Macromolecules **2008,** *41,* 579−590

Zirconocene Immobilization and Activation on $MgCl_2$-Based Supports: Factors Affecting Ethylene Polymerization Activity

Rubin Huang, Robbert Duchateau, Cor E. Koning, and John C. Chadwick*

Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands, and Dutch Polymer Institute (DPI), P.O. Box 902,
5600 AX Eindhoven, The Netherlands

Received November 6, 2007; Revised Manuscript Received November 26, 2007

ABSTRACT: The effect of cyclopentadienyl ring substitution on the immobilization and activation of zirconocenes on supports of type $MgCl_2/AlR_n(OEt)_{3-n}$ has been investigated. Comparison of the activity of immobilized zirconocenes $(RCp)_2ZrCl_2$ in ethylene polymerization, using simple aluminum alkyls such as $AlEt_3$ or $Al\textit{i}Bu_3$ as a cocatalyst, revealed a remarkable effect of the substituent R in the cyclopentadienyl ring. Low activity (<300 kg/mol bar h) was obtained with R = H or Et, but longer alkyl substituents, notably *n*-Pr or *n*-Bu, gave more than an order of magnitude increase in activity. Zirconocenes with branched substituents (*i*-Pr, *t*-Bu) were less easily immobilized and gave relatively low activity, while the activities of zirconocenes of composition $Cp(RCp)ZrCl_2$ (R = *n*-Pr, *n*-Bu, *n*-pentyl) were intermediate between those of Cp_2ZrCl_2 and $(RCp)_2ZrCl_2$. Experiments carried out under homogeneous conditions with aluminoxane cocatalysts indicated that the effect of cyclopentadienyl ring substitution can be related to differences in the ease of formation of the active species. An inverse relationship between activity and the catalyst loading on the support was found. At a low loading of 1 μmol $(n\text{-PrCp})_2ZrCl_2$/g support, an activity greater than 40 000 kg/mol bar h was obtained in ethylene polymerization at 70 °C, with $Al\textit{i}Bu_3$ as the cocatalyst. The results demonstrate that with certain $MgCl_2$-immobilized zirconocenes it is possible to achieve very high polymerization activity without the use of methylaluminoxane or a borate activator, but the strong effect of catalyst loading on activity implies the presence of a relatively low number of active species.

Introduction

The discovery[1] by Kaminsky, Sinn, and co-workers in the early 1980s that very high ethylene polymerization activity could be obtained using homogeneous catalyst systems comprising of a zirconocene and methylaluminoxane (MAO) sparked an intensive, worldwide research effort into the development of well-defined, single-center catalysts for olefin polymerization.[2] In the case of metallocenes, the ability to tailor the steric and electronic environment of the metal center by varying the ligand substitution pattern and symmetry has led to increasing control over catalyst activity and polymer structure and properties.[3] However, utilization of a single-center catalyst in a gas-phase or slurry process for olefin polymerization requires its immobilization on a carrier and considerable efforts have been made to develop procedures for catalyst immobilization on a variety of support materials.[4] Silica has been widely used, but it is generally found that the activity after heterogenization on a silica support is significantly lower than the activity that can be obtained in homogeneous polymerization.[5] Lower activity after the immobilization of a zirconocene has also been noted using zeolites.[6]

In the past few years, there has been a notable increase in research on the use of magnesium chloride-based supports for the immobilization and activation of a range of early and late-transition metal catalysts.[7−10] This interest stems partly from the utilization of methods for controlling the particle size, porosity, and morphology of $MgCl_2$ supports, which are widely used in the production of Ziegler−Natta catalysts. Such supports can also have the advantage of easier fragmentation than is generally the case with silica supports, facilitating polymer particle growth during polymerization.[11]

In certain cases, magnesium chloride can function as a catalyst activator even in the absence of any additional cocatalyst, as a result of its Lewis acidity. This has been reported by Marks, who demonstrated that $MgCl_2$ was able to activate $(C_5Me_5)_2ThMe_2$ by abstraction of a methide anion, generating a catalytically active actinide species $[(C_5Me_5)_2ThMe]^+$ for ethylene polymerization.[12] Somewhat more attention has been paid to the use of $MgCl_2$-immobilized metallocenes together with MAO as the cocatalyst.[13] Immobilization of the aluminoxane itself on a magnesium chloride support has also been reported,[14] as well as approaches for the tethering of borate activators to the support.[15] For a number of $MgCl_2$-immobilized catalysts, including Ti, V, Cr, Fe, and Ni complexes,[8−10] activation can be achieved using simple cocatalysts such as $AlEt_3$ or $Al\textit{i}Bu_3$, in many cases giving activities comparable to or even exceeding those obtained in homogeneous polymerization. Avoidance of the need for the more expensive and complicated aluminoxane or borate activators represents one of the major incentives for the use of magnesium chloride supports. However, attempts to activate $MgCl_2$-supported zirconocenes using cocatalysts of type AlR_3 have been relatively unsuccessful. For example, immobilization of Cp_2ZrCl_2 on a support of type $MgCl_2/AlR_n(OEt)_{3-n}$ gave only a third of the activity in ethylene polymerization that was obtained with Cp_2TiCl_2.[9a] Kissin et al. have used mixtures of MgR_2 and $AlEt_2Cl$ to generate $MgCl_2$ and AlR_3 in situ, obtaining activities 5−10 times lower than those obtained with MAO.[16] Kaminaka and Soga reported that ball-milled $MgCl_2/\textit{rac}\text{-Et(IndH4)}_2ZrCl_2$ was active in propylene polymerization with $AlMe_3$ or $AlEt_3$ as the cocatalyst, although the activity was about an order of magnitude less than that obtained in homogeneous polymerization using MAO.[17] A linear increase in polymer yield with increasing polymerization time indicated high catalyst stability.[18] A key role of the $MgCl_2$ support was inferred from the fact that no activity was obtained with the

---

* Corresponding author. E-mail: j.c.chadwick@polymers.nl.

10.1021/ma7024557 CCC: $40.75

systems *rac*-Et(IndH4)$_2$ZrCl$_2$−AlMe$_3$ or SiO$_2$/*rac*-Et(IndH4)$_2$-ZrCl$_2$−AlMe$_3$.[17] It is important in this respect that the support contains Lewis acidic centers, enabling catalyst activation without the use of MAO or borates. Echevskaya et al. have immobilized *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ on highly dispersed MgCl$_2$, prepared by the reaction of MgBu$_2$·*n*AlEt$_3$ with CCl$_4$. Using Al*i*Bu$_3$ as the cocatalyst, they obtained an ethylene polymerization activity similar to that obtained using a SiO$_2$/MAO support, albeit that the activity was much lower than that obtained in homogeneous polymerization with MAO as the cocatalyst.[19]

In the current work, we present the results of a study of the effects of alkyl substitution in one or both rings of bis(cyclopentadienyl)zirconium dichloride, immobilized on MgCl$_2$-based supports, using AlEt$_3$ or Al*i*Bu$_3$ as the cocatalyst. Remarkable differences in catalyst activity are obtained with catalysts of type (RCp)$_2$ZrCl$_2$, dependent on the alkyl substituent R. Comparative experiments carried out under homogeneous conditions with aluminoxane cocatalysts indicate that these effects can be related to differences in the ease of formation of the active species. An inverse relationship between catalyst activity and loading on the support indicates that only a limited proportion of surface sites on magnesium chloride are able to effectively immobilize and activate zirconocene catalysts.

Experimental Section

General Methods. All manipulations were performed under an argon atmosphere using a glove box (Braun MB-150 GI or LM-130) and Schlenk techniques. ^{1}H NMR spectroscopy was performed using a Varian 400 NMR spectrometer. Data were acquired using VNMR-software. Chemical shifts are reported relative to residual CHCl$_3$ (δ 7.26 for ^{1}H). Elemental analysis for MgCl$_2$/AlEt$_n$(OEt)$_{3-n}$ supports and synthesized metallocene catalysts was carried out by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Ethoxide contents in the MgCl$_2$/AlEt$_n$(OEt)$_{3-n}$ supports were determined by gas chromatography (GC) analysis of the ethanol content of a solution obtained by dissolving 100 mg of support in 5 mL of BuOH containing a known quantity of PrOH as an internal standard. Molecular weight and molecular weight distributions of the resulting polymers were determined by means of gel permeation chromatography on a PL-GPC210 at 135 °C using 1,2,4-trichlorobenzene as the solvent. Differential scanning calorimetry (DSC) was carried out with a Q100 differential scanning calorimeter (TA Instruments). The samples (4−6 mg) were heated to 160 °C and subsequently cooled to 20 °C at a rate of 10 °C/min. A second heating cycle was used for data analysis. The particle morphologies of the polymers were examined using a Philips S-250MK3 SEM-EDX. UV−vis absorption spectra were recorded with a Hewlett-Packard 8453 spectrometer operating between 200 and 1100 nm under ambient conditions, using a sealed 1.4 mL cuvette supplied by Hellma GmbH.

Materials. Light petroleum (bp 40−60 °C), *n*-pentane, tetrahydrofuran (THF), and toluene were purchased from Biosolve and passed over a column containing activated alumina. All solvents were freeze−thaw degassed twice before use. *n*-BuLi (1.6 M in hexane), ZrCl$_4$, CpZrCl$_3$, 1-bromopropane, 1-bromobutane, and 1-bromopentane were purchased from Aldrich and used directly. CDCl$_3$ was purchased from Cambridge Isotope Laboratories. Cp$_2$-ZrMe$_2$, Cp$_2$HfCl$_2$, (RCp)$_2$ZrCl$_2$ (R = H, Et, *i*-Pr, *n*-Bu, *t*-Bu), (C$_5$-HMe$_4$)$_2$ZrCl$_2$, and (C$_5$Me$_5$)$_2$ZrCl$_2$ were purchased from Strem Chemicals. (RCp)$_2$ZrCl$_2$ with R = *n*-Pr and *n*-dodecyl were purchased from Wako Pure Chemical Industries. (1,3-Me$_2$-Cp)$_2$ZrCl$_2$, (1-Me-3-*n*-BuCp)$_2$ZrCl$_2$, and (1,2,4-Me$_3$Cp)$_2$ZrCl$_2$ were generously donated by Borealis Polymers Oy. AlEt$_3$ (1.3 M in heptane) and Al*i*Bu$_3$ (25 wt % in toluene) were obtained from Acros and Akzo Nobel, respectively. Methylaluminoxane (MAO) (10 wt % in toluene) was purchased from Chemtura. AlEt$_2$Cl (1.0 M in heptane) and tetraisobutyldialuminoxane (10 wt % in toluene) were purchased from Aldrich. Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of BASF RS3-11 supported Cu oxygen scavenger and 4 Å molecular sieves.

