# SYNTHESIS OF ZIRCONOCENE SILSESQUIOXANE COMPLEXES AND THEIR ETHENE POLYMERIZATION ACTIVITY IN SYSTEMS WITH METHYLALUMINOXANE

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Protocols for obtaining defined zirconocene complexes with polyhedral oligomeric silsesquioxanes with mono-, di-, and trisilanol functionality (SIPOSS, DIPOSS, and TRIPOSS) were established. The TRIPOSS silanolates binding one zirconocene and one chlorozirconocene moiety, $[\{(c\text{-}C_5H_9)_7Si_7O_9O_3\}Zr_2Cl(\eta^5\text{-}C_5H_4R)_4]$ (**1**, R = Bu; **2**, R = H), were obtained by reacting the silanol with the respective zirconocene dichloride and triethylamine in $CH_2Cl_2$ in a 1.0:3.0:3.0 molar ratio, an excess of the zirconocene dichloride being required to suppress intramolecular dehydration of TRIPOSS. The related SIPOSS complex, $[\{(c\text{-}C_5H_9)_7Si_8O_{12}O\}_2\text{-}Zr(\eta^5\text{-}C_5H_4Bu)_2]$ (**3**), was prepared similarly at the stoichiometric ratio of $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$/SIPOSS/$NEt_3$ equal to 1.0:2.0:2.0. When employed in the 1.0:1.0:1.0 ratio, the same reagents afforded only the impure complex $[\{(c\text{-}C_5H_9)_7Si_8O_{12}O\}ZrCl(\eta^5\text{-}C_5H_4Bu)_2]$ (**4**), contaminated with **3** and unreacted $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$. Finally, the zirconocene complexes with SIPOSS and DIPOSS moiety, $[\{(c\text{-}C_5H_9)_7Si_8O_{12}O\}_2Zr(\eta^5\text{-}C_5H_5)_2]$ (**5**) and $[(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)O_2\}\text{-}Zr(\eta^5\text{-}C_5H_5)_2]$ (**6**), respectively, were obtained by reacting $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ with stoichiometric amounts of the appropriate silanols. All complexes were characterized by $^1H$, $^{13}C$, $^{29}Si$ NMR and IR spectra, and by elemental analysis from XPS spectra. Preliminary ethene polymerization experiments showed that compounds **5** or **6** when combined with an excess of methylaluminoxane were nearly as active as $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ whereas compound **2** was by about one order of magnitude less active.

**Keywords**: Zirconium; Zirconocene; Metallocenes; Sandwich complexes; Polyhedral oligomeric silsesquioxanes; Silsesquioxanes; NMR spectroscopy; Infrared spectroscopy; XPS spectroscopy; Ethene polymerization; X-ray diffraction.


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Polyhedral oligomeric silsesquioxanes (POSS) with silicon atoms bearing cyclopentyl substituents and containing monosilanol, e.g., $[(c\text{-}C_5H_9)_7Si_8O_{12}(OH)]$ (SIPOSS), disilanol, e.g., $[(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2]$ (DIPOSS), and trisilanol functionality, e.g., $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$ (TRIPOSS)[1] have been used as defined mimics of silica surface in studies aimed at understanding the behavior of homogeneous catalysts immobilized at silica support via the surface hydroxyl groups. Compared with the silica surface where a single site catalyst can hardly be obtained due to a variety of Si–O–H groups acting in isolated or cooperative modes[2], the POSS silanols offer the opportunity to study the stability and catalytic properties of well-defined single site catalytic centers with the siloxy environment that is encountered in silica-anchored catalytic species[3]. The use of POSS silanols for the preparation of metal silanolates and their utilization in catalysis have been reviewed several times[4]. The early transition metal (e.g., Ti, Zr, Hf) POSS silanolates have been mostly investigated as catalysts of olefin epoxidation[5] or catalyst precursors for polymerization of olefins[6]. The former were mostly alkoxy(siloxy)metallasilsesquioxanes, while the latter were typically half-sandwich metallocene silsesquioxanes derivatives.

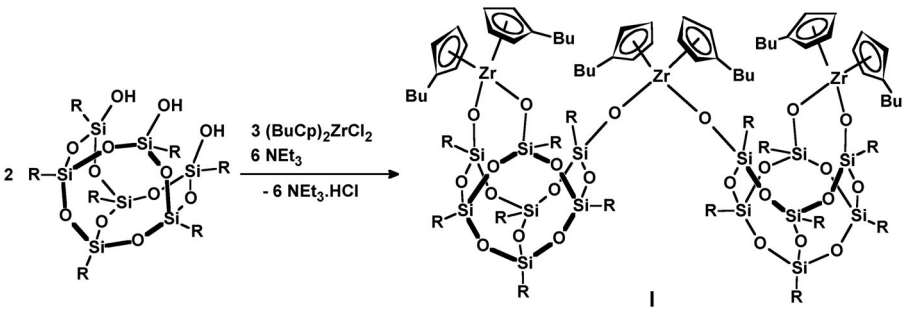
It was also of interest to model the interaction of a metallocene species with the silica surface leading to grafted catalysts using the above POSS silanols. As concerns the zirconocene–POSS complexes, the compound $[\{(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)O_2\}Zr(\eta^5\text{-}C_5H_5)_2]$ (**6**) was prepared by reacting DIPOSS with equimolar amount of $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ in chloroform in the presence of excess $NEt_3$, and its X-ray crystal structure was determined[7a]. The compounds possessing unsaturated siloxy moieties ($OSiMe_2CH{=}CH_2$ or $OSiMe_2CH_2CH{=}CH_2$) instead the $OSiMe_3$ group were obtained by the same procedure, and one representative was structurally characterized[5g]. A very similar compound, $[\{(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_2Ph)O_2\}Zr(\eta^5\text{-}C_5H_5)_2]$, was obtained by a transmetallation reaction of an aluminosesquioxane with $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ in moderate yield, and its crystal structure was found to be nearly identical with that of **6** [7b]. The related borylated derivative of **6**, $[\{(c\text{-}C_5H_9)_7Si_7O_9(OB(C_6F_5)_2)O_2\}Zr(\eta^5\text{-}C_5H_5)_2]$, was obtained by the reaction of $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ with the triborylated TRIPOSS using either $(C_6F_5)_2BH$ or $(C_6F_5)_2BCl$ as the boron reagent[6f]. TRIPOSS containing cyclohexyl organic substituents was also shown to react with $[ZrCl_3(\eta^5\text{-}C_5Me_5)]$ in $CH_2Cl_2$/pyridine or with $[Zr(CH_2Ph)_3(\eta^5\text{-}C_5Me_5)]$ in $CH_2Cl_2$ to give the half-sandwich tripodal complex $[\{(c\text{-}C_6H_{11})_7Si_7O_9(O)_3\}Zr(\eta^5\text{-}C_5Me_5)]$ (ref.[8]). However, no zirconocene–TRIPOSS complexes were so far described. Up to the best of our knowledge, there is also no report on the synthesis of

