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Grafting of the zirconium complexes [Zr(η^5-C_5H_5){NC-amidine}Cl_2] and [Zr(η^5-C_5H_5)(NC-NacNac)Cl_2] and the study of their behavior in ethylene polymerization

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ABSTRACT

The synthesis of the new zirconium complex [Zr(η^5-C_5H_5){NC-amidine}Cl_2] (**1**) has been achieved by reaction of the amidine (*E*)-*N*-(4-cyanophenyl)-*N*′-(2,6-diisopropylphenyl)acetimidamide with [Zr(η^5-C_5H_5)Cl_3] and the new complex has been characterized by spectroscopic methods. The reaction of one equivalent of $B(C_6F_5)_3$ with compound **1** produces the adduct [Zr(η^5-C_5H_5){$(C_6F_5)_3$B-NC-amidine}]Cl_2 (**2**). Complexes **1** and **2** have been tested as homogeneous catalysts in olefin polymerization using MAO as cocatalyst.

The grafting of **1** and the previously reported complex [Zr(η^5-C_5H_5)(NC-NacNac)Cl_2] (**3**) on to several inorganic solid supports, namely dehydroxylated silica (SiO_2(TEMP)) (**S_1**), dehydroxylated silica modified with $O(SiMe_3)_2$ (**S_2**) or MAO (**S_3**), and $MgCl_2$ (**S_4**) has been carried out by addition of a freshly prepared solution of **1** or **3** to the corresponding inorganic solid. FT-IR studies of the new materials showed that the links between complexes **1** or **3** and **S_1** and **S_2** occur through the zirconium center, whereas with **S_3** and **S_4** the links involve the CN functional group of the ligand. These new materials have been studied as catalysts in olefin polymerization reactions in the presence of MAO. A UV–vis study was carried out in order to identify the minimum amount of MAO necessary to produce the active species. A preliminary study into the activity in olefin polymerizations was also carried out.

1. Introduction

Olefin polymerization is still attracting considerable interest because the volume of polyolefin produced is increasing continuously due to its versatility for the production of new and very important materials in society. Control of the electronic and steric environments of polymerization catalysts has been shown to be very important in their activity and for the properties of the resulting polymers. Compared with conventional Ziegler–Natta systems, metallocene-based catalysts offer greater versatility and flexibility for both the synthesis and control of polyolefin structures. The influence of the nature of the metallocene on catalytic performance and the properties of the final polymer are the subject of considerable research in the field of applied organometallic chemistry [1]. In most cases modifications tend to affect the stereochemistry of the resulting materials (for instance syndio- vs. isotactic polypropylene) rather than the molecular weight of the polymer [2]. In contrast, the molecular weights of polymers obtained on using late transition catalysts are largely dependent on the steric volume of the ligands, where the presence of bulky groups in the catalyst leads to the production of high molecular weight materials [3] in what would otherwise be an oligomerization process. At the same time the design and synthesis of half-zirconocene complexes containing amidinate ligands as olefin polymerization catalysts is a growing area of interest [4].

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Recently, some of us reported the design and synthesis of new zirconium systems bearing a cyclopentadienyl ring as well as a bidentate diimine ligand with a functional group located remotely on the complex backbone [5]. It was shown that the polymerization activity of these systems could be increased by the action of a Lewis acid on a functional group located remotely on the complex backbone.

The main routes reported in the literature for metallocene immobilization [6] have been classified by Ribeiro et al. [7]. The first method involves direct impregnation of the metallocene onto the support, either with or without prior modification of the support. Soga et al. [8] prepared a number of supported catalysts in which silica was initially modified by treatment with Cl_2SiMe_2, followed by treatment with MAO and final grafting of $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$. Such systems were shown to be active in the presence of common trialkylaluminium cocatalysts. Moroz et al. [9] prepared a supported metallocene catalyst by treating a silylated silica, obtained by the reaction of dehydroxylated silica with $ClSiMe_3$, with $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$. A few years ago Otero et al. [10] presented results concerning a grafting link between substituted and unsubstituted metallocenes on the surfaces of several modified silicas through the Zr—Cl bond or through a pendant substituent on the cyclopentadienyl unit. One of the most promising methods for catalyst heterogenization involves the reaction between a functional group of the zirconium-containing molecule and a reactive group on the carrier surface. Recently, the synthesis and characterization of a series of indenyl zirconocenes bearing pendant chains with silicon ethers or heterocyclic moieties as donor groups was described [11].

The work described here is a continuation of our study of zirconium chemistry with bidentate ligands bearing a cyclopentadienyl ring and a bidentate ligand with a functional group located remotely on the complex backbone. The presence of the nitrile group as a functional group increase the catalytic activity of zirconium complexes interacting with Lewis acids and can also allow support it easily onto inorganic solids having such centers, improving at same time its catalytic activity in olefin polymerization processes.