Synthesis of Cp(*n*-BuCp)ZrCl$_2$. CpNa was prepared according to literature procedures.[20] Freshly distilled cyclopentadiene (6.0 g) was added with stirring at −78 °C under nitrogen to 2.09 g of Na in 100 mL of THF, and the mixture was refluxed overnight and then cooled to room temperature, after which the solvent was removed under vacuum. The solid was washed several times with light petroleum and dried until free flowing. An amount of 30 mL of light petroleum and 100 mL of THF was added slowly to CpNa (8.0 g, 90.8 mmol) at room temperature and stirred until a clear solution appeared. An amount of 12.5 g (90.8 mmol) of 1-bromobutane was then added dropwise. After stirring overnight, the solvent was removed in vacuo to give an oily product. After distillation, *n*-BuCpH was obtained as a pale yellow oil (7.0 g, 63.0%).

A 250 mL round-bottom flask equipped with stirring bar and dropping funnel was charged with *n*-BuCpH (5.0 g, 41.3 mmol) in THF (150 mL), after which *n*-BuLi (16.5 mL, 41.3 mmol, 2.5 M in hexane) was added dropwise at room temperature. The resulting suspension was stirred overnight. Volatiles were removed under vacuum, and the residue was washed with *n*-pentane (30 mL) to give the lithium salt *n*-BuCpLi (4.2 g, 80%) as a free flowing white powder after drying. At 0 °C, a THF (50 mL) solution of *n*-BuCpLi (0.24 g, 1.87 mmol) was added dropwise during 30 min to a solution of CpZrCl$_3$ (0.50 g, 1.87 mmol) in THF (50 mL). The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solvent was then removed in vacuo and hexane (150 mL) was added and the mixture was filtered. The filtrate was concentrated (30−50 mL) and cooled to −30 °C to give the title complex Cp(*n*-BuCp)ZrCl$_2$ (0.10 g, 15%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 0.92$ (t, 3 H, CH$_2$CH$_2$CH$_2$C***H$_3$***), 1.35 (m, 2 H, CH$_2$CH$_2$C***H$_2$***CH$_3$), 1.55 (m, 2 H, CH$_2$C***H$_2$***CH$_2$CH$_3$), 2.62 (t, 2 H, C***H$_2$***CH$_2$CH$_2$CH$_3$), 6.22, 6.32 (2 m, each 2 H, C$_5$***H$_4$***), 6.46 (s, 5 H, C$_5$***H$_5$***) ppm. C$_{14}$H$_{18}$Cl$_2$Zr (348): calcd, C 48.3, H 5.17; found, C 48.0, H 5.28.

Synthesis of Cp(*n*-PrCp)ZrCl$_2$ and Cp(*n*-pentylCp)ZrCl$_2$. These complexes were prepared using procedures similar to those described above. Details of synthesis and characterization can be found in the Supporting Information.

Synthesis of (*n*-PentylCp)$_2$ZrCl$_2$. *n*-PentylCpLi (1.0 g, 7.0 mmol) in THF (50 mL) was added dropwise during 20 min to a solution of ZrCl$_4$ (0.82 g, 3.50 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. Solvent was removed in vacuo, and hexane (100 mL) was added to the resulting solid. The mixture was filtered, and the filtrate was concentrated (20 mL) and cooled to −30 °C to give the title complex. Yield 0.60 g, 40%. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 0.92$ (2 t, 6 H, 2 × CH$_2$CH$_2$CH$_2$CH$_2$C***H$_3$***), 1.32 (2 m, 8 H, 2 × CH$_2$CH$_2$C***H$_2$***C***H$_2$***CH$_3$), 1.55 (2 m, 4 H, 2 × CH$_2$C***H$_2$***-CH$_2$CH$_2$CH$_3$), 2.61 (2 t, 4 H, 2 × C***H$_2$***CH$_2$CH$_2$CH$_2$CH$_3$), 6.22, 6.32 (2 m, each 4 H, 2 × C$_5$***H$_4$***) ppm. C$_{20}$H$_{30}$Cl$_2$Zr (432): calcd, C 55.6, H 6.94; found, C 55.3, H 7.01.

Synthesis of (*n*-BuCp)$_2$ZrMe$_2$. A 3 M solution of MgMeBr in diethyl ether (1.0 mL, 3.0 mmol) was added to a stirred solution of (*n*-BuCp)$_2$ZrCl$_2$ (0.60 g, 1.5 mmol) in diethyl ether (40 mL) at −78 °C. The solution was allowed to warm to room temperature and stirred for 4 h. After removal of diethyl ether in vacuo, (*n*-BuCp)$_2$ZrMe$_2$ was isolated by extraction with *n*-pentane (30 mL), which was subsequently removed in vacuo. The purity of the liquid product was verified by ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = -0.47$ (2 s, 6 H, 2 × Zr−C***H$_3$***), 0.94 (2 t, 6 H, 2 × CH$_2$CH$_2$-CH$_2$C***H$_3$***), 1.40 (2 m, 4 H, 2 × CH$_2$CH$_2$C***H$_2$***CH$_3$), 1.55 (2 m, 4 H, 2 × CH$_2$C***H$_2$***CH$_2$CH$_3$), 2.45 (2 t, 4 H, 2 × C***H$_2$***CH$_2$CH$_2$CH$_3$), 5.81, 5.91 (2 m, each 2 H, C$_5$***H$_4$***).

Details of the synthesis of (RCp)$_2$ZrMe$_2$ (R = Et, *n*-Pr, *n*-pentyl, and *n*-dodecyl), using similar procedures, are given in the Supporting Information.

X-ray Crystal Structure Determination of Cp(*n*-BuCp)ZrCl$_2$. Needle-shaped crystals of Cp(*n*-BuCp)ZrCl$_2$ were obtained by slow crystallization from diethyl ether. A suitable crystal was selected, mounted on a thin glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω scans at ϕ values of 0, 90, and 180°. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Complete crystallographic data are available in the Supporting Information. Data were integrated using SAINT, and an absorption correction was performed with the program SADABS. The structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Support Preparation and Catalyst Immobilization. The supports used in this work were prepared by addition of $AlEt_3$ to an adduct $MgCl_2 \cdot n EtOH$ ($n = 1.1$, 2.1 or 2.8) in light petroleum ($AlEt_3/EtOH = 2$) at 0 °C, after which the mixture was kept at room temperature for 2 days with occasional agitation. The resultant support was washed with light petroleum (3 × 20 mL) and dried under argon flow and subsequently under vacuum until free flowing. In the case of a second treatment of the support obtained above, a 2-fold excess of $AlEt_3$ with respect to residual ethoxide was used.

Catalyst immobilization was effected by mixing the support (100 mg) with a catalyst solution in toluene or dichloromethane (2 mL, containing 0.1−5.0 μmol of catalyst) and keeping at room temperature overnight. The slurry of the immobilized catalyst was diluted with light petroleum and used directly in ethylene polymerization.

Ethylene Polymerization. Polymerization was carried out in a l L Premex autoclave by charging the immobilized catalyst, slurried in approximately 100 mL of light petroleum, to 400 mL of light petroleum containing the desired amount of cocatalyst, at the desired temperature and at an ethylene pressure of 5 bar. In the case of homogeneous polymerization, MAO and catalyst solutions in toluene were injected successively at 50 °C and 5 bar ethylene pressure. After catalyst injection, polymerization was continued at constant pressure for 1 h for heterogeneous systems and 30 min for homogeneous catalysts, with a stirring rate of 1000 rpm. After venting the reactor, 20 mL of acidified ethanol were added and stirring was continued for 30 min. The polymer was recovered by filtration, washed with water and ethanol, and dried in vacuo overnight at 60 °C.

Under the above conditions, polymerization activities obtained in duplicate experiments with immobilized catalysts are repeatable to within 5−10%.[9g]

Results and Discussion

The activity of a metallocene catalyst is influenced by both electronic effects and steric encumbrance around the active site[21] and by the degree of interaction between the active cationic species and the counterion.[22] For zirconocenes of type $(RCp)_2ZrCl_2$ activated by ethylaluminoxane, it has been reported[21c] that an increase in ligand size produces a small increase in activity, while an increase in ligand electron donating capacity substantially increases the activity. However, a subsequent study in which MAO was used as the cocatalyst failed to provide a simple correlation between activity and either steric or electronic effects.[21d] MAO-activated ethylene polymerization with a series of zirconocenes $(RCp)_2ZrCl_2$ in which R was varied from H up to dodecyl has been investigated by Rytter and co-workers, who found that R = *n*-Pr and *n*-Bu increased the average polymerization activity at 50 °C by factors of 4 and 2.5, respectively, compared to R = H.[23] It was proposed that these higher activities resulted from an agostic interaction between the metal center and a hydrogen on the alkyl substituent. Higher activities with $(n\text{-}BuCp)_2ZrCl_2$ than with Cp_2ZrCl_2 have also been noted for SiO_2/MAO/metallocene systems, although the butyl-substituted zirconocenes exhibited more rapid deactivation during polymerization.[24]

Table 1. Ethylene Polymerization Using $(RCp)_2ZrCl_2$ Immobilized on a $MgCl_2$-Based Support[a]

entry	R	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
1	H	160	134.5	53.5	88 000	352 000	4.0
2	Et	260	135.1	55.6	113 000	394 000	3.5
3	Pr	2760	135.4	58.5	95 000	242 000	2.5
4	*i*-Pr	360	135.6	51.7	194 000	485 000	2.5
5	Bu	3680	135.3	56.9	120 000	271 000	2.3
6	*t*-Bu	120	135.1	53.7	126 000	425 000	3.4
7	pentyl	1120	134.5	57.9	98 000	302 000	3.1
8	dodecyl	700	135.6	53.8	122 000	344 000	2.8

[a] Support composition: $MgCl_2 \cdot 0.30AlEt_{2.46}(OEt)_{0.54}$. Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

In the present work, the effects of cyclopentadienyl ring substitution on the immobilization and activation of metallocenes of type $(RCp)_2ZrCl_2$ and $(Cp)(RCp)ZrCl_2$ have been investigated. Supports of type $MgCl_2/AlEt_n(OEt)_{3-n}$ were used, prepared mostly by the reaction of an adduct $MgCl_2 \cdot 1.1EtOH$ with excess $AlEt_3$. In previous studies we have found that this type of support can be used for the immobilization and activation of a range of early and late-transition metal complexes, giving high and stable polymerization activity and spherical polyethylene particle morphology.[9]

