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Ethylenebis(salicylideneiminato)zirconium Dichloride: Crystal Structure and Use as a Heterogeneous Catalyst in the Polymerization of Ethylene

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ABSTRACT: In the solid-state structure of the Schiff base salen [salen = *N*,*N′*-ethylenebis(salicylideneiminato)] zirconium dichloride complex Zr(salen)Cl_2(THF), $C_{20}H_{22}Cl_2N_2O_3Zr$, a quadridentate ligand, occupies four sites in the pseudopentagonal bipyramidal coordination. The coordination sphere is completed by one THF molecule, and two chloride ions are forced into the *trans*-position. Removal of THF, while Zr(salen)Cl_2(THF) is heated in toluene, leads to a six-coordinated complex with the two chloride ligands assuming the *cis*-position. This property was successfully utilized in the preparation of a homogeneous Zr(salen)Cl_2 catalyst precursor. Heating of Zr(salen)Cl_2(THF) in toluene in the presence of SiO_2 causes deposition of Zr(salen)Cl_2 on to the silica support, producing a heterogeneous catalyst, which shows an acceptable activity in ethylene polymerization at 80 °C and at low ethylene pressures in the presence of the cocatalyst methylaluminoxane.

Introduction

Bis(salicylaldehyde) *N*,*N′*-ethylenediimine (salen) is a well-known tetradentate Schiff base ligand which bonds metal ions in a pseudoplanar configuration. The syntheses, crystal structures, and reactions of numerous metal complexes of different Schiff bases have been studied, the focus being on transition metals of the middle and late d-block.[1] The motivation for studies of salen and other Schiff base complexes is their use as possible catalysts in epoxidation of olefins,[2] oxidation of alkynes[3] or sulfides,[4] addition of hydrogen or trimethylsilyl cyanide to aldehyde,[5] or Diels−Alder reactions.[6]

Titanium(IV) complexes, where the ligand forms the pseudoplanar configuration and the chlorides are in the *trans*-position, are the best known salen or salen-type complexes of the group 4 metals.[7] Reactions (e.g. alkylation and arylation)[8] and catalytic properties[5] of titanium salen complexes have also been studied. The literature references on zirconium salen (Schiff base) complexes are, unexpectedly, rather sparse.[9] The synthesis and the spectral properties of the title compound were published in 1990 by Corazza *et al.*[10]

The tetradentate Schiff base zirconium complexes, when isolated in solvated form, have seven-coordinated metal. The four donor atoms of the ligands are almost coplanar and the chlorides are in the *trans*-position to each other.[10] Solvated tetrahydrofuran (THF) adduct seems to be fairly easily removed when the complexes are heated in toluene. This reaction is especially well-studied with Zr(acen)Cl_2 and Hf(acen)Cl_2 [acen = *N*,*N′*-ethylenebis(acetylacetoneiminato)], where the solid-state structures of the complexes with and without THF have been characterized.[10] These structures reveal that removal of the THF leads to a six-coordinated complex, with chlorides in the *cis*-positions. A similar kind of behavior is also expected for other Schiff base zirconium complexes, but clear evidence of the stereochemistry of the chlorides is missing. The more rigid quadridentate ligands like salen or salphen [*N*,*N′*-*o*-phenylenebis(salicylideneiminato)] reduce the solubility of the complexes, and hence characterization is more difficult.[10]

cis-Arrangement of the chlorides in zirconium or hafnium Schiff base complexes is interesting, because it opens the possibility to use these complexes as a catalyst precursors in α-olefin polymerization. A catalytic active cationic center can be formed by replacing one chloride ion with an alkyl group and by substituting another chloride ion with a vacant coordination place, often occupied by a weakly coordinating anion. Activation can be completed either by using a cocatalyst such as methylaluminoxane (MAO) or by modifying the metal center synthetically. Because of great interest, both ways to activate the metal complex are especially well-studied with group 4 metallocenes.[11] For Schiff base complexes such studies are limited.