zirconocene–SIPOSS complexes although such complexes would mimic zirconocene catalysts grafted to isolated SiOH groups on a silica surface.

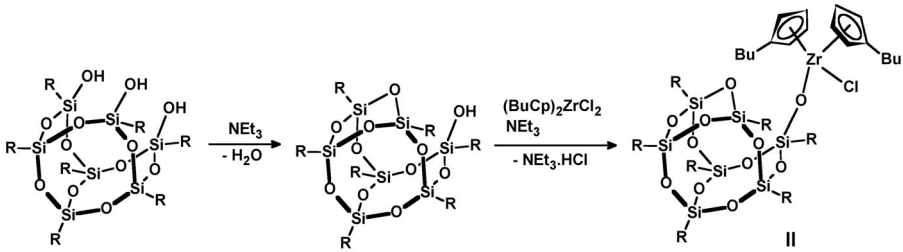
Here we report syntheses of zirconocene complexes with TRIPOSS, DIPOSS, and SIPOSS ligands from zirconocene dichlorides $[ZrCl_2(\eta^5\text{-}C_5H_4R)_4]$ (R = H, Bu) or zirconocene dimethyl exploring the above methods of deprotonation via HCl or alkane elimination. Furthermore, preliminary ethene polymerization experiments are described for these compounds activated with methylaluminoxane (MAO) co-catalyst.

## RESULTS AND DISCUSSION

Reactions of TRIPOSS with zirconocene dichlorides $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ and $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ were initially investigated under various reaction conditions with the latter compound because it is more soluble in toluene or chlorinated alkanes which were employed as the solvents. Moreover, this compound is cheap, being produced in large quantities as a catalyst precursor for industrial polymerization of ethene[9]. Previously, the toluene solvent was recommended for the reaction of DIPOSS with titanocene dichloride whereas chloroform was used for analogous reactions with zirconocene and hafnocene dichlorides, both in the presence of an excess of triethylamine[7a]. In our hands, dichloromethane appeared to be a better reaction medium than toluene for the above reactions that are ionic in nature. Attempts to use stoichiometric amounts of reactants for obtaining various products with defined ratio Zr/TRIPOSS failed because of the competitive elimination of water from TRIPOSS that is catalyzed both under acidic and basic conditions[1b–1d]. For example, the molar ratio Zr/TRIPOSS/$NEt_3$ 1.5:1.0:3.0, which should afford complex **I** (Scheme 1), gave an amorphous product whose IR spectra indicated the absence of free Si–OH groups and low contents of zirconocene moiety, which is compatible with complex **II** (Scheme 2).

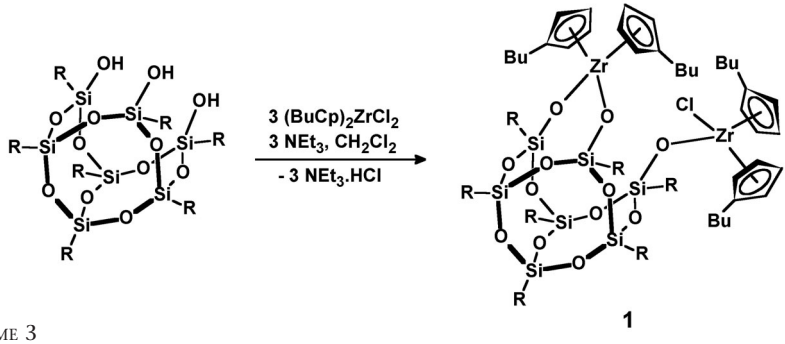



SCHEME 1




SCHEME 2

Apparently, the base-catalyzed intramolecular water elimination was faster than elimination of hydrogen chloride. To increase the rate of TRIPOSS reaction with zirconocene dichloride, a two-fold molar excess of the latter was applied to suppress the TRIPOSS dehydration. At the molar ratio Zr/TRIPOSS/$NEt_3$ 3.0:1.0:3.0, the reaction was accomplished within 10 min and yielded 75% of a white crystalline product after crystallization from hexane at a low temperature. The re-crystallized product was characterized by $^1H$ and $^{13}C\{^1H\}$ NMR and IR spectra, and by XPS elemental analysis. The NMR spectra showed the presence of two equally abundant $Zr(\eta^5\text{-}C_5H_4Bu)_2$ moieties, one having diastereotopic and the other enantiotopic cyclopentadienyl ligands. This together with the molar ratio Si/Zr/Cl 7.0:2.0:1.0 (±0.1) as established by XPS measurement allowed to assign the product to structure **1** (Scheme 3).




SCHEME 3

The formulation of **1** was confirmed by X-ray single crystal analysis. Unfortunately, an imperfect crystal and serious disorder over the cyclopentyl substituents of the TRIPOSS cage precluded a complete structure refinement. Nevertheless, the observed connectivities within the molecular framework were unambiguous, and corroborated the structure of **1** (Fig. 1) as it is schematically depicted in Scheme 3.

The formation of complex **II** (Scheme 2) could be disfavored here due to an increased concentration of $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ with respect to TRIPOSS. On the other hand, the presence of the butyl substituent at the cyclopentadienyl ligands did not affect reactivity of zirconocene dichloride since the analogous non-substituted zirconocene–TRIPOSS complex **2** was obtained in high yield at the same Zr/TRIPOSS/$NEt_3$ molar ratio equal to 3.0:1.0:3.0.

