considered to be fairly stable. However, most of these catalyst precursors are activated with strong Lewis acidic aluminum-based cocatalysts for which the Al–O bonds are competitively strong compared to the early-transition-metal–oxide bonds. Feher et al. demonstrated that  $Al(CH_2SiMe_3)_3$  readily splits two of the three vanadium–siloxy bonds in the vanadyl silsesquioxane  $(c-C_6H_{11})_7Si_7O_{12}V=O$ .<sup>72</sup> To study the stability of the group 4 metal–siloxy bonds, metallasilsesquioxane





**Figure 10.** Schematic presentation of a surface titanium site and the molecular structure of  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)]\text{-TiCp}^*[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})(\text{OSiMe}_3)]$ .<sup>159</sup>

species of the types  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{MCp}$ ,  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)]\text{MCp}_2$ , and  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{13}]_n\text{M}(\text{Cp})\text{-X}_{3-n}$  ( $\text{X} = \text{Cl}$ , alkyl;  $n = 1, 2$ ) were subjected to solutions of MAO in the presence of ethylene (Figure 11).<sup>47,74</sup> All metallasilsesquioxanes formed active



**Figure 11.** Schematic presentation of surface zirconium sites and molecular structures of  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{ZrCp}^*$  and  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)]\text{ZrCp}_2$ .<sup>159</sup>

catalysts after MAO-induced cleavage of the metal–siloxo bond. Even the terdentate ligand in  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{MCp}'$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ;  $\text{Cp}' = \text{C}_5\text{H}_5, 1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2, \text{Cp}^*$ ) was readily displaced by MAO to yield active catalysts. Do and co-workers<sup>184</sup> demonstrated that MMAO-induced metal–siloxo bond breaking in  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{MCp}^*$  is temperature dependent. At low to ambient temperature M–O bond breaking leads to a bimodal system (**II** and **III**, Scheme 3). At elevated temperatures, M–O bond

breaking is facile and affords a single-site, silsesquioxane-free catalyst (**III**, Scheme 3).

Protonolysis reaction of the monosilanol  $(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OH})$  with  $\text{Cp}''\text{TiR}_3$  yielded the monocyclopentadienylyltitanium silsesquioxane dialkyl species  $\text{Cp}''[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{13}]\text{TiR}_2$  ( $\text{Cp}'' = 1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ ;  $\text{R} = \text{Me}, \text{CH}_2\text{Ph}$ ),<sup>47,74</sup> which are realistic models for silica-grafted half-metallocenes and are very similar to the silica-grafted  $\text{Cp}''\text{ZrR}_3$  species reported by Basset et al.<sup>27</sup> Like the corresponding  $\text{SiO}_2(500)$ -supported  $(\equiv\text{SiO})\text{Cp}^*\text{ZrMe}_2$  system, the  $\text{Cp}''[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{13}]\text{TiR}_2$  complexes are themselves inactive but can be activated with “non-aluminum” cocatalysts such as  $\text{X}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  ( $\text{X}^+ = \text{Ph}_3\text{C}^+, \text{PhN}(\text{H})\text{Me}_2^+$ ) or  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 4). The thus obtained cationic titanasilsesquioxane species  $\{\text{Cp}''[(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{13}]\text{-TiR}\}^+[\text{RB}(\text{C}_6\text{F}_5)_3]^-$  proved to be single-site catalysts for the polymerization of ethylene ( $M_w = 260000$ ,  $M_w/M_n = 3.3$ ) and 1-hexene (atactic,  $M_w = 3000$ ,  $M_w/M_n = 2.0$ ).<sup>47,74</sup>