Effect of Zirconocene Ring Substitution. Investigation of substituent effects in zirconocenes of type $(RCp)_2ZrCl_2$ immobilized on magnesium chloride was first carried out using a support of composition $MgCl_2 \cdot 0.30AlEt_{2.46}(OEt)_{0.54}$. Catalyst immobilization was effected by contacting the support overnight with a solution of the metallocene in toluene, after which the slurry of the immobilized catalyst was simply diluted with light petroleum and used directly in ethylene polymerization, carried out at 50 °C with a constant monomer pressure of 5 bar. The results in Table 1 reveal a remarkable effect of cyclopentadienyl ring substitution on catalyst activity. Low activities were obtained with R = H or Et, but longer-chain alkyl substituents gave much higher activities. In the case of $(n\text{-}BuCp)_2ZrCl_2$, the activity was more than 20 times that obtained with Cp_2ZrCl_2. It was also observed that the ethylene mass flow remained essentially constant throughout polymerization, indicating negligible decay in catalyst activity. High activity was similarly obtained with R = *n*-Pr, while *n*-pentyl and *n*-dodecyl also gave much higher activities than the unsubstituted zirconocene. However, the introduction of branching into the alkyl substituent led to poor catalyst performance, seen from the low activities obtained with R = *i*-Pr or *t*-Bu. A relatively low activity of $(t\text{-}BuCp)_2ZrCl_2$ in homogeneous polymerization has been noted by Tait et al.[25] In the present system, the increased steric bulk imposed by branched substituents evidently impedes effective activation on the magnesium chloride support. It was previously observed[9a] that *rac*-$Et(Ind)_2ZrCl_2$, immobilized on a similar support, gave negligible polymerization activity. The polyethylene molecular weight data in Table 1 show M_w values in the range 200 000−500 000 g/mol, the highest molecular weights being obtained with R = *i*-Pr or *t*-Bu. Overall, the molecular weights are higher than those typically reported for homogeneous polymerization conditions, decreased susceptibility to chain transfer being a frequently observed feature of immobilized catalysts.[9,13d,26] The M_w/M_n values indicate in most cases a relatively narrow molecular weight distribution but significant deviations from the value of 2.0, expected for single-

Table 2. Effect of Number of Substituents in $(C_5H_nR_{5-n})_2ZrCl_2$ Immobilized on a $MgCl_2$-Based Support[a]

Cp ring substitution	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
1,3-Me_2	140	135.2	47.1	172 000	474 000	2.8
1-Me-3-*n*-Bu	880	135.9	54.3	217 000	467 000	2.2
1,2,4-Me_3	120	136.1	50.1	184 000	430 000	2.3
Me_4	140	139.2	47.3	119 000	392 000	3.3
Me_5	180	139.2	47.3	148 000	391 000	2.6

[a] Support composition: $MgCl_2 \cdot 0.30AlEt_{2.46}(OEt)_{0.54}$. Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

center catalysis, are apparent. Taking into account the difficulties and uncertainties in polydispersity measurement by high-temperature GPC, we have recently used melt rheometry for additional characterization and have established that a zirconocene can retain its single-center characteristics after immobilization on magnesium chloride, whereas this was not apparent for titanocenes.[27] The DSC data reveal that polymer crystallinities and melting temperatures fell within a fairly narrow range, irrespective of catalyst structure.

In view of the remarkable activity difference between Cp_2ZrCl_2 and $(n\text{-}BuCp)_2ZrCl_2$, the analogous hafnocenes were also investigated. At 50 °C, Cp_2HfCl_2 gave an activity of only 40 kg/mol bar h, while with $(n\text{-}BuCp)_2HfCl_2$ an activity of 240 kg/mol bar h was obtained. The polyethylene molecular weight (M_w) obtained with the latter was 627 000 g/mol, as opposed to 271 000 g/mol with the corresponding zirconocene. Higher molecular weight with Hf- than with Zr-based systems is a well-established feature of metallocene-catalyzed olefin polymerization.[28] A lower activity for hafnocene- as opposed to zirconocene-catalyzed polymerization is also expected, although it has been shown that hafnocenes can give very high activity when used together with a borate activator.[28c]

In addition to varying the substituent in zirconocenes of type $(C_5H_4R)_2ZrCl_2$, the effect of increasing the number of substituents was investigated. The results obtained with $(C_5H_nR_{5-n})_2ZrCl_2$ are shown in Table 2, from which it is apparent that low activities were obtained with methyl-substituted zirconocenes, irrespective of the number of methyl substituents. However, a 6-fold increase in activity was observed on going from 1,3-dimethyl to 1-methyl-3-*n*-butyl substitution in the cyclopentadienyl ring, again underlining the positive effect of a longer alkyl group.

The effect of alkyl substitution in only one of the cyclopentadienyl rings was investigated using $(Cp)(RCp)ZrCl_2$, synthesized by the reaction of $[C_5H_4R]Li$ with $CpZrCl_3$, as described in the Experimental Section. The X-ray crystal structure of $(Cp)(n\text{-}BuCp)ZrCl_2$ is shown in Figure 1. The polymerization results in Table 3 show that the activities of these complexes, immobilized on the same support, are intermediate between those of Cp_2ZrCl_2 and $(RCp)_2ZrCl_2$. In other words, an alkyl (in particular, *n*-propyl or *n*-butyl) substituent in each cyclopentadienyl ring is required for high activity.

The above polymerization studies consistently gave spherical polymer particle morphology, with no evidence of reactor fouling. A scanning electron micrograph of polyethylene produced with immobilized $(n\text{-}BuCp)_2ZrCl_2$ is shown in Figure 2, demonstrating that the spherical morphology of the original support had been retained and replicated throughout catalyst immobilization and polymerization.

Effect of Support Composition. Previous studies have shown variations in the activity of a bis(imino)pyridyl iron complex immobilized on different batches of $MgCl_2/AlEt_n(OEt)_{3-n}$ support, indicating that the support composition can have a significant effect on catalyst activity.[9g] This should also be the case for zirconocene activation on similar supports, taking into account the importance of acidic surface sites in the generation of active species.[12a,29] In order to determine the effect of support composition, three different $MgCl_2 \cdot nEtOH$ starting materials were used, each of which were reacted either once or twice with $AlEt_3$. The compositions of the supports obtained are given in Table 4. It is apparent that in each case a second treatment with $AlEt_3$ resulted in an increase in the Al content and a

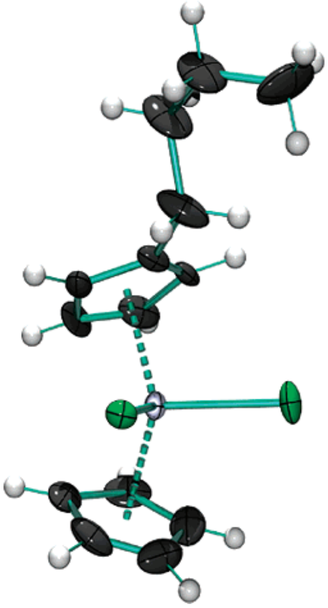


Figure 1. ORTEP view of $[Zr(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\{CH_2CH_2CH_2CH_3\})Cl_2]$.

Table 3. Ethylene Polymerization Using $Cp(RCp)ZrCl_2$ Immobilized on a $MgCl_2$-Based Support[a]

R	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
propyl	740	135.6	51.6	150 000	415 000	2.8
butyl	1020	135.5	51.4	148 000	404 000	2.7
pentyl	460	134.9	50.3	134 000	416 000	3.1

[a] Support composition: $MgCl_2 \cdot 0.30AlEt_{2.46}(OEt)_{0.54}$. Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

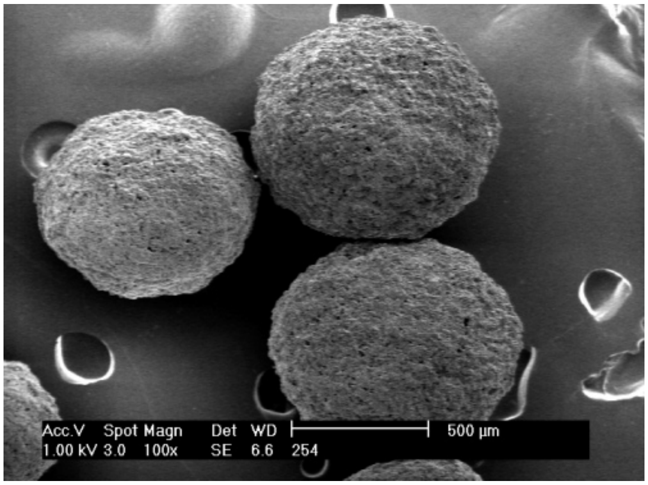


Figure 2. Scanning electron micrograph of polyethylene (entry 5, Table 1) prepared using $(n\text{-}BuCp)_2ZrCl_2$ immobilized on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support.

Table 4. Effect of Support Composition on Ethylene Polymerization Using (n-PrCp)$_2$ZrCl$_2$[a]

starting material[b]	$AlEt_3$ treatments	Al (wt %)	OEt (wt %)	overall composition	activity (kg/mol of Zr h bar)
$MgCl_2{\cdot}1.1EtOH$	1	4.12	7.89	$MgCl_2{\cdot}0.18AlEt_{1.85}(OEt)_{1.15}$	3940
$MgCl_2{\cdot}1.1EtOH$	2	4.53	5.84	$MgCl_2{\cdot}0.20AlEt_{2.23}(OEt)_{0.77}$	4300
$MgCl_2{\cdot}2.1EtOH$	1	7.50	5.33	$MgCl_2{\cdot}0.40AlEt_{2.57}(OEt)_{0.43}$	200
$MgCl_2{\cdot}2.1EtOH$	2	8.10	5.16	$MgCl_2{\cdot}0.45AlEt_{2.62}(OEt)_{0.38}$	160
$MgCl_2{\cdot}2.8EtOH$	1	7.06	6.43	$MgCl_2{\cdot}0.37AlEt_{2.45}(OEt)_{0.55}$	880
$MgCl_2{\cdot}2.8EtOH$	2	7.56	5.84	$MgCl_2{\cdot}0.40AlEt_{2.53}(OEt)_{0.47}$	1160
$MgCl_2$[c]				$MgCl_2$	720

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h. [b] Particle size (d_{50}): $MgCl_2{\cdot}1.1EtOH$, 82 μm; $MgCl_2{\cdot}2.1EtOH$, 61 μm; $MgCl_2{\cdot}2.8EtOH$, 15 μm. [c] Ball-milled $MgCl_2$.