A similar method was further applied for the reaction of $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ with SIPOSS, in which case no competing dehydration of the silanol could occur. Accordingly, the condensation at the stoichiometric ratio Zr/SIPOSS/$NEt_3$ equal to 1.0:2.0:2.0 in dichloromethane afforded virtually pure complex **3** (Scheme 4). Its purity was demonstrated by $^1H$ and $^{13}C\{^1H\}$ NMR spectra showing one set of signals for both cyclopentadienyl ligands and SIPOSS ligands in the complex of $C_{2v}$ symmetry. In contrast, attempted preparation of a zirconocene complex bearing only one SIPOSS silanolate by using equimolar amounts of all reagents proved unsuitable. The expected compound **4** was the main product (82%) according to NMR spectra. However, it was accompanied by minor amounts of **3** and unreacted $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ (both 9%), which could not be removed by fractional crystallization (Scheme 5).

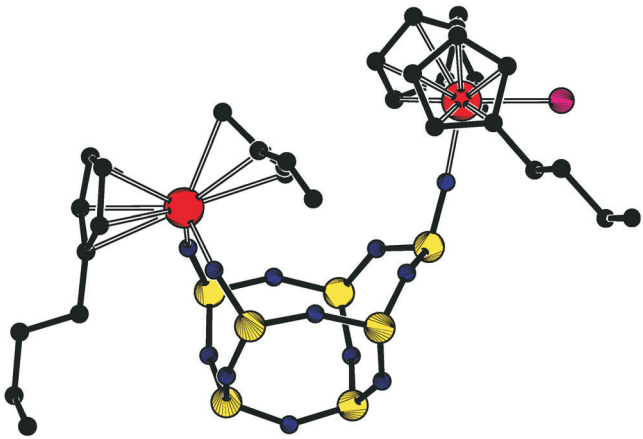
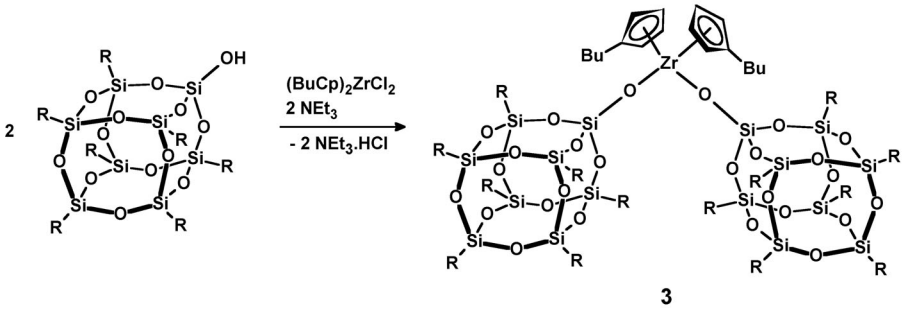
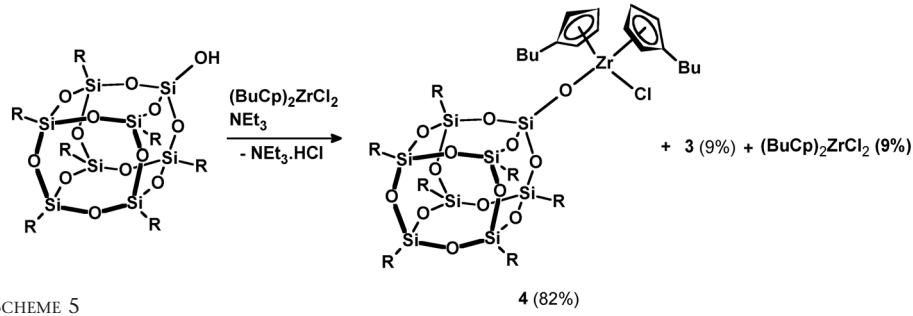


FIG. 1
A view of molecule **1** as obtained from X-ray diffraction patterns: Ti, red; Cl, purple; Si, yellow; O, blue; C, black. Cyclopentyl groups at the silicon atoms and all hydrogen atoms are omitted for clarity

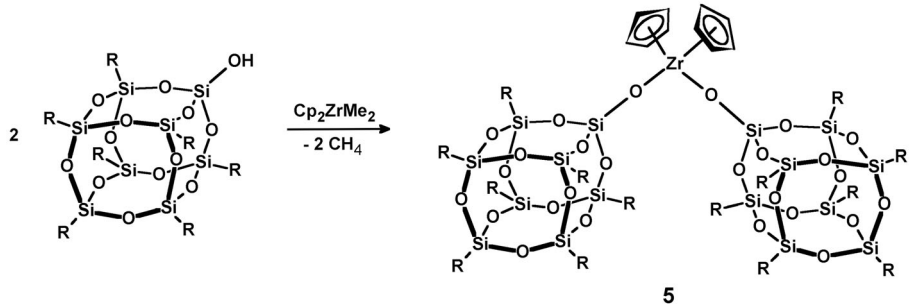



SCHEME 4

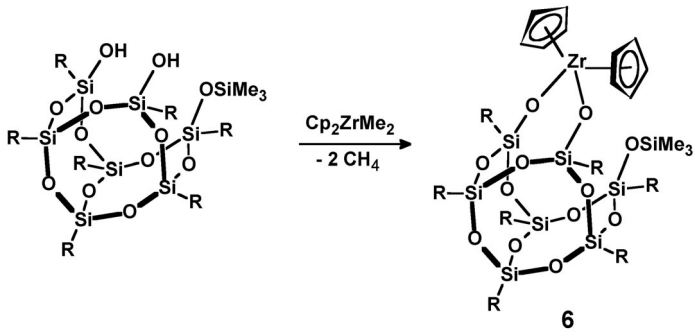



SCHEME 5

In order to prove whether commercially available zirconocene dimethyl can be employed for a straightforward synthesis of POSS complexes, the $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ solution in hexane was added to two molar equivalents of solid SIPOSS whereupon the solid SIPOSS was smoothly dissolving with methane evolution to give quantitatively **5** (Scheme 6). Likewise **3**, the purity of **5** was proved by $^1$H and $^{13}$C{$^1$H} NMR spectra indicating its $C_{2v}$ symmetry. In an analogous manner, the known zirconocene–DIPOSS complex **6** was obtained according to Scheme 7 in a quantitative yield. Its NMR spectra were consistent with the published data[7].