The alkylation and arylation of the zirconium Schiff base complexes have turned out to be difficult, leading to uncharacterized side products.[8] However, cationic metal complexes, if started from d^0 alkyl complexes, can be prepared.[12] This synthetic route to prepare a cationic Schiff base metal complex has been successfully used in the preparation of Zr(acen)R^+ catalyst for ethylene polymerization.[12,13]

In this work we present X-ray analysis of the title compound Zr(salen)Cl_2(THF) and the polymerization behavior of the MAO-activated Zr(salen)Cl_2 supported on SiO_2. This work is a part of our studies on transition

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metal coordination compound catalysts aimed at oligomerization and polymerization of α-olefins.

Experimental Section

Materials. All reactions and manipulations were carried out under inert nitrogen or argon atmosphere using standard syringe or Schlenk techniques. Solvents were dried and purified with standard methods. Silica gel with a specific surface area of 447 m^2/g, an N_2 pore volume of 3.0 mL/g, and a median particle size of 85 μm was used for immobilization of $Zr(salen)Cl_2(THF)$. Before use, SiO_2 was calcined at 500 °C for 10 h and stored under nitrogen.

The zirconium content of the supported catalysts was determined with the ICP method, and the chloride content was measured via potentiometric titration. The supported catalysts were also characterized under nitrogen atmosphere by the Nicolet Impact 400 D FTIR spectrometer using a diffuse reflectance (DC) technique. FT-IR spectra of the ligand, $Zr(salen)Cl_2$, and $Zr(salen)Cl_2(THF)$ were recorded with the Nicolet Magna 750 instrument. The samples were dispersed in KBr and pressed to disks. The standards (KBr and carrier) were subtracted from the sample spectra. The ^1H NMR spectra were recorded with a Bruker AM 250 NMR spectrometer. The cocatalyst MAO (10 wt % solution in toluene, $M = 800$ g/mol) was purchased from Witco GmbH. Ethylene (grade 3.5, AGA) was further purified by passing it through columns containing molecular sieves, Cu, and Al_2O_3. *N,N′*-Ethylenebis(salicylideneiminato)zirconium dichloride tetrahydrofuran was prepared by modifying the synthetic route published before.[10]

Crystal Data and Structure Determination. Crystals suitable for X-ray analysis were formed via a slow addition of *n*-hexane to THF solution of the complex. Intensities were collected at 193 K by the ω-scan mode with a Rigaku AFC-7S diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects and a ψ-scan correction was employed for absorption.[14] The structure was solved by direct methods and refined by full-matrix least squares using SHELXTL and SHELXL-93 programs.[15,16] All non-hydrogen atoms were refined anisotropically.

Preparation of the Supported $Zr(salen)Cl_2$ Catalyst Precursor. A suspension of $Zr(salen)Cl_2(THF)$ (342.5 mg, 0.684 mmol) and SiO_2 (6.80 g) in toluene (100 mL) was refluxed for 1 h. The resulting yellow solid material was separated from the colorless toluene solution with a double-tipped needle. The remaining solvent was removed under vacuum at 60 °C. Zr content: 0.85 wt %. FT-IR: ν (C═N) 1624 cm^{-1} (1619 cm^{-1} for $Zr(salen)Cl_2(THF)$, 1623 cm^{-1} for $Zr(salen)Cl_2$, and 1637 cm^{-1} for the ligand). Cl/Zr ratios were analyzed for catalysts with Zr contents 0.76 and 1.55 wt % and the values obtained were 1.81 and 1.99, respectively.

Method of Polymerization. Polymerizations were performed in toluene or *n*-heptane in a 0.5 dm^3 stainless steel reactor equipped with a propeller-like stirrer. The stirring speed was 400 rpm, temperature 80 °C, and ethylene overpressure 5.0 bar. Toluene or *n*-heptane and the cocatalyst solution were introduced to the nitrogen-purged reactor. Catalyst suspension (100 or 50 mg catalyst/ca. 40 cm^3 toluene or *n*-heptane) was prepared in a glovebox and added to the reactor with nitrogen pressure. The total volume of polymerization medium was 300 cm^3. The temperature in the reactor was controlled by circulating water in the reactor jacket. At the polymerization temperature ethylene feed was started. During polymerization the partial pressure of ethylene was maintained constant with an electronic pressure controller.