Table 5. Ethylene Polymerization Using (C_5H_4R)(C_5H_4R')ZrCl$_2$ on a Support of Composition $MgCl_2{\cdot}0.17AlEt_{1.92}(EtO)_{1.08}$[a]

entry	R	R′	activity (kg/mol of Zr h bar)
1	H	Pr	1500
2	Pr	Pr	7200
3	H	Bu	1760
4	Bu	Bu	4160
5	H	pentyl	1060
6	pentyl	pentyl	3560
7	dodecyl	dodecyl	2400

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

Table 6. Ethylene Polymerization Using Homogeneous (C_5H_4R)(C_5H_4R')ZrCl$_2$/MAO Catalysts[a]

entry	R	R′	Al/Zr	activity (kg/mol of Zr·h.bar)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
1	H	H	1 000	880	297 000	92 000	3.2
2	H	H	10 000	5 480	392 000	183 000	2.1
3	H	Pr	1 000	6 160	489 000	245 000	2.0
4	H	Bu	1 000	10 160	494 000	248 000	2.0
5	H	pentyl	1 000	2 160	566 000	238 000	2.4
6	Pr	Pr	1 000	7 600	482 000	244 000	2.0
7[b]	Pr	Pr	10 000	53 400	347 000	175 000	2.0
8	Bu	Bu	1 000	6 120	467 000	225 000	2.1
9	pentyl	pentyl	1 000	3 000	551 000	260 000	2.1
10	dodecyl	dodecyl	1 000	2 530	545 000	234 000	2.3

[a] Polymerization conditions: 500 mL of light petroleum, catalyst 1.0 μmol, 50 °C, ethylene pressure 5 bar, time 30 min. [b] Polymerization time 10 min.

decrease in the residual ethoxide content of the final support, although the differences are fairly small. It is likely that the residual ethoxide is present in the form of coordinatively bridged species of type Mg−O(Et)−Al, which cannot be easily removed from the support surface.[9a] The catalyst activities in Table 4 indicate that an additional treatment with $AlEt_3$ leads to small increases in activity for the supports prepared from $MgCl_2{\cdot}1.1EtOH$ and $MgCl_2{\cdot}2.8EtOH$. Very low activities were obtained with the $MgCl_2{\cdot}2.1EtOH$ support precursor. It is probable that the different activities obtained with the respective support precursors are related more to particle porosity than to chemical composition. Substantially dealcoholated supports such as $MgCl_2{\cdot}1.1EtOH$ have porosities in the range 0.40−0.60 mL/g, whereas the porosities of supports with a EtOH/$MgCl_2$ molar ratio $>$ 2 are in the 0.10−0.15 mL/g range.[30] The most effective supports are those having high porosity.[7] The difference in the activities obtained with the less porous $MgCl_2{\cdot}2.1EtOH$ and $MgCl_2{\cdot}2.8EtOH$ supports is likely to be due to their different particle sizes, the latter support having much smaller particle size. It can be seen from Table 4 that moderate activity could also be achieved using ball-milled magnesium chloride, indicating that the presence of alkylaluminum alkoxide species in the support is not necessary for catalyst activation.

High catalyst activities were obtained with a support of composition $MgCl_2{\cdot}0.17AlEt_{1.92}(OEt)_{1.08}$, obtained from the reaction of $MgCl_2{\cdot}1.1EtOH$ with $AlEt_3$. The results in Table 5 show that with this support (n-PrCp)$_2$ZrCl$_2$ gave an activity of 7200 kg/mol bar h at 50 °C, demonstrating the possibility of obtaining high activity with a $MgCl_2$-immobilized zirconocene without the use of an aluminoxane or borate activator. In a previous study, we have observed that titanocene dichloride could be activated on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support even without the use of additional aluminum alkyl.[9a] In the present work it was found that injection of immobilized (n-PrCp)$_2$ZrCl$_2$ into the polymerization reactor in the absence of a cocatalyst did not result in any observable uptake of ethylene. Subsequent injection of $AlEt_3$ did result in polymerization, however, demonstrating its function as a cocatalyst and not merely as a scavenger. An aluminum alkyl is of course required for the formation of a zirconium−carbon bond, and the formation of active zirconocenium species is dependent on both the acidic nature of the support and the alkylating power of the cocatalyst.

Comparison of Homogeneous and Heterogeneous Catalyst Systems. In order to gain more insight into the effects of immobilization and the efficiency of active site formation with $MgCl_2$-immobilized zirconocenes, a series of reference polymerizations was carried out without immobilization on a support, using MAO as the cocatalyst. The results in Table 6 show that, for a given Al/Zr ratio, all the alkyl-substituted zirconocenes had higher activities than Cp_2ZrCl_2 under homogeneous polymerization conditions. At an Al(MAO)/Zr ratio of 1000, (n-PrCp)$_2$ZrCl$_2$ gave an activity similar to that obtained using a $MgCl_2/AlEt_n(OEt)_{3-n}$ support and $AlEt_3$ as the cocatalyst (Table 5, entry 2). In the absence of the support, $AlEt_3$ was ineffective as the cocatalyst, giving an activity of only 240 kg/mol bar h at an Al/Zr molar ratio of 1000, in stark contrast to the $>$7000 kg/mol bar h obtained with MAO and with $AlEt_3$ after immobilization. In the immobilized system, the magnesium chloride support clearly plays an important role in the generation of active species. However, the activities of the immobilized systems only approached those of the MAO-activated, homogeneous systems when the “low” Al(MAO)/Zr ratio of 1000 was used. Increasing this ratio to 10000 resulted in much higher activities, as can be seen from entries 2 and 7 in Table 6. The requirement for a large excess of MAO for the effective activation of metallocenes is well-known, and differences in polymerization activity at different MAO/Zr ratios have been linked to different proportions of active species.[31] Whereas large quantities of MAO are required to activate zirconocene dichlorides, conversion of the dichloride to a dimethyl or dibenzyl analogue enables effective activation at relatively low MAO/Zr ratios.[32] The low activity of zirconocene dichlorides at low MAO concentrations was attributed to the negative role of the $[MAO-Cl]^-$ counterion in the activation process. Deffieux and

Table 7. Effect of Cocatalyst in Ethylene Polymerization Using $(n\text{-PrCp})_2ZrCl_2$ on a Support of Composition $MgCl_2 \cdot 0.17AlEt_{1.92}(EtO)_{1.08}$[a]

cocatalyst	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)
AlEt3	7200	135.8	57.2
MAO	8560	136.4	55.5
AliBu3	3440	135.6	58.7
*i*Bu$_2$AlOAl*i*Bu$_2$	5420	136.3	57.1

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), cocatalyst1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

co-workers have also reported that the amount of MAO required for catalyst activation could be decreased by precontacting the zirconocene and MAO in dichloromethane.[31] In the present work, however, it was found that the use of dichloromethane rather than toluene for the immobilization of $(n\text{-BuCp})_2ZrCl_2$ on a support $MgCl_2 \cdot 0.17AlEt_{1.92}(OEt)_{1.08}$ did not lead to higher activity, the respective activities being 3800 and 3960 kg/mol bar h.

Effects of Cocatalyst and Temperature. To compare the cocatalyst effects in the homogeneous polymerizations with those in heterogeneous polymerization, various aluminum alkyls and aluminoxanes were used as cocatalysts in polymerizations with $(n\text{-PrCp})_2ZrCl_2$ immobilized on $MgCl_2/AlEt_n(OEt)_{3-n}$. The results in Table 7 show that the use of MAO gave a slightly higher activity than $AlEt_3$. However, MAO also gave serious reactor fouling, indicative of catalyst leaching from the support. Good particle morphology, with no trace of leaching, was obtained with $AlEt_3$, Al*i*Bu$_3$, and *i*Bu$_2$AlOAl*i*Bu$_2$.

After this initial screening, the effects of various cocatalysts were investigated at polymerization temperatures of 50 and 70 °C. These experiments were carried out using not only $(n\text{-PrCp})_2ZrCl_2$ but also $(n\text{-PrCp})_2ZrMe_2$, derived from the dichloride by reaction with MgMeBr, following procedures similar to those reported by Otero and co-workers.[33] The results obtained are given in Tables 8 and 9 and reveal a number of significant findings. First, the relative activities obtained with $AlEt_3$ and Al*i*Bu$_3$ were strongly dependent on the polymerization temperature, with $AlEt_3$ giving high activity at 50 °C, whereas at 70 °C the highest activities were obtained with Al*i*Bu$_3$. The activities in the range 11 000−13 000 kg/mol bar h achieved in these experiments are particularly high and it may be noted that these polymerizations were carried out with a batch of support having a relatively low residual ethoxide content, providing a further indication of the dependence of catalyst activity on support composition. The different effects obtained with $AlEt_3$ and Al*i*Bu$_3$ were found to be due to a relatively rapid decay in activity when using $AlEt_3$ as the cocatalyst at 70 °C. Rapid deactivation was also observed with $AlEt_2Cl$. Activity profiles for polymerizations carried out at 70 °C, apparent from changes in monomer mass flow, are shown in Figure 3. With both $(n\text{-PrCp})_2ZrCl_2$ and $(n\text{-PrCp})_2ZrMe_2$, a rapid decrease in activity in the early stages of polymerization is apparent using $AlEt_3$, whereas the use of Al*i*Bu$_3$ as the cocatalyst results in an initial increase in activity, after which the activity decreases relatively slowly. Figure 3 also shows that increasing the Al*i*Bu$_3$ concentration from 1 to 3 mmol/L led to a further stabilization of the polymerization activity. The stabilizing effect of Al*i*Bu$_3$ may be due to the negligible tendency of an isobutyl group to bridge between Zr and Al, avoiding deactivation via the formation of alkylidene species analogous to those of type $[L_2Zr(\mu\text{-}CH_2)(\mu\text{-Me})AlMe_2]^+$ that can arise in zirconocene/MAO systems.[34] The polyethylene molecular weight data in Tables 8 and 9 show that in all cases a narrow molecular weight distribution was obtained, with M_w/M_n values in the range 2.0−2.2.

A further observation that can be made from the results presented in Tables 8 and 9 concerns the similarity in the activities (and also the molecular weights) obtained with $(n\text{-PrCp})_2ZrCl_2$ and $(n\text{-PrCp})_2ZrMe_2$. In other words, prealkylation of the catalyst prior to immobilization does not, in most cases, lead to increased activity, signifying that the limiting factor in the generation of active species in this system is not the alkylation step. Further polymerizations with a series of zirconocenes of type $(RCp)_2ZrX_2$, where R was varied from H up to dodecyl, were carried out at 50 °C and with $AlEt_3$ as the cocatalyst to compare the effect of prealkylation. The results in Table 10 reveal a consistent trend of somewhat lower activity with $(RCp)_2ZrMe_2$ compared to the parent dichloride.

Effect of Catalyst Loading on the Support. In a previous study, involving the immobilization and activation of titanocenes and half-titanocenes on $MgCl_2$-based supports, it was found that the catalyst activity increased as its loading on the support was lowered.[9b] Echevskaya et al. have found similar effects with a Ziegler−Natta catalyst of type $MgCl_2/TiCl_4$ and reported that the proportion of active centers increased greatly when the titanium loading was lowered to less than 0.1 wt %.[35] These results indicate that magnesium chloride supports contain relatively low proportions of surface coordination sites for effective catalyst activation. We therefore investigated the effect of different loadings of various catalysts on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support. The results in Table 11 show that, with $(n\text{-PrCp})_2ZrCl_2$ as the catalyst and $AlEt_3$ as the cocatalyst, the activity increased from 1560 to 17 600 kg/mol bar h on decreasing the loading from 50 to 1 μmol/g. A similar trend was found when *i*Bu$_2$AlOAl*i*Bu$_2$ was employed as the cocatalyst.