SCHEME 6




SCHEME 7

Infrared spectra of **1**–**6** (see Fig. 2 for representative spectra of **2**, **5** and **6**) were dominated by absorption bands in the range 1045–1100 $cm^{-1}$ due to Si–O(Si) valence vibrations of POSS cages. Shapes of these composed bands changed only slightly from those of parent POSS silanols[1b,10]. The formation of zirconocene complexes was evidenced by strong absorption bands in the range 983–1018 $cm^{-1}$ attributable to stretching Si–O(Zr) vibrations. The Zr–O(Si) valence vibration is believed to be obscured by the broad, strong band of POSS cages at 500 $cm^{-1}$. In simple $[M(OSiR_3)_4]$ (M = Ti or Zr), the ν(Si–O) and ν(M–O) vibrations were found at 912–918 and 510–521 $cm^{-1}$,

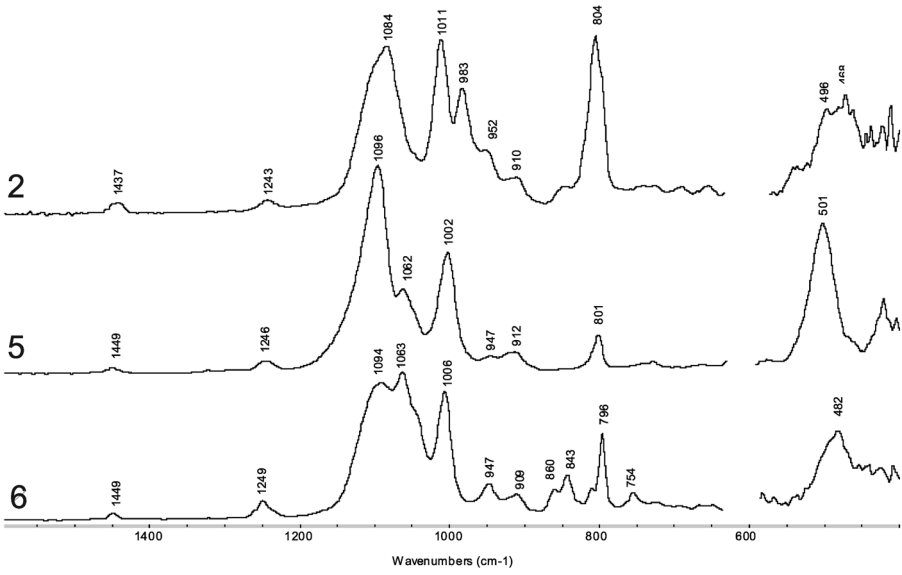



FIG. 2
IR (ATR Si) spectra of compounds **2**, **5**, and **6**

respectively[11]. However, the ν(Si–O) vibration for the actual $(SiO)_3Si–O(Zr)$ species in POSS complexes is to be expected at higher wavenumbers since the valence Si–O(Ti) vibration was found for $[(\eta^5\text{-}C_5Me_5)_2TiOSi(O\textit{t}\text{-}Bu)_3]$ at 964 $cm^{-1}$ and for $[(\eta^5\text{-}C_5Me_5)_2Ti(SIPOSS)]$ at 1038 $cm^{-1}$ (ref.[12]). The presence of zirconocene species is most pronouncedly demonstrated by the absorption band of strong-to-medium intensity in the range 795–807 $cm^{-1}$, assigned to the δ(C–H) vibration of the cyclopentadienyl ligands[13]. Shifts of this band to higher wavenumbers indicate a higher Lewis acidity of the zirconium atom[14], however, the effects of the siloxy and chloro substituents on the band position differ only slightly. Other vibrations of $\eta^5\text{-}C_5H_5$ ligands[13] in **1–6** are observable with lower intensities.

### *Ethene Polymerization*

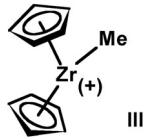
In order to study the catalytic properties of silica-grafted bidentate zirconocene species, the homogeneous "model complexes" **2**, **5**, and **6**, and $[ZrCl_2\text{-}(\eta^5\text{-}C_5H_5)_2]$ as a reference were activated by methylaluminoxane at the constant molar Al/Zr ratio of 1000, and the activity of the resulting catalytic systems in polymerization of ethene was determined (Table I). The mononuclear complexes **5** and **6** displayed a high activity that was only slightly lower than that of the $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$/MAO reference system. This indi-

TABLE I
Ethene polymerization activities of zirconocene complexes $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$, **2**, **5**, and **6** combined with MAO[a]

| Run | Zirconocene complex | PE<br>g | Activity<br>kg(PE) mol(Zr)$^{-1}$ h$^{-1}$ Pa$^{-5}$ |
|---|---|---|---|
| 1 | $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ | 0.80 | 6400 |
| 2 | $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ | 0.73 | 5840 |
| 3 | **2** | 0.11 | 440 |
| 4 | **2** | 0.08 | 320 |
| 5 | **5** | 0.58 | 4640 |
| 6 | **5** | 0.58 | 4640 |
| 7 | **6** | 0.48 | 3840 |
| 8 | **6** | 0.56 | 4480 |

[a] Polymerization conditions: [Zr] = 5 × $10^{-6}$ mol $l^{-1}$, Al/Zr = 1000 (mol/mol), time 10 min, ethene pressure 3 × $10^5$ Pa, temperature 25 °C, solvent toluene, total volume 50 ml, rpm 800.

cates that Zr–O(Si) bonds in POSS complexes **5** and **6** are cleaved by MAO similarly like Zr–Cl bonds in $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ to give the generally assumed cationic polymerization centre (**III**, Chart 1)[15].