After the polymerization time of 60 min, the reactor was degassed and the product was stirred for 6 h with a mixture of ethanol and a small amount of concentrated hydrochloric acid. The polymer was filtered from the mixture, washed with ethanol, and dried under vacuum.

Polymer Characterization. Molar masses and molar mass distributions were determined with a Waters 150-C GPC instrument operating at 135 °C and equipped with two Shodex A-80M/S columns and one Shodex AC-806/S column and a RI-detector. Solvent 1,2,4-trichlorobenzene was applied at a flow rate of 0.6 cm^3/min. The columns were universally calibrated with broad-molar-mass-distribution polyethylene standards.

Melting temperatures were recorded with a Perkin-Elmer DSC-7 differential scanning calorimeter. The melting endotherms were measured upon reheating the polymer sample to 150 °C at a heating rate of 10°C/min. The crystallinities were determined from melting range integrals (ΔH_f/290 J/g).

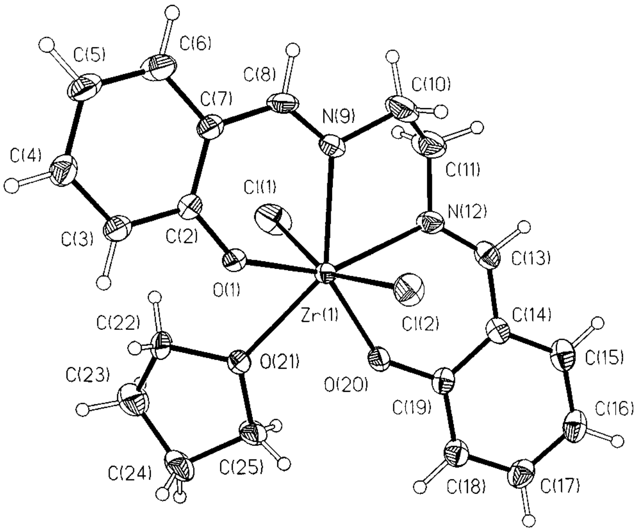

Figure 1. $Zr(salen)Cl_2(THF)$ molecule with the 30% probability level displacement ellipsoids.

Results and Discussion

The crystal structure of the title compound consists of discrete $Zr(salen)Cl_2(THF)$ molecules, where the metal is seven-coordinated in a pseudopentagonal bipyramid.[17] The four donor atoms of salen ligand are nearly coplanar, having a very small tetrahedral distortion of about 0.020(3) Å from the mean plane through N_2O_2 (Figure 1). Zirconium is 0.169(2) Å below that plane toward Cl(1). The planes passing through O(1), C(2)−C(8), N(9) and O(20), C(13)−C(19), N(12) are inclined by 1,6(2)° and 19.2(2)°, respectively, with respected to N_2O_2 coordination plane. The distortion of the salen molecule might be described by a stepped or even better a half-stepped conformation as defined by Calligaris *et al.*[18] The ethylene carbon atoms are above and below the coordination plane, and the five-membered chelate ring has the *gauche* orientation.

Bond distances and angles in the coordination sphere are typical for zirconium bearing tetradentate salen type ligands, furnished with a *trans*-dichloro and THF arrangement.[10] The oxygen atoms of the salen ligand are closest to zirconium, Zr(1)−O(1) 2.024(3) Å and Zr(1)−O(20) 2.002(4) Å, having the bite angle O(1)−Zr−O(20) 133.9(1)°, which allows the coordination of one THF molecule. The imine nitrogen atoms and the THF oxygen atom have almost equal bond lengths of about 2.34(±1) Å. The chloride ions are almost equidistant from the central atom. The low temperature contraction effect (193 K) may be seen in the coordination sphere, where the sum of all bonds to central zirconium atom is 16.033(4) Å compared to corresponding seven-coordinate salen derivatives of zirconium, $Zr(acen)Cl_2(THF)$ (16.090(3) Å) and $[Zr(salphen)Cl_2(THF)]\cdot 0.5THF$ (16.067(3) Å), measured at room temperature.[10] The complete crystal data of $Zr(salen)Cl_2(THF)$ are available as Supporting Information.