Further experiments to determine the effects of loading were carried out at 70 °C with a support of composition $MgCl_2 \cdot 0.25AlEt_{2.51}(EtO)_{0.49}$ and with Al*i*Bu$_3$ as the cocatalyst, the data in Tables 8 and 9 having shown that the highest activities were obtained under these conditions. It was found that, when the catalyst loading was decreased to 1 μmol/g, the activities obtained with $(n\text{-PrCp})_2ZrCl_2$ and $(n\text{-PrCp})_2ZrMe_2$ were 44 000 and 28 600 kg/mol bar h, respectively. These are spectacularly high activities, but it should be taken into account that an activity of 44 000 kg/mol bar h at a catalyst loading of 1 μmol/g corresponds to a productivity of only 44 g/(g support) bar h.

In order to establish a broader picture of the effect of catalyst loading on activity, polymerizations were also carried out with vanadium complexes containing amidinate[36] or pincer[37] ligands. Complexes having heteroatom-containing ligands are considered[8e] to be particularly suitable for immobilization on $MgCl_2$ supports, although the above results show that certain $MgCl_2$-immobilized metallocenes can also give high activity even though no heteroatom is present in the ligand. We have previously shown that the amidinate complex $\{PhC(NSiMe_3)_2\}VCl_2(THF)_2$ (**1**, Scheme 1) can be immobilized and activated on $MgCl_2/AlEt_n(OEt)_{3-n}$, with retention of its single-center characteristics.[9c] Recently, it has been found that the pincer complex **2** (Scheme 1) gives very high polymerization activity when immobilized on $MgCl_2$-based supports.[37] The effects of loading with these amidinate and pincer complexes are given in Tables 12 and 13, respectively. It is apparent that these complexes also give higher activity as the loading is decreased, although the effect is not quite as large as with the zirconocene. For example, a decrease in loading from 20 to 1 μmol/g increased the zirconocene

Table 8. Effect of Cocatalyst and Temperature on Ethylene Polymerization Activity Using (n-PrCp)$_2$ZrCl$_2$ on a Support of Composition MgCl$_2$·0.25AlEt$_{2.51}$(EtO)$_{0.49}$ [a]

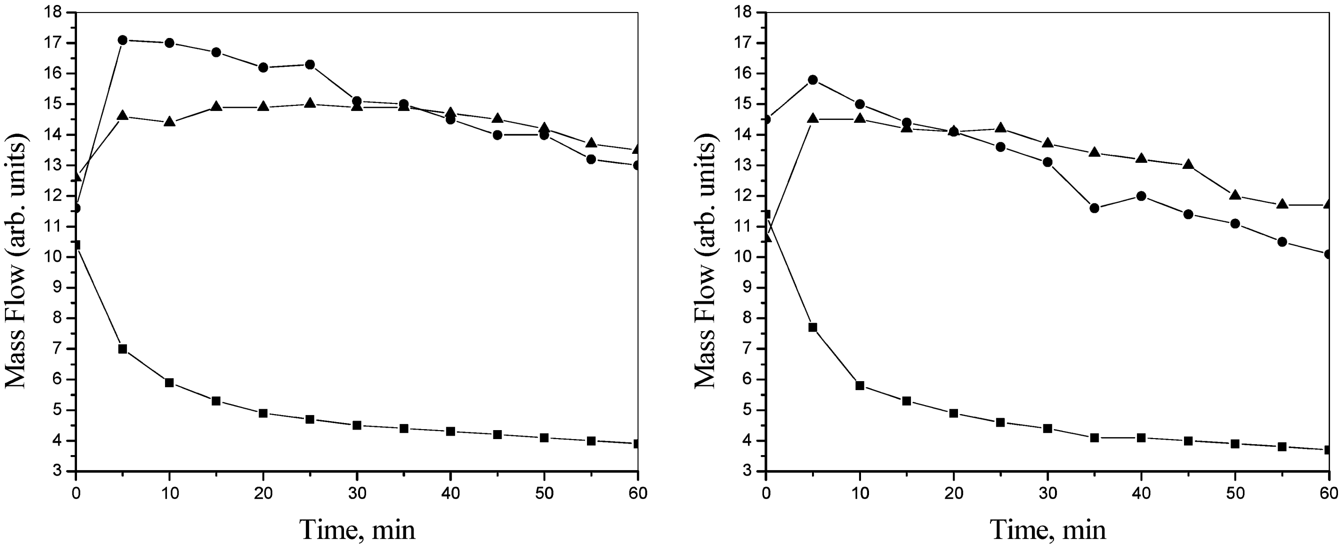
entry	cocatalyst	temperature (°C)	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
1	AlEt$_3$	50	9 360	135.9	62.1	250 300	120 000	2.1
2	AlEt$_3$	70	3 900	134.7	60.3	185 300	89 100	2.1
3	Al*i*Bu$_3$	50	8 960	136.1	60.4	212 800	104 300	2.0
4	Al*i*Bu$_3$	70	12 680	135.3	61.3	179 300	86 000	2.1
5[b]	Al*i*Bu$_3$	70	11 660	135.8	63.2			
6	*i*Bu$_2$AlOAl*i*Bu$_2$	50	9 080	135.7	60.5	212 600	102 900	2.1
7	*i*Bu$_2$AlOAl*i*Bu$_2$	70	10 400	134.6	60.8			
8	AlEt$_2$Cl	50	2 000	135.3	59.7	265 100	121 500	2.2
9	AlEt$_2$Cl	70	200	133.4	62.0			

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), cocatalyst1 mmol, ethylene pressure 5 bar, time 1 h. [b] 3 mmol Al*i*Bu$_3$.

Table 9. Effect of Cocatalyst and Temperature on Ethylene Polymerization Activity Using (n-PrCp)$_2$ZrMe$_2$ on a Support of Composition MgCl$_2$·0.25AlEt$_{2.51}$(EtO)$_{0.49}$ [a]

entry	cocatalyst	temperature (°C)	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
1	AlEt$_3$	50	5 860	135.4	58.0	253 400	119 100	2.1
2	AlEt$_3$	70	3 700	134.9	60.1	189 100	91 200	2.1
3	Al*i*Bu$_3$	50	9 800	136.3	59.3	203 900	97 800	2.1
4	Al*i*Bu$_3$	70	11 640	135.3	62.3	175 500	82 800	2.1
5[b]	Al*i*Bu$_3$	70	10 800	135.2	62.9			
6	*i*Bu$_2$AlOAl*i*Bu$_2$	50	9 000	135.9	59.5	204 400	97 200	2.1
7	*i*Bu$_2$AlOAl*i*Bu$_2$	70	9 360	135.2	62.7			
8	AlEt$_2$Cl	50	2 220	135.4	58.8	272 300	126 200	2.2
9	AlEt$_2$Cl	70	240	133.8	64.2			

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), cocatalyst1 mmol, ethylene pressure 5 bar, time 1 h. [b] 3 mmol of Al*i*Bu$_3$.



(a) (b)

Figure 3. Rate-time profiles for polymerizations carried out at 70 °C with (a) (n-PrCp)$_2$ZrCl$_2$ and (b) (n-PrCp)$_2$ZrMe$_2$ immobilized on a MgCl$_2$/AlEt$_n$(OEt)$_{3-n}$ support. Cocatalyst: ●, Al*i*Bu$_3$ (1 mmol); ▲, Al*i*Bu$_3$ (3 mmol); ■, AlEt$_3$ (1 mmol).

activity by a factor 5.5, whereas the activity of the vanadium pincer complex **2** increased by a factor 3.5. Furthermore, it is apparent from Table 13 that complex **2** gave an activity greater than 5000 kg/mol bar h even at a high loading of 40 μmol/g, making it more attractive than the Zr-based system in terms of kg of polymer obtainable per g of support.

UV−Visible Studies on Zirconocene Immobilization and Activation. It is well documented that the active species in zirconocene-catalyzed olefin polymerization are zirconocenium cations. The formation of cationic active species in the presence of MAO has been detected by X-ray photoelectron spectroscopy (XPS) as well as by ^{1}H and ^{13}C NMR.[38,39] A particularly convenient method for the investigation of zirconocene alkylation and activation by aluminoxanes is ultraviolet−visible (UV−vis) spectroscopy.[40] The ligand to metal charge-transfer bands in the UV−vis spectrum of a zirconocene are sensitive to changes in the electron density on zirconium. Replacement of a chlorine by a methyl group leads to a hypsochromic shift to lower wavelength due to a decrease in net positive charge on the metal atom, whereas a bathochromic shift to higher wavelength is indicative of the formation of cationic active species. UV−vis spectra taken at various time intervals in the

Table 10. Ethylene Polymerization Using $(RCp)_2ZrX_2$ (X = Cl or Me) on a Support of Composition $MgCl_2{\cdot}0.25AlEt_{2.51}(EtO)_{0.49}$[a]

entry	R	X	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)
1	H	Cl	300	134.7	52.9
2	H	Me	240	134.0	51.1
3	Et	Cl	480	135.2	54.8
4	Et	Me	400	135.4	54.6
5	Bu	Cl	5540	135.2	59.9
6	Bu	Me	4560	135.1	58.8
7	pentyl	Cl	4480	136.1	58.1
8	pentyl	Me	3720	135.8	59.5
9	dodecyl	Cl	2880	133.9	58.3
10	dodecyl	Me	2100	135.1	57.7

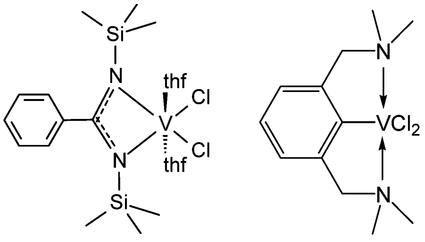
[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (1 μmol Zr), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

Table 11. Effect of Catalyst Loading on Ethylene Polymerization Activity Using $(n\text{-}PrCp)_2ZrCl_2$ on a Support of Composition $MgCl_2{\cdot}0.22AlEt_{2.35}(EtO)_{0.65}$[a]

loading (μmol/g)	cocatalyst	activity (kg/mol of Zr h bar)	T_{m2} (°C)	χ_c (%)
1	$AlEt_3$	17 600	134.8	58.1
5	$AlEt_3$	7 840	135.6	57.6
10	$AlEt_3$	6 520	135.0	56.7
20	$AlEt_3$	3 200	135.7	57.3
50	$AlEt_3$	1 560	136.0	57.9
1	$iBu_2AlOAliBu_2$	14 400	135.1	58.2
5	$iBu_2AlOAliBu_2$	4 000	135.9	58.1
10	$iBu_2AlOAliBu_2$	3 300	135.5	59.1
20	$iBu_2AlOAliBu_2$	2 720	137.2	59.2

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (0.1−5 μmol Zr), cocatalyst1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

Scheme 1. Structures of Vanadium Amidinate and Pincer Complexes



(1) (2)

Table 12. Effect of Catalyst Loading on Ethylene Polymerization Activity Using a Vanadium Amidinate Complex (1) on a Support of Composition $MgCl_2{\cdot}0.22AlEt_{2.35}(EtO)_{0.65}$[a]

loading (μmol/g)	activity (kg/mol of V h bar)	T_{m2} (°C)	χ_c (%)
1	9000	135.6	46.3
5	3880	135.5	47.7
10	3040	135.7	45.2
20	2080	136.1	48.5

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (0.1−2 μmol V), $AlEt_3$ 1 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

reaction of $(n\text{-}BuCp)_2ZrCl_2$ with MAO in toluene, at an Al/Zr ratio of 3000 and a MAO concentration of 1 mol/L, are shown in Figure 4. Alkylation of the zirconocene is apparent from a hypsochromic shift of the main absorption band, while the gradual formation of cationic species is evident from the formation of an absorption band at around 365−370 nm.