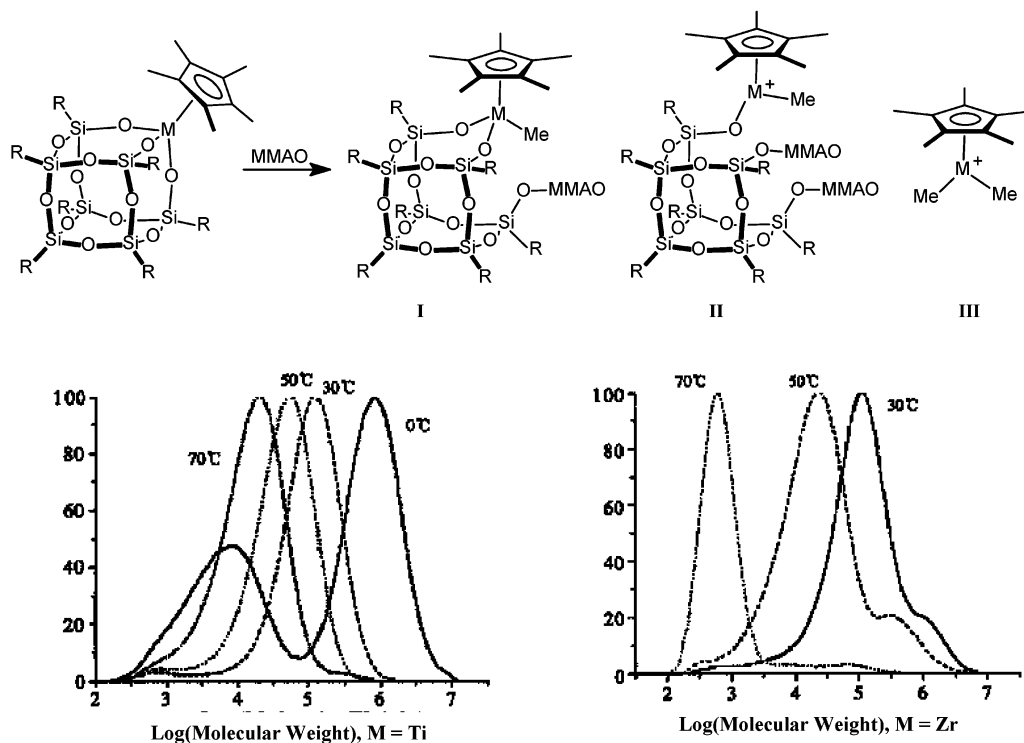
In the studies discussed above silsesquioxanes representing a variety of silanol sites present on silica surfaces were used, particularly with regard to the denticity of the siloxy chelates. It is therefore suggested that silica-grafted early-transition-metal polymerization catalysts might leach upon activation with MAO or other aluminum alkyls. On the other hand, when aluminum-based cocatalysts can be avoided, stable silica-grafted olefin polymerization catalysts are very feasible.

## 2. Tethering of Catalyst Precursors

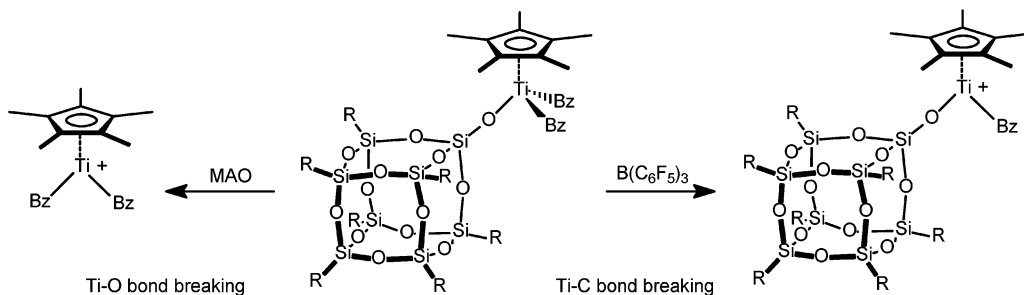
Tethering of organometallic compounds to a silica support is, with respect to leaching, probably the best method to anchor a homogeneous catalyst to the support. Unfortunately, it is also the most laborious route. Tethering is a versatile method of anchoring virtually any homogeneous catalyst onto a support and is gaining more and more attention in the recent literature.<sup>175–183</sup> While several studies on tethering of olefin polymerization catalysts to silicas are reported, curiously enough hardly any information is available on the effectiveness of the applied immobilization method, the stability of the catalysts, and the effect of the support on these immobilized catalysts.<sup>178–181</sup> There are two general routes that are applied: (i) building-up the ligand and subsequently the metal complex at the surface and (ii) immobilizing a presynthesized catalyst precursor containing an anchorable functionality (Scheme 5). Both routes clearly have their limitations and advantages.<sup>175–183</sup> Studies using silsesquioxanes to mimic catalyst tethering have shown that these model supports are also very suitable for optimizing synthetic strategies.<sup>81,115,126,127,130,132</sup>

Three general routes have been applied to tether cyclopentadienes and various other organic functionalities to surface supports. They consist of (i) grafting of a silyl chloride- or silyl ether-functionalized cyclopentadiene (Scheme 5), (ii) salt elimination reaction of a cyclopentadienyl alkali-metal salt with an alkyl chloride group previously tethered onto the surface by method i or, e.g., sol–gel synthesis, and (iii) hydrosilylation of an olefin-substituted cyclopenta-