**III**

CHART 1

Rather suprisingly, the dinuclear complex **2** combined with MAO showed an activity by about one order of magnitude lower (Table I). Kinetic measurement consisting in following ethene consumption in all polymerization runs (Table I) revealed that the **2**/MAO system was much more rapidly deactivated than all the other systems. In view of a close proximity of zirconium atoms in **2** one can suggest that the formed cationic centres III are rapidly deactivated by mutual interaction with elimination of methane (or a hydrocarbon from growing alkyl chain). The mechanism for bimolecular deactivation in homogeneous zirconocene–aluminoxane systems has been established[16].

The above results for the **5**/MAO and **6**/MAO systems are of relevance to the heterogeneous systems involving zirconocene dichlorides grafted on silica and activated with excess MAO (Al/Zr = 1000 (ref.[17])). For silica and zirconocene dichlorides, a monodentate $[ZrCl(OSi{\equiv})Cp'_2]$ and bidentate $[Zr(OSi{\equiv})_2Cp'_2]$ species, where Cp′ is $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5H_4Bu$, were considered to be formed depending on the density of OH groups on the silica surface. The bidentate species were suggested to result on silica with a high density of surface OH groups, and were assumed to be polymerization inactive[17c]. The present results show that both disiloxy complexes **5** and **6** form highly effective catalysts with activities comparable to the most active zirconocene–silica systems, where the monodentate species were established[17]. Since the interaction with MAO results in metathesis reaction of MAO methyls with the zirconocene siloxy bonds in the homogeneous as well as silica-grafted catalysts, aluminoxane–POSS complexes (for methylaluminum–POSS complexes, see ref.[7b]) and silica-grafted aluminoxane species must form anionic counterparts to the zirconocene cation **III** (Chart 1)[2c]. As the complexes **5** and **6** mimic the bidentate zirconocene silica-grafted species these should after MAO activation also afford the active catalysts. Reasons for the very low activity of the silica-grafted bidentate zirconocene centres can be sought in their proximity allowing for their intermolecular deactivation similar to that known for homogeneous systems[16].

## EXPERIMENTAL

### General

All manipulations with the silanol POSS compounds or $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ were done under vacuum (~20 mPa) or under a high purity argon using a high-vacuum/argon line. $^1H$ (300 MHz), $^{13}C$ (75 MHz), and $^{29}Si$ (59.6 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer in $C_6D_6$ solutions at 25 °C. Chemical shifts (δ, ppm) are given relative to the solvent signals or tetramethylsilane, coupling constants (*J*) are given in Hz. The $^{29}Si$ NMR spectra were measured without polarization transfer with the acquisition time of 4.27 s and the delay time $d_1$ = 52 s. Sample tubes were filled on a vacuum line and sealed off with flame. IR spectra (ν, $cm^{-1}$) were measured on a Nicolet 380 FT IR spectrometer with attenuated total reflectance (ATR) cell equipped with a silicon crystal in the range 650–4000 $cm^{-1}$ (resolution 4 $cm^{-1}$, 32 scans). A special air-protected cell was charged with the solid sample in a glovebag under argon. Since the silicon crystal does not allow measurement in the range 550–650 $cm^{-1}$, hexane solutions of the products were also measured in the range 400–1300 $cm^{-1}$ except for **2** and **5** which were too poorly soluble. Hexane solutions were filled into KBr cells ($d$ = 0.025–0.1 cm) under argon in a glovebag. XPS analysis of **1** for the content of Zr, Si, and Cl was carried out using VG ESCA3 MkII electron spectrometer equipped with an AlKα X-ray source and electrostatic hemispherical electron analyzer. The pressure of residual gases in analyzer chamber during spectra accumulation was $3 \times 10^{-3}$ mPa. The estimated error in binding energy determination was ±0.1 eV. Theoretical photoionization cross-sections were used to convert peak integrated intensities into the elemental concentrations. Curve fitting of overlapping spectral lines was carried out using the lines of a Gaussian–Lorentzian shape. The measured core level binding energies relative to C 1s line located at 284.8 eV were: Zr $3d_{5/2}$ (182.04 eV), Zr $3d_{3/2}$ (184.44 eV), Si 2p (102.41 eV), and Cl $2p_{3/2}$ (198.82 eV).

### Chemicals

The solvents toluene and hexane were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4C_5H_4)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$ (ref.[18]). Dichloromethane (Aldrich) was refluxed over $CaH_2$, and distilled into a storage ampule under argon. Commercial zirconium compounds, $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ (Aldrich) and $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ (Strem Chemicals), were weighed on air and degassed. $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ (Strem Chemicals) was weighed under argon and degassed. TRIPOSS $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$ and SIPOSS $[(c\text{-}C_5H_9)_7\text{-}Si_7O_{12}SiOH]$ (both Aldrich) were degassed and stored under argon. DIPOSS $[(c\text{-}C_5H_9)_7Si_7O_9\text{-}(OSiMe_3)(OH)_2]$ was prepared from TRIPOSS by a partial trimethylsilylation according to the literature[1b]. Triethylamine (Aldrich) was dried with sodium/benzophenone mixture, distilled at normal pressure under argon, and stored under argon. Methylaluminoxane (10 wt.% in toluene) (Aldrich) was used as received.

### Preparation of $[\{(c\text{-}C_5H_9)_7Si_7O_9O_3\}Zr_2Cl(\eta^5\text{-}C_5H_4Bu)_4]$ (**1**)

Under argon, a reaction ampoule equipped with a magnetic stirring bar was charged subsequently with TRIPOSS (0.85 g, 0.98 mmol), $CH_2Cl_2$ (60 ml), $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ (1.2 g, 2.95 mmol), and $NEt_3$ (0.35 g, 3.4 mmol). The resulting mixture was stirred at ambient temperature for 3 h, and then left standing overnight. All volatiles were evaporated in vacuum,