Table 13. Effect of Catalyst Loading on Ethylene Polymerization Activity Using a Vanadium Pincer Complex (2) on a Support $MgCl_2{\cdot}0.22AlEt_{2.35}(EtO)_{0.65}$[a]

loading (μmol/g)	activity (kg/mol of V h bar)	T_{m2} (°C)	χ_c (%)
1	26 400	136.2	41.5
5	12 400	136.0	42.4
10	8 600	136.0	42.7
20	7 480	135.7	43.2
40	5 560	136.6	41.2

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg (0.1−4 μmol V), $AliBu_3$ 2 mmol, 50 °C, ethylene pressure 5 bar, time 1 h.

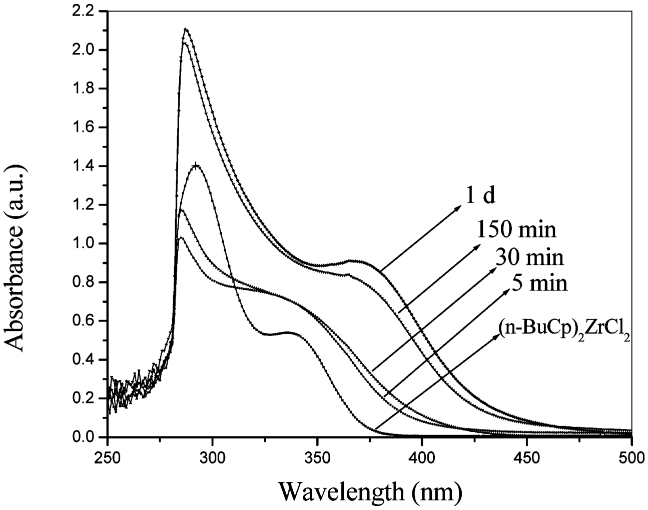
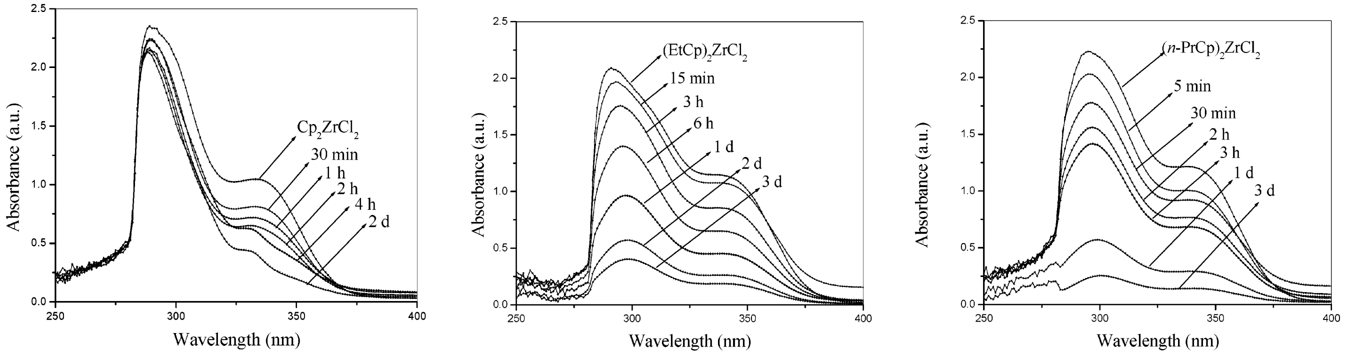


Figure 4. UV−vis determination of the reaction of $(n\text{-}BuCp)_2ZrCl_2$ with MAO in toluene (Al/Zr = 3000).

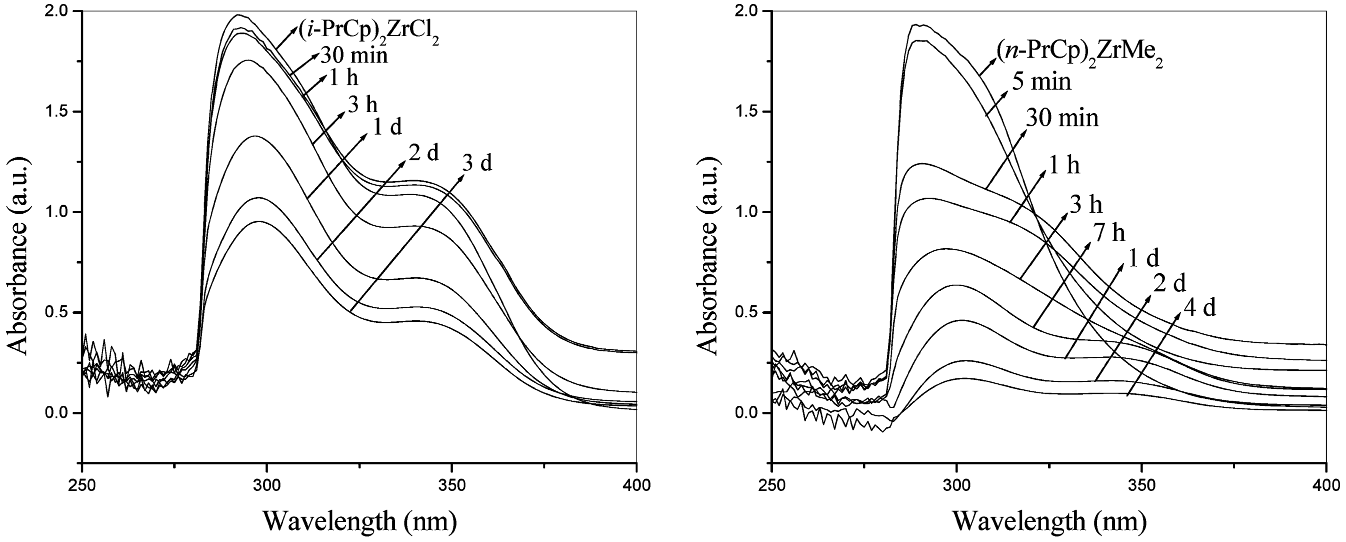
In the present work, UV−vis was also found to be useful to investigate the rate of immobilization of a zirconocene on a support, by following the decrease in UV−vis absorbance from solution when the zirconocene was brought into contact with a support of composition $MgCl_2{\cdot}0.14AlEt_{1.92}(OEt)_{1.08}$. These experiments were carried out in a sealed 1.4 mL cuvette, containing 100 mg of support and 1 μmol zirconocene dissolved in 1 mL of toluene. The immobilization rate was found to be strongly related to catalyst structure. As can be seen from Figure 5, the uptake of Cp_2ZrCl_2 from solution was much slower than that of $(EtCp)_2ZrCl_2$ or $(n\text{-}PrCp)_2ZrCl_2$, indicating a beneficial effect of an electron-donating alkyl substituent in the cyclopentadienyl ring on the rate of immobilization on the support. However, this does not explain the different activities obtained with these systems, as the data in Table 1 show that, despite their similar ease of immobilization, $(EtCp)_2ZrCl_2$ gives much lower activity than $(n\text{-}PrCp)_2ZrCl_2$. A somewhat lower rate of immobilization was observed with $(i\text{-}PrCp)_2ZrCl_2$ (Figure 6a), but the rate of immobilization of $(n\text{-}PrCp)_2ZrMe_2$ (Figure 6b) was similar to that of $(n\text{-}PrCp)_2ZrCl_2$. UV−vis spectroscopy can also be used to study species formed after immobilization, and silica-supported metallocenes have been investigated by various groups.[41] However, UV−vis spectra of $MgCl_2$-immobilized zirconocenes prepared in the present studies failed to provide useful information, probably as a result of the low catalyst loading on the support.

General Considerations. It is interesting to compare the large effects of cyclopentadienyl ring substitution on the activation of $MgCl_2$-immobilized zirconocenes with results obtained by Resconi et al. using $iBu_2AlOAliBu_2$.[42] The latter aluminoxane



(a) (b) (c)

Figure 5. UV−vis determination of the rate of immobilization on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support of (a) Cp_2ZrCl_2, (b) $(EtCp)_2ZrCl_2$, and (c) $(n\text{-}PrCp)_2ZrCl_2$.