## Scheme 3. MAO-Induced M–O Bond Breaking in Group 4 Metal Silsesquioxane Complexes



## Scheme 4. MAO-Induced M–O versus Borane-Induced M–C Bond Breaking in Titanium Silsesquioxane Complexes



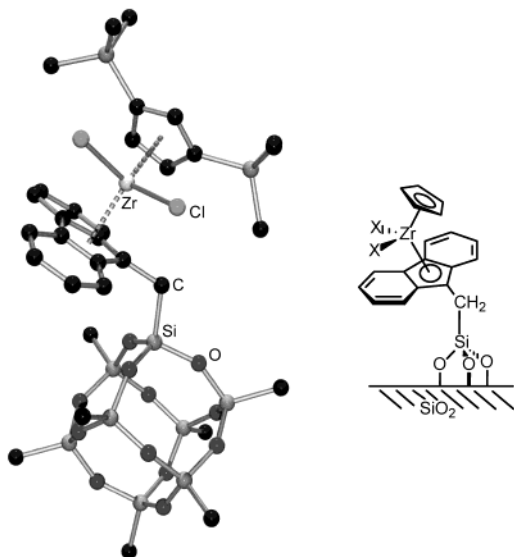
dienyl. Once the cyclopentadienyl ligand is attached to the silsesquioxane, it can be deprotonated and treated with the metal precursor (Scheme 5). For silsesquioxanes, these are convenient routes since the silsesquioxane-bonded cyclopentadienyl ligand can be purified and, more importantly, there are no adjacent silanol functionalities that can interfere with the intended reaction (Scheme 5).<sup>81</sup> Figure 12 shows an example of such a complex, a silsesquioxane-tethered fluorenylcyclopentadienylzirconium dichloride species, [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>13</sub>CH<sub>2</sub>C<sub>9</sub>H<sub>8</sub>](Cp'')ZrCl<sub>2</sub> (Cp'' = 1,3-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>).<sup>81</sup>

The second strategy, consisting of treating the support with a catalyst precursor containing an anchorable functionality, has the highest chance of forming a uniform surface-metal complex. Nevertheless, several side reactions can result in decomposition of the catalyst precursor. Furthermore, synthesis of such metal complexes containing a pendant anchorable, reactive functionality is often not trivial. Reacting Cp''[EtOSi(Me)<sub>2</sub>CH<sub>2</sub>Flu]ZrCl<sub>2</sub> with (*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> resulted in loss of the fluorenyl ligand and formation of the corner-capped zirconium silsesquioxane [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>12</sub>]ZrCp''.<sup>225</sup>

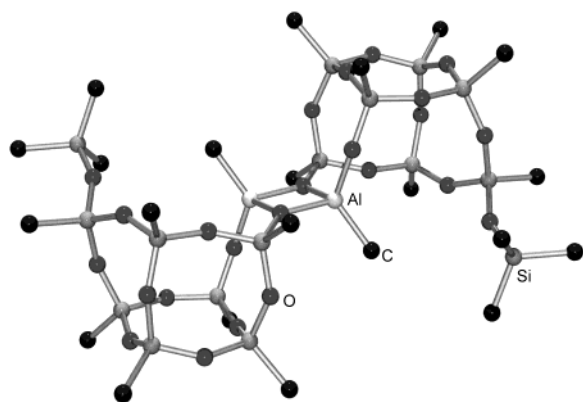
The same reaction of (*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> with the more-hydrolysis-stable Cp[C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>OEt]ZrCl<sub>2</sub> initially resulted in (*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)(O<sub>2</sub>ZrCp)-(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>OEt), which slowly reacted further under formation of ethanol and the silsesquioxane-tethered [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(O<sub>2</sub>ZrCp)(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>O-)]<sub>n</sub> (Scheme 5). Clearly, reaction of the zirconium chloride substituents is faster than grafting of the pendant silyl ether. As long as the cyclopentadienyl ligands remain attached to the zirconium, this route can still lead to a uniform silica-tethered metallocene catalyst. As we have seen previously, silsesquioxane-grafted zirconocenes form active olefin polymerization catalysts after activation with MAO, as the latter effectively splits Zr–OSi bonds. Hence, complexes of the type [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(O<sub>2</sub>ZrCp)(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>O-)]<sub>n</sub> can be activated in the same way albeit now the metallocene remains attached to the surface by the tethered cyclopentadienyl group (Scheme 5).