Homogeneous Polymerization. $Zr(salen)Cl_2(THF)$ was directly activated with MAO and used as a homogeneous catalyst (run E1, Table 2) in ethylene polymerization (at 80 °C and 5 bar). Moderate activity, 130 kg of PE/(mol of Zr·h), was observed. Zr(salen)Cl_2, which was obtained from Zr(salen)Cl_2(THF), where THF was removed by refluxing for 2 h in toluene,[19] gave a similar activity of 120 kg of PE/(mol of Zr·h) under the same conditions. The activated complexes have comparable activity with the cationic counterion system of Zr(F_6-acen)(CH_2CMe_3)$^+$, but they show clearly higher activity than the cationic Zr(acen)(CH_2CMe_3)$^+$ complex.[13] Al(*i*-Bu)$_3$, which was used with counterion complexes, was not needed in the present systems. Even though Zr(salen)Cl_2 complexes have moderate activity in ethylene polymerizations, all trials to polymerize propene failed.

Titanium and zirconium alkoxides have achieved currently new interest as a polymerization catalyst precursors.[20] These complexes, together with activator, typically MAO, show moderate activity for α-olefins. In ethylene polymerization molecular weights are relatively high, but molecular weight distributions are fairly broad. Broad molecular weight distributions implicate that reactions of the titanium or zirconium alkoxides and MAO do not form only one uniform catalytically active species. Relatively narrow molecular weight distributions of the polymers prepared by Zr(salen)Cl_2(THF) (run E1 Table 2), when toluene was used as reaction medium, indicate that one main species may be involved in the polymerization process.

Activation Process of Zr(salen)Cl_2 with MAO was followed by ^{1}H NMR. The toluene solvent of MAO solution (1 mL 30% in toluene) was removed in vacuum. The solid residue was dissolved back into 1 mL of toluene-d_8 and Zr(salen)Cl_2 (50 mg, 0.11 mmol) was added (Al/Zr ratio ≈ 20:1). After 0.5 h the ^{1}H NMR spectrum was measured. When compared to the spectrum of pure MAO in toluene two new peaks rise at −0.041 and 0.681 ppm. A similar high field shift of the methyl protons can be observed for $Cp_2ZrClMe$ and Cp_2ZrMe_2.[21] The signal of free $AlMe_3$ at −0.362 ppm is partly reduced. Direct comparison of ^{1}H NMR spectra of Zr(salen)Cl_2 and Zr(salen)Cl_2 treated with MAO cannot be done, because Zr(salen)Cl_2 is poorly soluble in toluene-d_8 and measurement of complex spectra cannot be executed. After 0.5 h reaction time with MAO, the complex solution turned orange, which clearly indicated a change in solubility. The sharp singlet of the ethylene bridge protons (acetone-d_6 at 4.18 ppm) transformed into two multiplets at 3.3 and 3.7 ppm, probably due to the reorientation of the salen ligand around the zirconium center. Aromatic protons of Zr(salen)Cl_2 appear at 7.56 (triplet) and 6.80 (multiplet) ppm [acetone-d_6 $\delta = 7.46$ ppm (2H, multiplet), 6.84 (4H, triplet) and 6.76 (2H, doublet)]. The imine proton at 7.86 ppm (8.67 ppm in acetone-d_6) was followed in order to see if the methyl groups migrates as in the case of Ti(salen)Me_2, but migration could not be observed. A new doublet at 5.43 ppm arose, indicating some side reactions. Whatever other side reactions are taking place, products are not soluble in toluene-d_8.

Heterogeneous Polymerization. In order to prepare a heterogeneous polymerization catalyst, Zr(salen)Cl_2(THF) was immobilized on an inorganic oxide support. Heating of Zr(salen)Cl_2(THF) in toluene in the presence of SiO_2 causes deposition of Zr(salen)Cl_2 onto the silica, producing a yellow powder. A series of supported catalysts (A−D) with a varying zirconium content of the catalysts were analyzed with the ICP method (Table 1). FT-IR measurements and the Cl/Zr ratio indicated that the supported zirconium complex remains intact.