and the residue was repeatedly extracted with 30 ml of hexane. The hexane was slowly distilled into a distant arm of the ampule leaving a yellowish crystalline product. This was rinsed with condensing hexane vapor, and dissolved in 10 ml of warm hexane. Crystallization by slow cooling, finally to –28 °C yielded a white crystalline product. Yield 1.2 g (75%). $^1$H NMR ($C_6D_6$): 0.88 (t, $^3J_{HH}$ = 7.3, 6 H, Me); 0.92 (t, $^3J_{HH}$ = 7.3, 3 H, Me); 0.97 (t, $^3J_{HH}$ = 7.4, 3 H, Me); 1.12–2.24 (m, 79 H, $C_5H_9$ and C**H**$_2$C**H**$_2$Me); 2.66–2.80 (m, 8 H, $C_5H_4$C**H**$_2$); 5.73–5.78 (m, 4 H, $C_5H_4$); 6.00 (apparent t, 2 H, $C_5H_4$); 6.05 (apparent t, 2 H, $C_5H_4$); 6.16 (apparent q, 2 H, $C_5H_4$); 6.27 (apparent q, 2 H, $C_5H_4$); 6.38 (apparent t, 2 H, $C_5H_4$); 6.46 (apparent t, 2 H, $C_5H_4$). $^{13}$C{$^1$H} NMR ($C_6D_6$): 14.13 (2 C), 14.17, 14.23 (Me); 22.80 (2 C), 22.86 ($CH_2$ of Bu); 23.24, 23.39 (CH of $C_5H_9$); 23.48 ($CH_2$ of Bu); 24.48 (2 C), 24.67 (2 C), 26.14 (CH of $C_5H_9$); 27.34, 27.52 (2 C), 27.58 (2 C), 27.62 (2 C), 27.78, 28.07, 28.21, 28.33 (2 C), 28.55, 28.74, 28.82 ($CH_2$ of $C_5H_9$); 29.86, 30.03, 30.17 (2 C) ($CH_2$ of Bu); 32.77, 33.60 (2 C), 34.01 ($CH_2$ of Bu); 108.83, 110.74, 112.90, 113.01, 113.54, 113.67, 115.31, 117.68 (CH of $C_5H_4$); 130.31, 131.18, 133.30 (2 C) ($C_{ipso}$ of $C_5H_4$). $^{29}$Si NMR ($C_6D_6$): –66.66 (2 Si); –65.97 (1 Si); –65.39 (2 Si); –64.68 (1 Si); –61.89 (1 Si). IR (ATR Si): 3092 (vw), 2948 (s), 2932 (s, sh), 2908 (w, sh), 2862 (m), 1492 (w), 1465 (w, sh), 1451 (m), 1437 (vw, sh), 1424 (vw), 1378 (w), 1340 (vw), 1321 (vw), 1294 (vw), 1242 (m), 1099 (vs), 1077 (vs), 1050 (s, sh), 1040 (s), 1010 (vs), 985 (vs), 951 (m), 930 (m), 909 (m), 872 (w), 855 (w), 828 (m), 807 (s), 795 (s), 748 (w), 727 (m), 653 (m), 540 (w), 501 (s), 481 (s), 467 (s). IR (hexane): 1241 (m), 1104 (vs), 1093 (vs, sh), 1049 (m), 1038 (m), 1010 (vs), 981 (s), 746 (m), 933 (m, sh), 911 (m), 855 (w), 820 (w, sh), 804 (m), 793 (m), 653 (w), 542 (w), 498 (m), 481 (m), 463 (m, sh).

### Preparation of [{(*c*-$C_5H_9$)$_7$Si$_7$O$_9$O$_3$}Zr$_2$Cl($\eta^5$-$C_5H_5$)$_4$] (**2**)

To a suspension of dry TRIPOSS (3.31 g, 3.78 mmol) in $CH_2Cl_2$ was added under argon dry powdery [ZrCl$_2$($\eta^5$-$C_5H_5$)$_2$] (2.2 g, 7.56 mmol) and neat $NEt_3$ (1.15 g, 11.34 mmol), and the mixture was stirred at room temperature for 3 h. After standing overnight, the clear reaction solution was decanted from a precipitate of $Et_3N{\cdot}HCl$. The solution was evaporated under vacuum, the residue was rinsed twice with 15 ml of hexane and after drying in vacuum dissolved in 30 ml of toluene. The volume of the solution was reduced, and the saturated solution was left to crystallize at 5 °C. Pure colorless crystalline product was obtained by repeated crystallization. Yield 3.6 g (73%). $^1$H NMR ($C_6D_6$): 1.07–1.38 (m, 7 H, CH, cyclopentyl); 1.46–2.07 (m, 56 H, $CH_2$, cyclopentyl); 6.06 (s, 10 H, $C_5H_5$); 6.14, 6.34 (2 × s, 2 × 5 H, 2 × $C_5H_5$). $^{13}$C {$^1$H} NMR ($C_6D_6$): 23.19 (1 C), 23.23 (1 C), 23.97 (2 C), 24.09 (2 C), 25.70 (1 C) (CH, cyclopentyl); 27.32, 27.54, 27.62, 27.64, 27.69, 27.84, 28.03, 28.07, 28.15, 28.19, 28.38, 28.53, 28.62 ($CH_2$, cyclopentyl); 113.89, 114.12 (2 × 5 C, $C_5H_5$); 114.61 (10 C, $C_5H_5$). $^{29}$Si NMR ($C_6D_6$): –66.61 (2 Si); –66.75 (1 Si); –65.29 (2 Si); –64.66 (1 Si); –61.97 (1 Si). IR (ATR Si): 3102 (w), 2945 (m), 2908 (w, sh), 2862 (m), 1448 (w, sh), 1437 (w), 1363 (vw), 1320 (vw), 1291 (vw), 1243 (w), 1102 (vs, sh), 1084 (vs), 1045 (s, sh), 1011 (vs), 983 (vs), 952 (s), 910 (m), 849 (w, sh), 804 (vs), 796 (vs, sh), 725 (w), 689 (w), 654 (w), 538 (m, sh), 488 (s). IR (KBr): 3098 (w), 2948 (s), 2911 (m, sh), 2863 (m), 1447 (m), 1365 (vw), 1318 (vw), 1290 (vw), 1244 (m), 1098 (vs), 1011 (s), 979 (s), 947 (m), 912 (m), 805 (s), 798 (s, sh), 727 (w, br), 652 (w), 611 (vw), 541 (w), 489 (m), 448 (w), 427 (w).