Complexes containing non-cyclopentadienyl ligands have also been tethered onto silsesquioxanes.<sup>192</sup> For example, the silsesquioxane-tethered guanidine ligand [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>]C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>N(*i*-Pr)C(=N-*i*-Pr)(N(H)-*i*-Pr) could easily be synthesized by reacting [(*c*-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>-





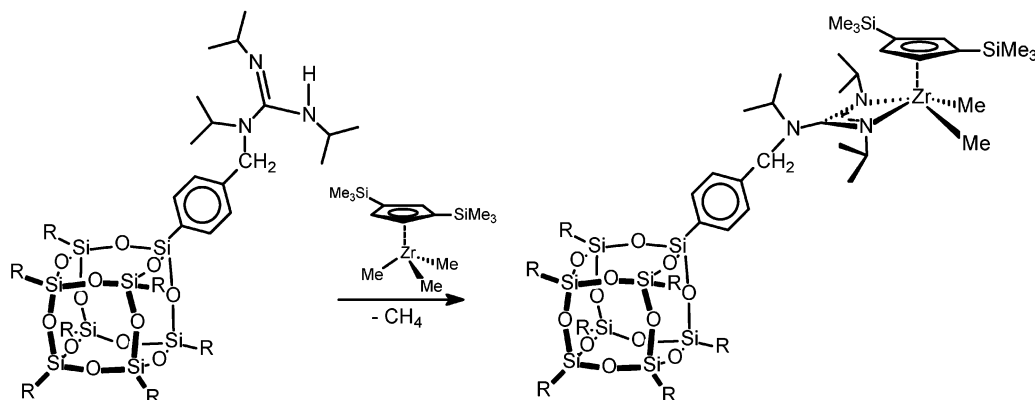
**Figure 12.** Schematic and molecular structure of  $[(c-C_5H_9)_7Si_7O_{13}CH_2C_9H_8](Cp'')ZrCl_2$ .<sup>159</sup>



**Figure 13.** Molecular structure of one of the three conformers of the aluminosilsesquioxane  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)_2AlMe_2]\}$ .<sup>159</sup>

gregated into electronically saturated dimers. Silsesquioxane silanols react in various ratios with TMA, for example, the dimeric silsesquioxane disiloxaluminum methyl complex  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)_2AlMe_2]\}$ , which exists in three different isomeric forms (Figure 13). These dimeric structures are very stable, and prolonged heating (400 h, 76 °C) is required for these conformers to isomerize

#### Scheme 6. Synthesis of a Guanidinate-Tethered Zirconium Complex



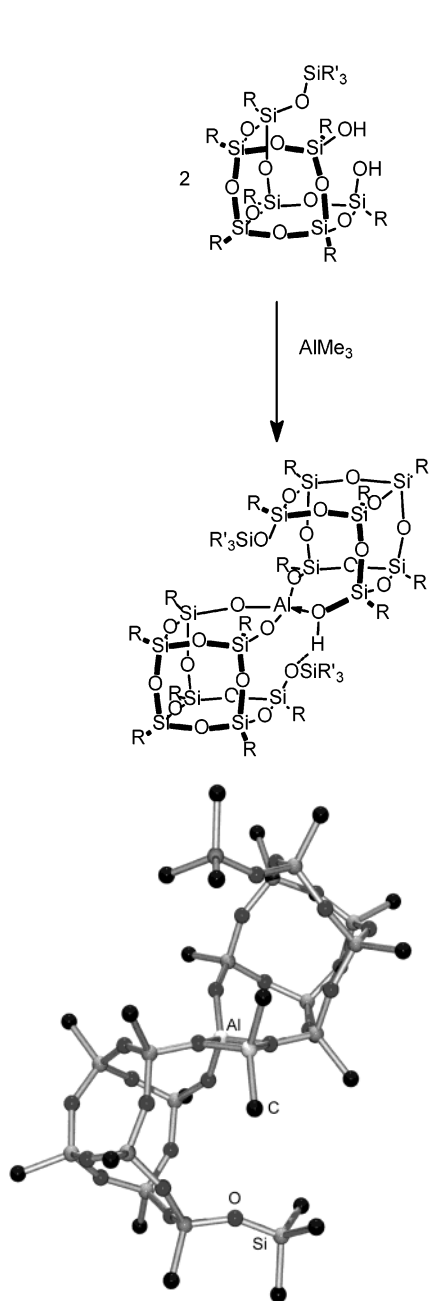
into the thermodynamically most stable mixture (Scheme 7).

For the preparation of supported MAO, silicas are used that contain large amounts of silanol groups and even physisorbed water.<sup>14,193–198</sup> Reacting such silicas with aluminum alkyls might result in Brønsted acidic aluminosilicate structures, which in turn can react further with additional aluminum alkyls. As expected, the Brønsted acidic  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)_2Al^-]\{H^+\}$ <sup>146</sup> is readily deprotonated by TMA, affording the novel  $C_2$ -symmetric  $[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)_2Al_2Me_2]$  (Scheme 7, Figure 14).<sup>80</sup> The structure of this complex is also very robust and isomerizes to the thermodynamically most stable mixture of  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)]AlMe_2\}$  only after prolonged heating (1000 h, 76 °C).