Table 1. Zirconium Content of Immobilized Zr(salen)Cl_2(THF) on SiO_2

catalyst	Zr(salen)Cl_2/SiO_2 (mg/100 mg)	zirconium content (wt %)
A	1.0	0.145
B	2.0	0.300
C	5.0	0.780
D	5.0	0.850

The supported zirconium complex was used in ethylene polymerizations in the presence of MAO as a cocatalyst. These heterogeneous systems are more active than homogeneous systems in ethylene polymerizations. This behavior differs from the results obtained for corresponding zirconocene systems. Catalysts prepared by direct deposition of zirconocene onto the support surface have lower activity than homogeneous zirconocene does.[22−25] The polymerization results of the supported Zr(salen)Cl_2 catalyst are summarized in Table 2.

The measured polymerization activities of the heterogeneous catalyst increase when the amount of Zr in the catalyst decreases (Figure 2). The highest activity of 3020 kg of PE/(mol of Zr·h) in *n*-heptane was obtained for the SiO_2/Zr(complex) ratio of 100 (run A1, Table 2). For the SiO_2/Zr(complex) ratio of 20, an activity of 190 kg of PE/(mol of Zr·h) (run C1) and of 94 kg of PE/(mol of Zr·h) (run D1) in *n*-heptane was observed. These last two activities are close to the value measured for the homogeneous catalyst system (run E1).

Effect of Polymerization Medium and Al/Zr Mole Ratio. The activity of SiO_2-supported catalyst D was studied in different polymerization media (*n*-heptane and toluene) using different Al/Zr mole ratios. The results illustrated in Figure 3 indicate that the catalyst is more effectively activated in toluene than in *n*-heptane. The result is in accordance with observations made in olefin polymerizations with metallocene/MAO catalyst systems where more polar polymerization medium results in an increase in the activity of catalyst.[24,26] Also the lower solubility of MAO in *n*-heptane might play a role in the polymerization processes.

The polymerization activity of the SiO_2-supported Zr(salen)Cl_2 catalyst is strongly dependent on the Al/Zr mole ratio (Figure 3). This behavior is also well-known with metallocene/MAO catalyst systems, where Al/Zr mole ratios up to and above 15 000 have been used.[24,27] In addition, a linear dependence on Al/Zr ratio was observed when toluene and *n*-heptane were used as a polymerization medium. This is in accordance with the behavior of SiO_2-supported Cp_2ZrCl_2/MAO reported before.[23]

Polymer Properties. The gel permeation chromatography studies show that homogeneous Zr(salen)Cl_2(THF)/MAO catalyst is capable of producing polyethylene with moderate molar mass (run E1, Table 2). In polyethylene prepared with homogeneous catalyst, the molar mass distribution is narrow and monomodal.

When supported onto SiO_2 surface and activated with MAO, Zr(salen)Cl_2 produces polyethylene with similar molecular weights and molecular weight distributions as homogeneous catalyst system (runs D5−D7). This observation is contradictory to SiO_2-supported Cp_2ZrCl_2/MAO systems, where direct immobilization increases molecular weights of the polymer.[23,25]

Molecular weights are considerably higher when *n*-heptane was used as a polymerization medium for

Table 2. Results of Ethylene Polymerizations Promoted by $Zr(salen)Cl_2/SiO_2$ Catalysts[a]