(a) (b)

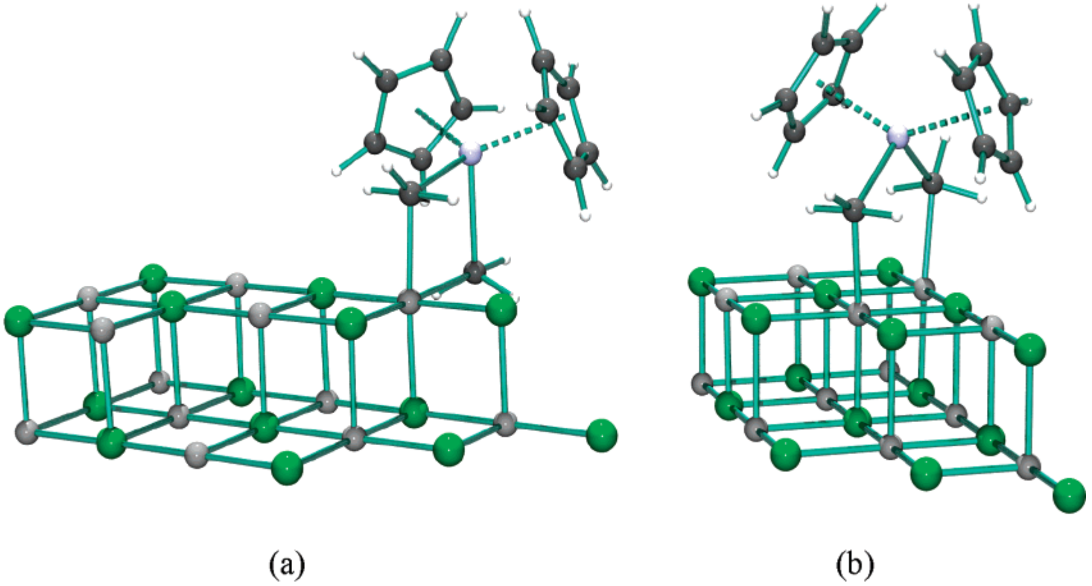
Figure 6. UV−vis determination of the rate of immobilization on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support of (a) $(i\text{-}PrCp)_2ZrCl_2$ and (b) $(n\text{-}PrCp)_2ZrMe_2$.

was found to be able to activate $(RCp)_2ZrCl_2$ but not Cp_2ZrCl_2. It was suggested that iBu$_2$AlOAliBu$_2$ was insufficiently Lewis acidic to activate Cp_2ZrCl_2, but activation became possible when an electron-donating substituent was present in the ligand. Likewise, recent studies with an $AlPO_4$ support and AliBu$_3$ have indicated much easier activation with $(n\text{-}BuCp)_2ZrCl_2$ than with Cp_2ZrCl_2.[43] A particularly strong effect of an electron-donating substituent on metallocene activation has been noted with siloxy-substituted *ansa*-zirconocenes.[40e,44] Electron donation from the siloxy group was proposed to decrease the local Lewis acidity of the Zr atom, influencing alkylation and/or ionization and weakening the coordination of the MAO counterion, so that high activities could be obtained at low Al/Zr ratios. Bryliakov et al.[39d,e] have investigated the active intermediates formed on contacting zirconocenes of type $(RCp)_2ZrCl_2$ with MAO. Increased ethylene polymerization activity with increasing MAO/Zr was ascribed to the formation of $[(RCp)_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$, the main precursor for the active species in that system. At a MAO/Zr ratio of 1000, the activities obtained[39e] with Cp_2ZrCl_2 and $(n\text{-}BuCp)_2ZrCl_2$ differed by less than 30%, however, whereas in the present work (Tables 1 and 6) and in ref 23, large differences in activity were noted. Other reports, describing zirconocenes immobilized on $MgCl_2$ or SiO_2/MAO and used with MAO as the cocatalyst, have even indicated lower activity for $(n\text{-}BuCp)_2ZrCl_2$ than for Cp_2ZrCl_2.[13d,26] A uniform picture of the effect of cyclopentadienyl ring substitution on catalyst activity in ethylene polymerization is therefore lacking.

Our results indicate that, in both $MgCl_2$-immobilized and homogeneous systems, much higher activities are obtained with $(n\text{-}PrCp)_2ZrCl_2$ or $(n\text{-}BuCp)_2ZrCl_2$ than with Cp_2ZrCl_2. The requirement for a linear alkyl substituent having at least three carbon atoms is in agreement with the results presented by Rytter and co-workers[23] and supports their proposal of a strong agostic interaction between Zr and a γ-H on the alkyl substituent R in $(RCp)_2ZrCl_2$. Immobilization and activation of a zirconocene on the $MgCl_2/AlEt_n(OEt)_{3-n}$ supports used in the present studies is clearly impeded by the introduction of branched alkyl substituents. Zirconocenes of type L_2ZrMe_2 are immobilized as easily as L_2ZrCl_2 but do not give increased activity. The limiting factor in achieving high activity with $MgCl_2$-immobilized zirconocenes is therefore not the alkylation step but the generation of active species on the support. The large increase in catalyst activity observed when the loading on the support is decreased indicates that catalyst activation is by no means quantitative, but the very high activities obtained at low loading demonstrate that a limited number of highly active catalytic centers can be generated in these systems.

The nature of the active species present in $MgCl_2$-supported catalysts is still far from being resolved. This applies both to immobilized single-center catalysts and to Ziegler−Natta catalysts. For the latter, a fundamental question is whether the active

Scheme 2. Possible Modes of Coordination of a Zirconocene on (a) a (110) and (b) a (100) Face of Magnesium Chloride



species derive from $TiCl_4$ adsorption on the (100) or the (110) face of $MgCl_2$. Modeling studies carried out by Cavallo and co-workers have indicated that, for monomeric $TiCl_4$, coordination on the (110) face is favored.[45] The most stable geometry of $TiCl_4$ epitactically adsorbed on the (110) face of $MgCl_2$ is one in which the Ti atom is octahedrally coordinated, but adsorption of a metallocene on the (110) face is more likely to occur via bridging coordination to a single Mg atom, as illustrated in Scheme 2a for Cp_2ZrMe_2.[46] A second possibility for adsorption of a metallocene on $MgCl_2$ is illustrated in Scheme 2b; in this case, coordination of the zirconocene on the (100) face of $MgCl_2$ is analogous to that of a single $TiCl_4$ molecule. Abstraction of a methyl group from either of the species depicted in Scheme 2 will give rise to a zirconocenium cation potentially active in polymerization. The formation of catalytically active species will therefore depend on which crystallite faces of $MgCl_2$ are formed in the support preparation, the energetics of formation of adsorbed species on a particular crystallite face, and the ease of cationization of such species. For the present supports, another factor to be taken into account is competition between the metallocene and residual alkylaluminum ethoxide species with respect to coordination on $MgCl_2$ surface sites. An alkoxy group can also form a strong bridge between Al and Zr in complexes of R_2AlOR' with Cp_2ZrX_2 (X = Cl or Me), although no reaction takes place between the zirconocene and strongly associated dimers of type $R_2Al(\mu\text{-}OR')_2AlR_2$.[47] Supports containing relatively low contents of residual ethoxide would therefore be expected to give the highest activities for immobilized zirconocenes, and this is in line with the trends observed in the present work.

Conclusions

The activity in ethylene polymerization of zirconocenes of type $(RCp)_2ZrCl_2$, immobilized on $MgCl_2$-based supports and used with $AlEt_3$ or Al*i*Bu_3 as the cocatalyst, is strongly dependent on the substituent R. High activity can be achieved when R is a linear alkyl chain containing at least three carbon atoms, indicating the probability of a γ-agostic interaction between the metal center and a hydrogen on the alkyl substituent. Positive effects of an alkyl substituent in one or both cyclopentadienyl rings of a zirconocene are also apparent in MAO-activated homogeneous polymerization. For the immobilized systems, relatively low activity is obtained when R is H, Et, *i*-Pr, or *t*-Bu. The activity is also dependent on the loading of metallocene on the support and is highest at very low loadings. Similar effects with other immobilized single-site catalysts, as well as $MgCl_2/TiCl_4$ Ziegler−Natta catalysts, indicate a relatively low proportion of highly active species in these systems. The limiting factor in the AlR_3-assisted activation of a zirconocene immobilized on $MgCl_2$ is not the alkylation step; activities obtained with $(RCp)_2ZrMe_2$ are slightly lower than those obtained using $(RCp)_2ZrCl_2$. The dimethyl derivatives were immobilized as easily as the parent dichlorides, indicating that effective immobilization on the support is not dependent on the presence of a Cl bridge between Mg and Zr.

The $MgCl_2$ support plays an important role in the generation of active species, and activity is influenced by support composition, the highest activities being obtained with supports of the type $MgCl_2/AlEt_n(OEt)_{3-n}$ with relatively low ethoxide contents. The stability of the polymerization activity is dependent on the aluminum alkyl used as a cocatalyst. At 50 °C $AlEt_3$ gives higher activities than Al*i*Bu_3, but at 70 °C the highest activities are achieved with Al*i*Bu_3, as a result of relatively little decay in activity during polymerization.

Further studies are in progress to define the nature of the active species in these and other catalysts, with particular reference to the similarities and differences between support-catalyst interaction in $MgCl_2$-immobilized single-center catalysts and in related Ziegler−Natta systems.

Acknowledgment. This research forms part of the research program of the Dutch Polymer Institute (DPI), Project No. 495. We thank Drs. A. P. Jekel of the Center for Catalytic Olefin Polymerization at the Rijksuniversiteit Groningen for GPC analysis and Dr. K. Lu of Eindhoven University of Technology for SEM characterization of the polymer particle morphology. We also thank Dr. A. Chuchuryukin and Dr. G. P. M. van Klink of the University of Utrecht for the vanadium pincer complex and Prof. V. Busico of the University of Naples for a sample of ball-milled $MgCl_2$.

Supporting Information Available: Details of the synthesis of Cp(*n*-PrCp)$ZrCl_2$, Cp(*n*-pentylCp)$ZrCl_2$, and $(RCp)_2ZrMe_2$ (R = Et, *n*-Pr, *n*-pentyl, *n*-dodecyl). Complete crystallographic data for Cp(*n*-BuCp)$ZrCl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Sinn, H.; Kaminsky, W.; Vollmer, H.-J.; Woldt, R. *Angew. Chem., Int. Ed.* **1980**, *19*, 390−392. (b) Kaminsky, W.; Engehausen, R.; Zoumis, K.; Spaleck, W.; Rohrmann, W. *Makromol. Chem.* **1992**, *193*, 1643−1651. (c) Kaminsky, W.; Miri, M.; Sinn, H.; Woldt, R. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 417−421.

(2) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143−1170. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429−447. (c) Ittel, S.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203. (d) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315. (e) Kaminsky, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3911−3921.

(3) (a) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1346.

(4) (a) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347−1376. (b) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friederichs, N. *Chem. Rev.* **2005**, *105*, 4073−4147.

(5) Galland, G. B.; Seferin, M.; Guimarães, R.; Rohrmann, J. A.; Stedile, F. C.; dos Santos, J. H. Z. *J. Mol. Catal. A: Chem.* **2002**, *189*, 233−240.

(6) (a) Woo, S. I.; Ko, Y. S.; Han, T. K. *Macromol. Rapid Commun.* **1995**, *16*, 489−494. (b) Ko, Y. S.; Woo, S. I. *J. Polym. Sci., Part. A: Polym. Chem.* **2003**, *41*, 2171−2179.

(7) Sacchetti, M.; Pasquali, S.; Govoni, G. Components and Catalysts for the Polymerization of Olefins. U.S. Patent 5,698,487, December 16, 1997

(8) (a) Nakayama, Y.; Bando, H.; Sonobe, Y.; Kaneko, H.; Kashiwa, N.; Fujita, T. *J. Catal.* **2003**, *215*, 171−175. (b) Nakayama, Y.; Bando, H.; Sonobe, Y.; Suzuki, Y.; Fujita, T. *Chem. Lett.* (*Jpn.*) **2003**, *32*, 766−767. (c) Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *J. Mol. Catal. A: Chem.* **2004**, *213*, 141−150. (d) Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 617−625. (e) Nakayama, Y.; Saito, J.; Bando, H.; Fujita, T. *Chem.*—*Eur. J.* **2006**, *12*, 7546−7556.