Preparation of $[\{(c\text{-}C_5H_9)_7Si_8O_{12}O\}_2Zr(\eta^5\text{-}C_5H_4Bu)_2]$ (**3**)

A solution of $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ (0.43 g, 1.06 mmol) in a mixture of $NEt_3$ (0.26 g, 2.57 mmol) and 20 ml of dichloromethane was poured under argon onto solid SIPOSS (1.95 g, 2.126 mmol). The reaction mixture was stirred at ambient temperature for 14 h, after which time all volatiles were evaporated in vacuum, and the residue was extracted with hexane. The hexane solution was evaporated until becoming saturated. Crystallization in a refrigerator with the temperature decreasing from 5 to –5 °C afforded colorless crystalline material. Yield 2.1 g (95%). $^1$H NMR ($C_6D_6$): 1.01 (t, $^3J_{HH}$ = 7.3, 6 H, Me); 1.14–2.11 (m, 134 H, $C_5H_9$ and C**H**$_2$C**H**$_2$Me); 2.79 (apparent t, 4 H, $C_5H_4$C**H**$_2$); 6.18 (apparent t, 4 H); 6.28 (apparent t, 4 H). $^{13}$C{$^1$H} NMR ($C_6D_6$): 14.35 (1 C, Me), 22.77 (4 C; degenerate); 22.89 (3 C) (CH of $C_5H_9$); 23.08 (1 C, $CH_2$ of Bu); 27.48 (2 C), 27.50 (6 C), 27.62 (6 C), 27.85 (2 C), 27.88 (6 C), 27.99 (6 C) ($CH_2$ of $C_5H_9$); 29.57 (1 C), 34.10 (1 C) ($CH_2$ of Bu); 110.45 (2 C), 115.27 (2 C) (CH of $C_5H_4$); 131.39 (1 C) ($C_{ipso}$ of $C_5H_4$). $^{29}$Si NMR ($C_6D_6$): –106.60 (1 Si); –66.02 (7 Si). IR (ATR Si): 2949 (m), 2911 (w, sh), 2864 (m), 1449 (w), 1377 (vw), 1322 (vw), 1245 (m), 1118 (s, sh), 1097 (vs), 1050 (m), 1001 (s), 946 (vw), 913 (w), 807 (w), 794 (w), 502 (s), 419 (m). IR (hexane): 1322 (vw), 1244 (m), 1138 (s, sh), 1117 (vs), 1060 (m), 1048 (m, sh), 1004 (s), 947 (w), 917 (w), 808 (w, sh), 796 (w), 693 (vw), 512 (s), 422 (m).

Preparation of Impure $[\{(c\text{-}C_5H_9)_7Si_8O_{12}O\}ZrCl(\eta^5\text{-}C_5H_4Bu)_2]$ (**4**)

To a suspension of SIPOSS (1.91 g, 2.08 mmol) in dichloromethane (40 ml) under argon was added $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ (0.84 g, 2.08 mmol) and $NEt_3$ (0.21 g, 2.08 mmol), and the mixture was stirred at ambient temperature for 14 h. All volatiles were evaporated under vacuum, and the residue was extracted with 20 ml of hexane. A clear solution was decanted from a white precipitate of triethylammonium chloride. The solution was concentrated close to saturation. A white crystalline material was obtained by crystallization at –28 °C. This was rinsed with condensing hexane vapor and dried in vacuum. Yield 2.1 g (82%). According to $^1$H, $^{13}$C, and $^{29}$Si NMR spectra this material contained **4** (82%), $[ZrCl_2(\eta^5\text{-}C_5H_4Bu)_2]$ (9%), and **3** (9%). The NMR data below were easily distinguished from those of the known impurities. The IR ATR data are overwhelmed by those due to the SIPOSS ligand in **4** and those belonging to **3** were not observed (but they can slightly alter shapes of the absorption bands of **4**). $^1$H NMR ($C_6D_6$): 0.93 (t, $^3J_{HH}$ = 7.2, 6 H, **Me**, butyl); 1.11–1.44 (m, 11 H, C**H**, cyclopentyl and C**H**$_2$Me, butyl); 1.44–2.09 (m, 60 H, C**H**$_2$, cyclopentyl and C**H**$_2$CH$_2$Me, butyl); 2.72 (apparent t, 4 H, $C_5H_5$C**H**$_2$, butyl); 5.84–5.88 (m, 2 H, $C_5H_4$); 5.98–6.04 (m, 4 H, $C_5H_4$); 6.13–6.17 (m, 2 H, $C_5H_4$). $^{13}$C {$^1$H} NMR ($C_6D_6$): 14.17 (Me), 22.75 (4 C, CH, cyclopentyl); 22.94 (**C**H$_2$Me, butyl); 22.96 (3 C, CH, cyclopentyl); 27.47, 27.51, 27.86, 27.98 ($CH_2$, cyclopentyl); 29.82 (**C**H$_2$CH$_2$Me, butyl); 33.35 ($C_5H_4$**C**H$_2$, butyl); 110.83, 110.94, 115.86, 116.11 (CH, $C_5H_4$); 133.10 ($C_{ipso}$ of $C_5H_5$). $^{29}$Si NMR ($C_6D_6$): –106.82 (1 Si, $SiO_4$); –65.95 (1 Si); –65.93 (3 Si); –65.70 (3 Si). IR (ATR Si): 2949 (s), 2911 (w, sh), 2863 (m), 1491 (vw), 1464 (w, sh), 1450 (w), 1377 (vw), 1322 (vw), 1245 (m), 1098 (vs), 1050 (s, sh), 1017 (vs), 950 (w, sh), 931 (w, sh), 913 (m), 819 (m, sh), 801 (s), 728 (w, br), 504 (vs), 422 (s). IR (hexane): 1322 (vw), 1262 (w, sh), 1243 (m), 1117 (vs), 1051 (m, sh), 1021 (s), 945 (m), 917 (m), 816 (m, sh), 801 (m), 747 (w), 620 (vw), 577 (vw), 513 (s), 462 (vw), 422 (m).