run	cat.[b] (mg)	n_{Zr} (μmol)	medium	Al/Zr (mol/mol)	yield (g)	activity[c]	$M_W \times 10^{-3}$	M_w/M_n	T_m (°C)
A1	A (100)	1.6	heptane	1200	4.8	3020	394	3.5	134.4
B1	B (50)	1.6	heptane	1200	1.9	1160	358	4.4	133.9
C1	C (50)	4.3	heptane	1200	0.8	190	604	5.4	135.7
D1	D (100)	9.3	heptane	1100	0.9	94	668	15.1	137.7
D2	D (100)	9.3	heptane	500	0.7	70	1054	20.6	137.7
D3	D (100)	9.3	heptane	1600	1.6	170	197	5.8	135.0
D4	D (100)	9.3	heptane	3200	2.7	290	432	9.5	133.7
D5	D (100)	9.3	toluene	500	5.0	540	88	2.7	132.9
D6	D (100)	9.3	toluene	1100	8.9	960	121	3.7	135.6
D7	D (50)	4.7	toluene	3200	15.6	3350	77	2.5	133.3
E1	E (5.0)	10.0	toluene	1500	1.3	130	88	2.3	134.5

[a] Polymerization conditions: $T_p = 80$ °C, $p(C_2H_4) = 5.0$ bar, Al as MAO, $t_p = 60$ min. [b] Catalysts: (A) $Zr(salen)Cl_2/SiO_2$, Zr = 0.145 wt %, (B) $Zr(salen)Cl_2/SiO_2$, Zr = 0.300 wt %, (C) $Zr(salen)Cl_2/SiO_2$, Zr = 0.780 wt %, (D) $Zr(salen)Cl_2/SiO_2$, Zr = 0.850 wt %, (E) $Zr(salen)Cl_2(THF)$. [c] Catalyst activity in kg of PE/(mol of Zr·h).

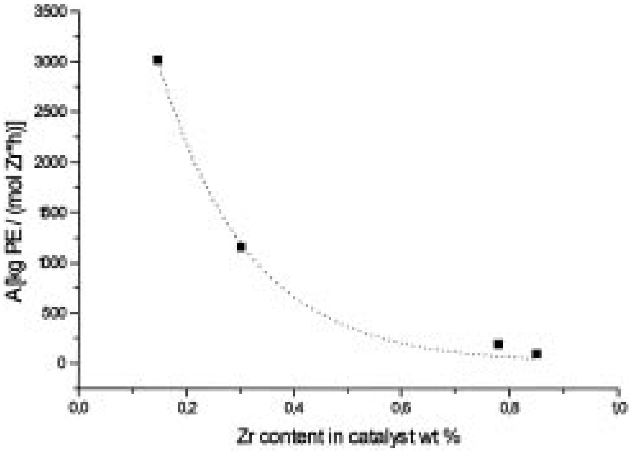

Figure 2. Dependence of catalyst activity on Zr content of the catalyst. Polymerizations were done in *n*-heptane, $T_p = 80$ °C, $p(C_2H_4) = 5.0$ bar, Al as MAO, $T_p = 60$ min.

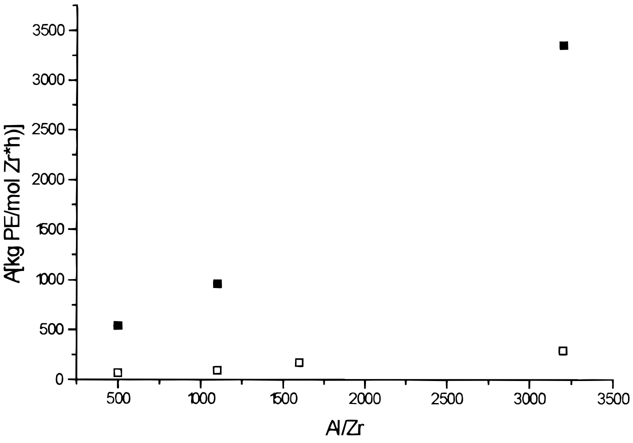

Figure 3. Effect of polymerization medium (■ toluene and □ *n*-heptane) and Al/Zr mole ratio on the activity of catalyst D, Zr content 0.85 wt %. Polymerization conditions: $T_p = 80$ °C, $p(C_2H_4) = 5.0$ bar, Al as MAO, $t_p = 60$ min.

supported $Zr(salen)Cl_2/MAO$ catalysts (run D1–D4). Molecular weight distributions (MWD) are broader and are also influenced by the amount of $Zr(salen)Cl_2$ on the carrier; the higher the amount of complex on the support, the broader the MWD (A1–D1). Also molecular weights rise with the SiO_2/Zr(complex) ratio (Table 2). Besides this, the products from polymerizations D1–D4 are clearly bimodal, indicating the possible presence of different active sites in the heterogeneous catalyst when the concentration of active compound on SiO_2 is higher.