It was argued that deprotonating the Brønsted acids  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiR_3)_2Al^-]\{H^+\}$  ( $SiR_3 = SiMe_3, SiMePh_2$ )<sup>145,146</sup> might afford weakly coordinating anions supporting cationic metallocene species, in a fashion similar to, for example, that reported by Marks et al. for strongly acidic sulfonated zirconia.<sup>199</sup> However, reaction of  $Cp_2ZrMe_2$  with the Brønsted acidic aluminosilsesquioxane did not afford a cationic zirconocene species but instead resulted in a clean redistribution reaction yielding  $[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)]ZrCp_2$ , methane, and various methylaluminosilsesquioxane species (Scheme 8).<sup>80,184</sup>

Although the Lewis acidic methylaluminosilsesquioxane complexes are poor models for supported MAO, like Barron's *tert*-butylaluminum complexes they could possibly be applied as olefin polymerization cocatalysts.<sup>200,201</sup> Whereas  $Cp_2ZrMe_2$  definitely interacts with the Lewis acidic aluminosilsesquioxanes (Scheme 8), no active olefin polymerization catalyst is formed. In the presence of  $Cp_2ZrMe_2$ , both  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)]AlMe_2\}$  (76 °C, 1.5 h) and  $[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)_2Al_2Me_2]$  (76 °C, 8 h) equilibrate over 2 orders of magnitude faster than without  $Cp_2ZrMe_2$  (Schemes 7 and 8). It is proposed that  $\{[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)]AlMe_2\}$  and  $[(c-C_5H_9)_7Si_7O_{11}(OSiMePh_2)_2Al_2Me_2]$  react as Lewis acids with  $Cp_2ZrMe_2$ ,<sup>80</sup> similar to homogeneous Lewis acids such as  $B(C_6F_5)_3$ .<sup>202–207</sup> However, for the Lewis acidic aluminosilsesquioxanes, the interaction with  $Cp_2ZrMe_2$  is clearly too weak to effectively abstract a methyl to form a cationic zirconocene complex.<sup>200,201,206</sup>

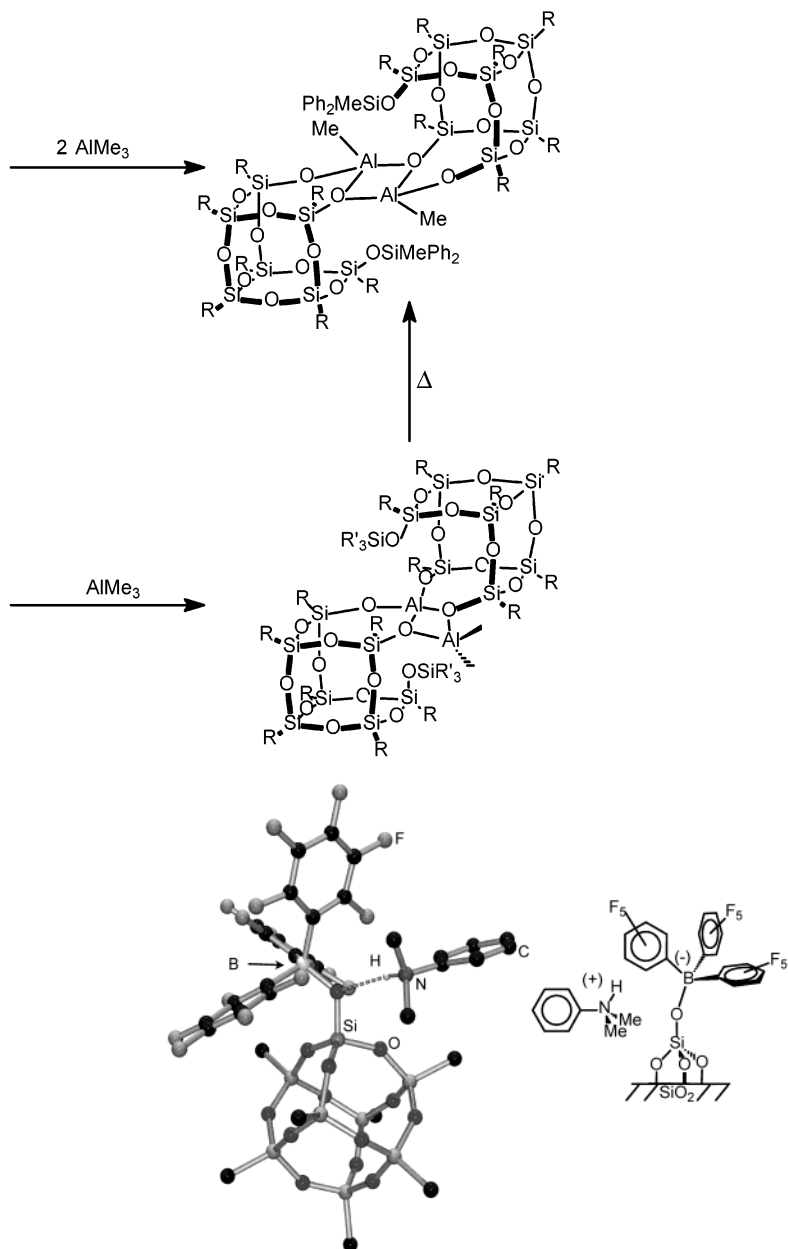
## Scheme 7. Synthesis and Thermal Behavior of Aluminosilsesquioxanes