Preparation of $[\{(c\text{-}C_5H_9)_7Si_8O_{12}O\}_2Zr(\eta^5\text{-}C_5H_5)_2]$ (**5**)

Compounds $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ (0.19 g, 0.75 mmol) and SIPOSS (1.37 g, 1.5 mmol) were weighed under argon into a reaction ampule attached to a vacuum line, and degassed. Then, 15 ml of hexane were vacuum distilled to the solid mixture under cooling with liquid nitrogen. A slow warming of the mixture to room temperature under stirring was accompanied by intense bubbling of evolved methane, and a voluminous white precipitate was formed. After stirring for 1 h, the methane was largely pumped off, and the precipitate was left to sedimentate for 5 h. Then, the reaction solution was carefully decanted from the precipitate. This was dried in vacuum, and dissolved in 20 ml of toluene. A crystalline colorless product was obtained by crystallization from warm saturated solution upon slow cooling to room temperature. Yield of **5** was 1.4 g (92%). $^1$H NMR ($C_6D_6$): 1.12–1.37 (m, 14 H, CH, cyclopentyl); 1.44–1.60 (m, 28 H, $CH_2$, cyclopentyl); 1.60–2.07 (m, 84 H, $CH_2$, cyclopentyl); 6.28 (s, 10 H, $C_5H_5$). $^{13}$C {$^1$H} NMR ($C_6D_6$): 22.80 (CH, cyclopentyl); 27.49, 27.59, 27.85, 27.90, 27.96 ($CH_2$, cyclopentyl); 113.87 ($C_5H_5$). $^{29}$Si NMR ($C_6D_6$): –106.39 (1 Si, $SiO_4$); –65.90 (1 Si); –65.86 (3 Si); –65.69 (3 Si). IR (ATR Si): 2948 (m), 2910 (w, sh), 2865 (m), 1448 (w), 1321 (vw), 1245 (w), 1095 (vs), 1062 (s), 1048 (s, sh), 1001 (vs), 946 (w), 913 (m), 847 (vw), 801 (m), 741 (w), 727 (w), 664 (vw), 502 (vs), 421 (s).

Preparation of $[\{(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)O_2\}Zr(\eta^5\text{-}C_5H_5)_2]$ (**6**)

Analogously to the synthesis of **5**, a mixture of solid compounds $[ZrMe_2(\eta^5\text{-}C_5H_5)_2]$ (0.164 g, 0.65 mmol) and DIPOSS (0.615 g, 0.65 mmol) was reacted after addition of hexane (15 ml) with evolution of methane. In distinction from **5**, the product was highly soluble in hexane. Therefore, after pumping off methane and some hexane a crude product was crystallized out by a slow evaporation of hexane at ambient temperature. A dim crystalline product was separated from the mother liquor, and rinsed with condensing hexane vapour. A repeated crystallization in the same manner yielded after drying in vacuum a white crystalline material. Yield 0.50 g (67%). $^1$H NMR ($C_6D_6$): 0.12 (s, 9 H, $SiMe_3$); 1.07–1.26 (m, 7 H, CH, cyclopentyl); 1.45–1.62 (m, 14 H, $CH_2$, cyclopentyl); 1.62–1.87 (m, 28 H, $CH_2$, cyclopentyl); 1.87–2.10 (m, 14 H, $CH_2$, cyclopentyl); 6.10, 6.33 (2 × s, 2 × 5 H, $C_5H_5$). $^{13}$C {$^1$H} NMR ($C_6D_6$): 2.13 ($SiMe_3$), 23.28 (2 C), 24.11 (2 C), 24.14 (2 C), 25.53(1 C) (CH, cyclopentyl); 27.34 (2 C), 27.53 (6 C), 27.56 (2 C), 27.69 (2 C), 27.82 (2 C), 28.07 (2 C), 28.11 (2 C), 28.20 (2 C), 28.25 (2 C), 28.42 (2 C), 28.47 (2 C), 28.59 (2 C) ($CH_2$, cyclopentyl); 113.71, 114.42 ($C_5H_5$). $^{29}$Si NMR ($C_6D_6$): –67.42 (2 Si); –66.09 (1 Si); –65.89 (1 Si); –65.45 (2 Si); –64.84 (1 Si); 7.79 (1 Si, $SiMe_3$). IR (ATR Si): 2948 (m), 2910 (w, sh), 2864 (m), 1450 (w), 1321 (vw), 1290 (vw), 1260 (w, sh), 1250 (m), 1237 (w, sh), 1090 (vs), 1062 (vs), 1045 (vs, sh), 1006 (vs), 947 (m), 910 (m), 860 (m), 843 (m), 810 (m), 796 (s), 754 (m), 723 (w), 506 (m, sh), 493 (s, sh), 482 (s). IR (hexane): 1321 (w), 1290 (vw), 1259 (m, sh), 1251 (m), 1239 (m, sh), 1112 (vs), 1066 (vs), 1045 (s, sh), 1010 (s), 948 (m), 913 (m), 861 (m), 843 (m), 809 (m), 796 (s), 745 (m), 580 (w), 530 (w, sh), 499 (m), 485 (m), 445 (w), 427 (w, sh).

Polymerization of Ethene

The polymerization of ethene was performed at constant ethene pressure (3 bars) in a 250 ml Büchi glass double-jacketed autoclave equipped with a magnetic stirrer. The hot autoclave was three times evacuated and filled with argon, charged with toluene, and the solution of methylaluminoxane (10 wt.% in toluene, molar ratio Al/Zr = 1000) was consecutively in-

jected. The autoclave was thermostated to 25 °C and the temperature was maintained by using the external Pt100 sensor connected to Julabo F31-C bath. The atmosphere of argon was replaced with ethene by cyclic pressuring and venting. The polymerization was started by injecting of the desired amount of dissolved zirconocene catalyst precursor (final volume of polymerization solution was 50 ml and [Zr] = $5 \times 10^{-6}$ mol $l^{-1}$ for all experiments), followed by pressuring autoclave with ethene to $3 \times 10^5$ Pa. After 10 min, the autoclave was vented and the residual mixture in autoclave was quenched with 80 ml of a 10% solution of HCl in ethanol. Precipitated polymer was stirred for 1 h, filtered off, washed with ethanol and acetone, and dried in vacuum to constant weight.

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