The thermal properties of the polyethylenes prepared were investigated by the DSC method. The melting temperatures were 133–138 °C and crystallinities 51–67%. Also, the bimodal samples (runs D1–D4) showed only one melting transition temperature. This indicates that the structures of polyethylenes are quite uniform.

Table 3. Polymerization Results of $Zr(salen)Cl_2/SiO_2$ before and after MAO/Toluene Treatment

run	Zr_{cat} (wt %)	m_{cat} (mg)	m_{Zr} (mg)	Al/Zr	yield (g)	activity[a]
1	1.55	31	0.47	5800	1.1	210
2	0.70	68	0.48	5800	2.7	520

[a] kg of PE/(mol of Zr·h). Polymerization time was 1 h, temperature 80 °C, and pressure of ethene 5.0 bar.

Properties of $Zr(salen)Cl_2$ on the Silica Surface. Leaching of the catalyst from the carrier during a polymerization experiment was also studied. Supported catalyst, containing 1.55 wt % Zr, was stirred at 80 °C in toluene for 1 h. According to ICP measurement 7% of the total Zr dissolved into toluene. When the same experiment was done in the presence of MAO with a Zr:Al ratio of 1:1000, leaching was severe; more than 50% of the metal complex was lost and the final amount of Zr on the silica was 0.70 wt %. Polymerization activities of the supported $Zr(salen)Cl_2$ were tested before (run 1) and after MAO/toluene treatment (run 2), and results are summarized in Table 3.

Reduction of $Zr(salen)Cl_2$ content to half results in a catalyst with two times higher activity than the untreated catalyst. This phenomenon is in accordance with the observations obtained in the studies on the effect of Zr content on the support to activity (Table 2).

The title complex was shown to be more active on the carrier than as a homogeneous catalyst. Activity also rises when the amount of catalyst on the silica is reduced. The FT-IR measurements and Cl/Zr ratio of the supported catalysts indicate that no major chemical reactions are taking place between silica and $Zr(salen)Cl_2$. Hence, variations in activity cannot be explained with the formation of new cationic centers with different activities on the carrier, but rather with a different amount of active centers in the polymerization processes.

The deactivation process of polymerization catalyst systems is especially well-studied with zirconocenes. The tendency of cationic metal centers to dimerize, for example via CH_2 and C_2H_2 bridges, leads to dominating nonactive species in polymerization processes.[11] One possible explanation for the polymerization results described above might be that MAO-activated $Zr(salen)Cl_2$ has also a susceptibility to dimerize or otherwise form nonactive species. The formation of nonactive species happens more readily in homogeneous systems than in heterogeneous ones. Silica support seems to protect the activated centers and in way reduces deactivation process. The density of Zr(salen)Cl_2 on the silica surface has a major role. When the amount of Zr(salen)Cl_2 on the silica is reduced, the average distance between zirconium centers on the silica surface increases and hence the possibility for dimerization decreases. With the lower amount of zirconium on the support, the number of activated centers rises, and for this reason the observed overall activity is higher.

Conclusions

For the homogeneous Zr(salen)Cl_2/MAO catalysts, moderate activity was observed in ethylene polymerizations. On the silica support the complex showed higher activities which were also dependent on the amount of the complex on the support. The deposition of (salen) zirconium dichloride onto the silica support did not seem to have a great effect on polymer properties when polymerizations were carried out in toluene. When *n*-heptane, instead of toluene, was used as polymerization medium, a considerable increase in molecular weights and broadening of molecular weight distributions were observed.

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Supporting Information Available: Crystal structure of Zr(salen)Cl_2(THF) and experimental details, non-H atomic coordinates, bond lengths, bond angles, anisotropic displacement factors, H-atom coordinates + U_{eq}, and least squares planes (8 pages). Ordering information is given on any current masthead page.

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