**Figure 14.** Molecular structure of the aluminosilsesquioxane  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMePh}_2)]_2\text{Al}_2\text{Me}_2$ .<sup>159</sup>

#### 4. Electrostatic Interaction with Immobilized Cocatalyst. Supported Boranes/Borates

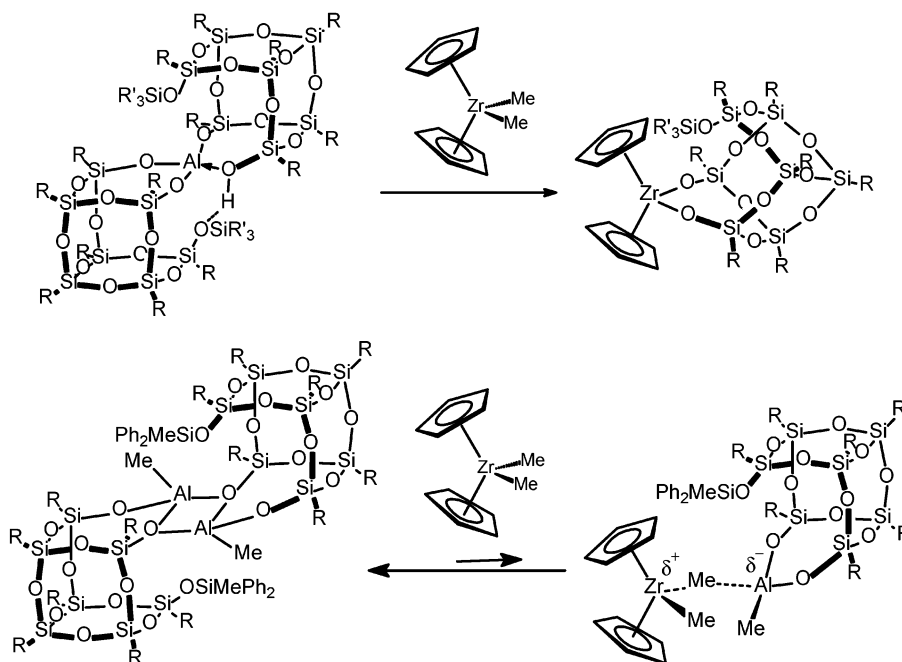
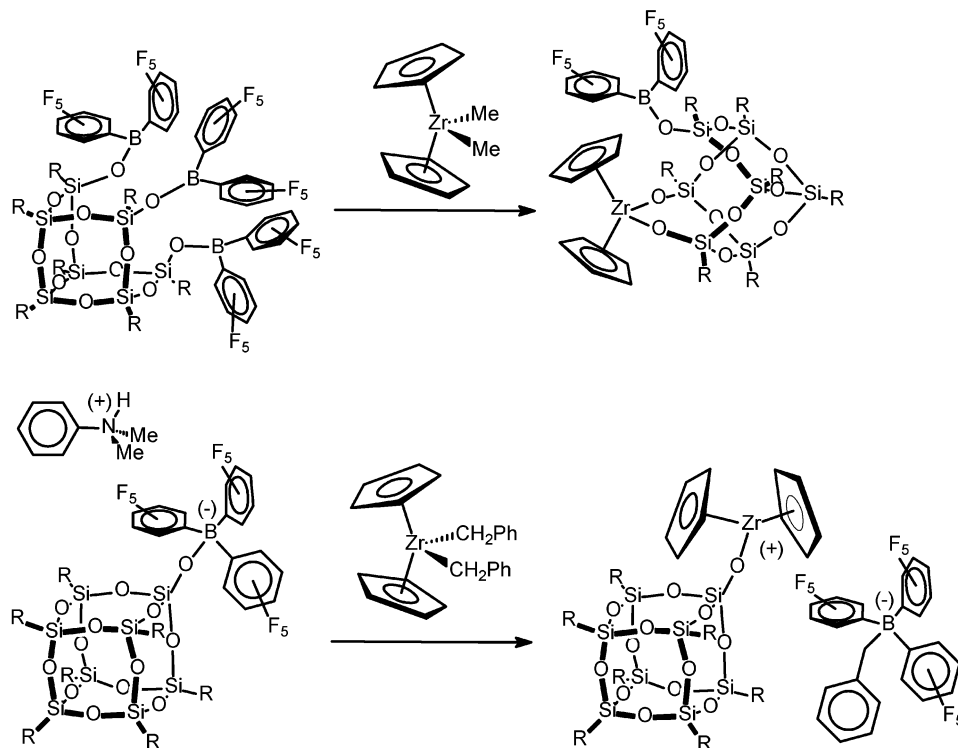
Recently, immobilized boranes and borates have also been reported as suitable cocatalysts.<sup>57,208–224</sup> Whereas physisorbed, tethered, and grafted boron species have been reported, so far only silica-grafted boranes and borates have been modeled using silsesquioxanes.<sup>57,77,82</sup> Representative examples are the neutral silsesquioxane trisborane  $\text{R}_7\text{Si}_7\text{O}_{12}[\text{B}(\text{C}_6\text{F}_5)_2]_3$  and the silsesquioxane borato ammonium salt  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{B}(\text{C}_6\text{F}_5)_3\}^- \{\text{PhN}(\text{H})\text{Me}_2\}^+$  (Figure 15). Recently Basset reported a comparative study on silica-grafted ammonium borates and hydroxyammonium, siloxyammonium, and silsesquioxane ammonium borates.<sup>57</sup> With the help of homogeneous