(9) (a) Severn, J. R.; Chadwick, J. C. *Macromol. Rapid Commun.* **2004**, *25*, 1024−1028. (b) Severn, J. R.; Chadwick, J. C. *Macromol. Chem. Phys.* **2004**, *205*, 1987−1994. (c) Severn, J. R.; Duchateau, R.; Chadwick, J. C. *Polym. Int.* **2005**, *54*, 837−841. (d) Severn, J. R.; Chadwick, J. C.; Van Axel Castelli, V. *Macromolecules* **2004**, *37*, 6258−6259. (e) Severn, J. R.; Kukalyekar, N.; Rastogi, S.; Chadwick, J. C. *Macromol. Rapid Commun.* **2005**, *26*, 150−154. (f) Huang, R.; Kukalyekar, N.; Koning, C. E.; Chadwick, J. C. *J. Mol. Catal. A: Chem.* **2006**, *260*, 135−143. (g) Huang, R.; Koning, C. E.; Chadwick, J. C. *Macromolecules* **2007**, *40*, 3021−3029.

(10) (a) Huang, R.; Liu, D.; Wang, S.; Mao, B. *Macromol. Chem. Phys.* **2004**, *205*, 966−972. (b) Huang, R.; Liu, D.; Wang, S.; Mao, B. *J. Mol. Catal. A: Chem.* **2005**, *233*, 91−97. (c) Xu, R.; Liu, D.; Wang, S.; Mao, B. *Macromol. Chem. Phys.* **2006**, *207*, 779−786.

(11) (a) McKenna, T. F.; Soares, J. B. P. *Chem. Eng. Sci.* **2001**, *56*, 3931−3949. (b) Abboud, M.; Denifl, P.; Reichert, K.-H.; *J. Appl. Polym. Sci.* **2005**, *98*, 2191−2200.

(12) (a) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65. (b) Finch, W. C.; Gillespie, R. D.; Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 6221−6232.

(13) (a) Silveira, F. D.; Forte, M. C.; Santos, J. H. Z.; Stedile, F. C.; Zacca, J. J. *Polim. Cienc. Technol.* **2000**, *10*, 42−48. (b) Cho, H. S.; Lee, W. Y. *J. Mol. Catal. A: Chem.* **2003**, *191*, 155−165. (c) Ochędzan-Siodłak, W.; Nowakowska, M. *Eur. Polym. J.* **2005**, *41*, 941−947. (d) Białek, M.; Czaja, K.; Reska, A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5562−5570.

(14) Guan, Z.; Zheng, Y.; Jiao, S. *J. Mol. Catal. A: Chem.* **2002**, *188*, 123−131.

(15) (a) Busico, V.; Guardasole, M.; Cipullo, R.; Resconi, L.; Morini, G. Catalyst System for the Polymerization of Olefins. World Patent WO 2004/078804, 2004. (b) Smit, M.; Severn, J. R.; Zheng, X.; Loos, J.; Chadwick, J. C. *J. Appl. Polym. Sci.* **2006**, *99*, 986−993.

(16) Kissin, Y. V.; Nowlin, T. E.; Mink, R. I.; Brandoloni, A. J. *Macromolecules* **2000**, *33*, 4599−4601.

(17) Kaminaka, M.; Soga, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 367−372.

(18) Soga, K.; Kaminaka, M. *Makromol. Chem.* **1993**, *194*, 1745−1755.

(19) Echevskaya, L. G.; Zakharov, V. A.; Semikolenova, N. V.; Mikenas, T. B.; Sobolev, A. P. *Polym. Sci. Ser. A* **2001**, *43*, 220−227.

(20) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99−115.

(21) (a) Ewen, J. A. *Stud. Surf. Sci. Catal.* **1986**, *25*, 271−292. (b) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098−3105. (c) Möhring, P. C.; Coville, N. J. *J. Mol. Catal.* **1992**, *77*, 41−50. (d) Grimmer, N. E.; Coville, N. J.; de Koning, C. B. *J. Mol. Catal. A: Chem.* **2002**, *188*, 105−113.

(22) (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. (b) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982−3998.

(23) Thorshaug, K.; Støvneng, J. A.; Rytter, E. *Macromolecules* **2000**, *33*, 8136−8145.

(24) Andersen, A.; Blom, R.; Dahl, I. M. *Macromol. Chem. Phys.* **2001**, *202*, 726−733.

(25) Tait, P. J. T.; Booth, B. L.; Jejelowo, M. O. *ACS Symp. Ser.* **1992**, *496*, 78−87.

(26) Guimarães, R.; Stedile, F. C.; dos Santos, J. H. Z. *J. Mol. Catal. A: Chem.* **2003**, *206*, 353−362.

(27) Kukalyekar, N.; Huang, R.; Rastogi, S.; Chadwick, J. C. *Macromolecules* **2007**, *40*, 9443−9450.

(28) (a) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544−6545. (b) Heiland, K.; Kaminsky, W. *Makromol. Chem.* **1992**, *193*, 601−610. (c) Rieger, B.; Troll, C.; Preuschen, J. *Macromolecules* **2002**, *35*, 5742−5743.

(29) (a) Ahn, H.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 13533−13534. (b) Costa Vayá, V. I.; Belelli, P. G.; dos Santos, J. H. Z.; Ferreira, M. L.; Damiani, D. E. *J. Catal.* **2001**, *204*, 1−10. (c) Nicholas, C. P.; Ahn, H.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 4325−4331. (d) Van Grieken, R.; Carrero, A.; Suarez, I.; Paredes, B. *Eur. Polym. J.* **2007**, *43*, 1267−1277.

(30) Ferraro, A.; Camurati, I.; Dall' Occo, T.; Piemontesi, F.; Cecchin, G. *Kinet. Catal.* **2006**, *47*, 176−185.

(31) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1996**, *197*, 855−867.

(32) (a) Pédeutour, J.-N.; Cramail, H.; Deffieux, A. *J. Mol. Catal. A: Chem.* **2001**, *174*, 81−87. (b) Pédeutour, J.-N.; Cramail, H.; Deffieux, A. *J. Mol. Catal. A: Chem.* **2001**, *176*, 87−94. (c) Cramail, H.; Deffieux, A.; Pédeutour, J.-N.; Radhakrishnan, K. *Macromol. Symp.* **2002**, *183*, 113−119.

(33) Antiñolo, A.; Fernández-Galán, R.; Otero, A.; Prashar, S.; Rivilla, I.; Rodríguez, A. M. *J. Organomet. Chem.* **2006**, *691*, 2924−2932.

(34) Babushkin, D. E.; Brintzinger, H. H. *Chem.*—*Eur. J.* **2007**, *13*, 5294−5299.

(35) Echevskaya, L. G.; Matsko, M. A.; Mikenas, T. B.; Nikitin, V. E.; Zakharov, V. A. *J. Appl. Polym. Sci.* **2006**, *102*, 5436−5442.

(36) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867−1870.

(37) Chuchuryukin, A. V.; Huang, R.; van Faassen, E. E.; van Klink, G. P. M.; Lutz, M.; Chadwick, J. C.; Spek, A. L.; van Koten, G. Manuscript in preparation.

(38) Gassmann, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875−7876.

(39) (a) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112−1114. (b) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247−1252. (c) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558−567. (d) Bryliakov, K. P.; Semikolenova, N. V.; Yudaev, D. V.; Ystenes, M.; Rytter, E.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2003**, *204*, 1110−1117. (e) Bryliakov, K. P.; Semikolenova, N. V.; Yudaev, D. V.; Zakharov, V. A.; Brintzinger, H. H.; Ystenes, M.; Rytter, E.; Talsi, E. P. *J. Organomet. Chem.* **2003**, *683*, 92−102.

(40) (a) Pieters, P. J. J.; van Beek, J. A. M.; van Tol, M. F. H. *Macromol. Rapid Commun.* **1995**, *16*, 463−467. (b) Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 1451−1457. Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 1459−1464. (c) Pédeutour, J.-N.; Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1999**, *200*, 1215−1221. (d) Wang, Q.; Song, L.; Zhao, Y.; Feng, L. *Macromol. Rapid Commun.* **2001**, *22*, 1030−1034. (e) Mäkelä-Vaarne, N. I.; Linnolahti, M.; Pakkanen, T. A.; Leskelä, M. A. *Macromolecules* **2003**, *36*, 3854−3860. (f) Alonso-Moreno, C.; Antiñolo, A.; Carillo-Hermosilla, F.; Carrión, P.; Rodríguez, A. M.; Otero, A.; Sancho, J. *J. Mol. Catal. A: Chem.* **2007**, *261*, 53−63.

(41) (a) Mäkelä-Vaarne, N. I.; Nicholson, D. G.; Ramstad, A. L. *J. Mol. Catal. A: Chem.* **2003**, *200*, 323−332. (b) Panchenko, V. N.; Zakharov, V. A.; Paukshtis, E. A. *J. Mol. Catal. A: Chem.* **2005**, *240*, 33−39. (c) Carrión, P.; Carillo-Hermosilla, F.; Alonso-Moreno, C.; Otero, A.; Antiñolo, A.; Sancho, J.; Villaseñor, E. *J. Mol. Catal. A: Chem.* **2006**, *258*, 236−245.

(42) Resconi, L.; Giannini, U.; Dall'Occo, T. In *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chicester, U.K., 2000; Vol. 1, p 69.

(43) Ikenaga, K.; Chen, S.; Ohshima, M.; Kurokawa, H.; Miura, H. *Catal. Commun.* **2007**, *8*, 36−38.

(44) (a) Leino, R.; Luttikhedde, H. J. G.; Lehmus, P.; Wilén, C.-E.; Sjöholm, R.; Lehtonen, A.; Seppälä, J. V.; Näsman, J. H. *Macromolecules* **1997**, *30*, 3477−3483. (b) Lehmus, P.; Kokko, E.; Härkki, O.; Leino, R.;

Luttikhedde, H. J. G.; Näsman, J. H.; Seppälä, J. V. *Macromolecules* **1999**, *32*, 3547−3552.

(45) Monaco, G.; Toto, M.; Guerra, G.; Corradini, P.; Cavallo, L. *Macromolecules* **2000**, *33*, 8953−8962.

(46) The figures in Scheme 2 were prepared in SPARTAN '04 (Wavefunctions Inc.). The $MgCl_2$ and zirconocene structures were optimized using molecular mechanics (MMFF) methodology and DFT calculations (B3LYP, 6−31G), respectively. Docking of the zirconocene onto the $MgCl_2$ resulted in the figures shown.

(47) Goodall, B. L. In *Transition Metal Catalyzed Polymerizations: Alkenes and Dienes*; Quirk, R. P., Ed.; Harwood Academic Publishers: New York, 1983; p 355.

MA7024557