**Figure 15.** Molecular structure of  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}][\text{OB}(\text{C}_6\text{F}_5)_3]\}^- \{\text{PhN}(\text{H})\text{Me}_2\}^+$ <sup>159</sup> and a corresponding surface structure it should represent.

models they found experimental conditions in which surface silanols are efficiently transformed into well-defined ammonium borate functionalities.

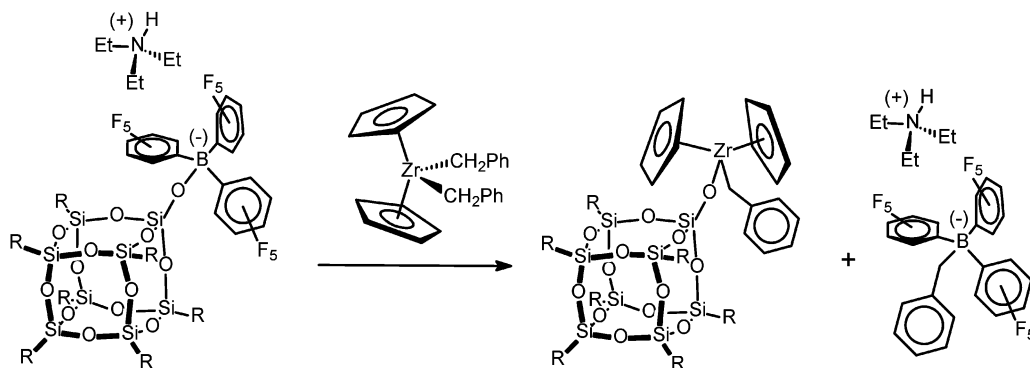
While stable in the absence of  $\text{Cp}_2\text{ZrMe}_2$ , already at low temperature the silsesquioxane borane complex  $\text{R}_7\text{Si}_7\text{O}_9[\text{OB}(\text{C}_6\text{F}_5)_2]_3$  reacts with  $\text{Cp}_2\text{ZrMe}_2$  to form the inactive  $\text{R}_7\text{Si}_7\text{O}_{11}\text{ZrCp}_2[\text{OB}(\text{C}_6\text{F}_5)_2]$  and  $(\text{C}_6\text{F}_5)_2\text{BMe}$ , indicating that the B–O bond is readily split (Scheme 9).<sup>82</sup> When zirconocene dibenzyl  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$  is reacted with the silsesquioxane borato ammonium salt  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{B}(\text{C}_6\text{F}_5)_3\}^- \{\text{PhN}(\text{H})\text{Me}_2\}^+$  in the presence of ethylene or 1-hexene, an active polymerization catalyst is obtained.<sup>77</sup> However, mechanistic studies showed that the expected  $\{\text{Cp}_2\text{ZrCH}_2\text{Ph}\}^+ \{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{B}(\text{C}_6\text{F}_5)_3\}^-$  was not formed. As a result of the relatively labile

**Scheme 8. Reaction of  $\text{Cp}_2\text{ZrMe}_2$  with Brønsted and Lewis Acidic Aluminum Silsesquioxanes****Scheme 9. B–O Bond Splitting and Zr–O Bond Forming upon Treatment of  $\text{Cp}_2\text{ZrR}_2$  with Silsesquioxane-Based Boranes and Borates**

B–O bond, the cationic zirconocene silsesquioxane  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{ZrCp}_2\}^+\{\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}^-$  was obtained instead (Scheme 9). This complex is in equilibrium with the neutral  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{Zr}(\text{CH}_2\text{Ph})\text{Cp}_2$  and free borane  $\text{B}(\text{C}_6\text{F}_5)_3$ . It was demonstrated that exclusively in the presence of an excess of  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$  an active catalyst is formed. The free borane, that is, together with  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{Zr}(\text{CH}_2\text{Ph})\text{Cp}_2$  in equilibrium with  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{ZrCp}_2\}^+\{\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}^-$ , reacts with  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$  to yield  $\{\text{Cp}_2\text{ZrCH}_2\text{Ph}\}^+\{\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}^-$ ,

the actual active catalyst of this system.<sup>77</sup> Further proof for the lability of the B–O bond in silsesquioxane borates was given by the reaction of the triethylammonium salt of the silsesquioxane borate  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{B}(\text{C}_6\text{F}_5)_3\}^-\{\text{Et}_3\text{NH}\}^+$  with  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$ , which selectively resulted in the formation of  $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{13}]\text{Zr}(\text{CH}_2\text{Ph})\text{Cp}_2$  and  $\{\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}^-\{\text{Et}_3\text{NH}\}^+$  (Scheme 10).<sup>77</sup>

Clearly, the lability of the B–O bond makes the silsesquioxane borane and borato systems unsuitable as cocatalysts. On the basis of these results, it is not

**Scheme 10. Ligand Exchange between  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$  and a Silsesquioxane-Based Ammonium Borate**

unlikely that the B–O bonds in silica-grafted boranes and borates are also labile. They are however a source of unsupported borane ( $\text{MeB}(\text{C}_6\text{F}_5)_2$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ ) that can be considered as being the actual cocatalyst and explain the fact that ethylene polymerization activity is still observed for the silica-grafted borate cocatalysts.<sup>217–219</sup> Nevertheless, Okuda recently proved that polyethylene with very nice particle morphology (spherical, high bulk density) and no reactor fouling can be obtained using silica-grafted borates, irrespective of any possible leaching of the borate cocatalyst.<sup>219</sup>

**V. Conclusions**

The results presented here demonstrate that silsesquioxanes resemble several features of silica surface silanol sites. It is now evident that metallasilsesquioxane complexes are capable of mimicking some characteristics of heterogeneous silica-supported transition-metal catalysts. Important features of silica-supported catalysts that can be observed in the corresponding metal-containing silsesquioxane complexes include a rigid, electron-withdrawing siloxide structure and, for example, the possibility of adjacent oxygen donors to interact with the metal center. With these model supports, features such as the stability and reactivity of metal–siloxo bonds in the presence of cocatalysts during catalytic reactions afford detailed insight that would be difficult to obtain with heterogeneous catalyst systems. However, since their mobility in solution allows aggregation reactions to thermodynamically stable complexes, many of the metallasilsesquioxane complexes do not structurally resemble the silica-supported systems for which they were intended to serve as a model. Nevertheless, with activities sometimes exceeding those of commercial silica-supported olefin polymerization catalysts, they still are interesting catalysts themselves.

The use of (metalla)silsesquioxanes as a tool to better understand processes taking place at silica surfaces and supported metal sites has gained more attention in different areas of heterogeneous catalysis and will most probably continue to do so. However, as already mentioned, one of the shortcomings of all homogeneous model systems, including silsesquioxane compounds, is that the mobility of the species in solution allows the electronically unsaturated species (the potential active catalysts) to form thermody-

namically stable, often inactive complexes. Only the development of larger and even more rigid silsesquioxane structures that might possibly prevent this problem will lift the usefulness of homogeneous model systems for heterogeneous catalysts to a higher level. The first example of not so much more rigid but less mobile metallasilsesquioxane complexes forms the study of Skworonska-Ptasinska et al., who have prepared well-separated titanasilsesquioxane epoxidation catalysts immobilized onto polysiloxanes.<sup>65</sup>

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