The investigation concerns the synthesis and characterization of a new amidinate zirconium bearing nitrile terminal groups, complex **1**, and its adduct with tris(pentafluorophenyl)borane (**2**). We also present new results on the grafting of the half sandwich zirconium complexes **1** and the previously reported complex $[Zr(\eta^5\text{-}C_5H_5)(NC\text{-}NacNac)Cl_2]$ (**3**) [5], both of which are supported by a ligand bearing nitrile terminal groups, onto commercial partially dehydroxylated silica and silica modified with MAO or silicon ethers and $MgCl_2$. The influence of the nature of these materials after MAO activation with the lowest possible Al/Zr ratio was also studied. The surface reactions were monitored by transmission infrared spectroscopy (FT-IR).

2. Experimental

2.1. Material

Degussa silica (200 m^2/g, according to the supplier) was dehydroxylated under vacuum (10^{-2} mm Hg) for 16 h at the desired temperature [$SiO_2(763)$] and the sample was cooled and stored under dry nitrogen. $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$, $AliBu_3$ (TIBA), methylalumoxane (MAO) and $B(C_6F_5)_3$ were supplied by Aldrich and were used without further purification. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure). Toluene, THF, ether and pentane were distilled from benzophenone ketyl.

2.2. Synthesis and characterization of $[Zr(\eta^5\text{-}C_5H_5)\{NC\text{-}amidine\}Cl_2]$ (**1**) and $[Zr(\eta^5\text{-}C_5H_5)\{(C_6F_5)_3B\text{-}NC\text{-}amidine\}Cl_2]$ (**2**)

2.2.1. (**1**) $[Zr(\eta^5\text{-}C_5H_5)\{NC\text{-}amidine\}Cl_2]$

N′-(2,6-diisopropylphenyl)-*N*-(4-cyanophenyl) acetimidamide [12] (100 mg, 0.32 mmol) and KH (16 mg, 0.39 mmol) were stirred in THF for 4 h. Gas was evolved during the reaction. The slightly cloudy mixture was filtered through Celite and added dropwise to $[Zr(\eta^5\text{-}C_5H_5)Cl_3]$ (84 mg, 0.32 mmol) in THF. The reaction mixture was stirred for 12 h. The resulting light brown solution was filtered through Celite. The solvent was extracted and the yellow solid was washed three times with ether. A pale yellow powder corresponding to complex **1** was isolated in 55% yield (96 mg, 0.18 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = 7.74 (d, *J* = 8.1 Hz, 2*H*, NH), 7.06 (t, *J* = 7.7 Hz, 1*H*, *m*-Ph(CN)), 7.19 (d, *J* = 8.1 Hz, 2*H*, *o*-Ph(CN)), 7.13 (m, 2*H*, *m*-Ar), 7.12 (m, 1*H*, *p*-Ar), 6.20 (s, 5*H*, *Cp*), 3.32 (hept, *J* = 6.9 Hz, 2*H*, HCiPr), 1.55 (s, 3*H*, MeC), 1.35 (d, *J* = 6.9 Hz, 6*H*, MeiPr), 1.21 (d, *J* = 6.9 Hz, 6*H*, MeiPr’). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ/ppm = 172.7 ($^{Ar\text{–}N}C^{N\text{–}Ph(F)}$), 153.9 (*i*-Ph(CN)), 144.3 (*o*-Ar), 142.1 (*i*-Ar), 134.1 (*m*-Ph(CN)), 126.7 (*o*-Ph(CN)), 125.2 (*p*-Ar), 123.9 (*m*-Ar), 119.5 (C≡N), 113.8 (*Cp*), 107.5 (*p*-Ph(CN)), 28.1 (HCiPr), 25.3 (MeiPr), 24.6 (MeiPr’), 17.1 (MeC). FT-IR (KBr) = 2222 cm^{-1} ($\tilde{\nu}$(C≡N), s). Elemental analysis (%): $C_{26}H_{29}Cl_2N_3Zr$ (M = 545.66 g/mol): calculated C 57.23, H 5.36, N 7.70; found C 57.13, H 5.30, N 7.61%. For additional 2D NMR data see Supporting information.

2.2.2. (**2**) $[Zr(\eta^5\text{-}C_5H_5)\{(C_6F_5)_3B\text{-}NC\text{-}amidine\}Cl_2]$

1 eq Of tris(pentafluorophenyl)borane (50 mg, 0.098 mmol in 1 mL of toluene) was added to a toluene suspension of **1** (53 mg, 0.098 mmol). The reaction mixture was stirred for 1 h at room temperature, filtered through Celite, and the volatiles were removed under vacuum and the residue was washed with pentane. Adduct **2** was isolated as a pale yellow solid in 95% yield (98.5 mg, 0.093 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = 7.96 (d, *J* = 8.46 Hz, 2*H*, *m*-Ph(CN)), 7.25 (d, *J* = 8.46 Hz, 2*H*, *o*-Ph(CN)), 7.15 (m, 3*H*, *m*,*p*-Ar), 6.21 (s, 5*H*, *Cp*), 3.24 (hept, *J* = 6.86 Hz, 2*H*, HC^{iPr}), 1.69 (s, 3*H*, Me^C), 1.36 (d, *J* = 6.86 Hz, 6*H*, Me^{iPr}), 1.22 (d, *J* = 6.86 Hz, 6*H*, $Me^{iPr'}$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ/ppm = 173.8 ($^{Ar\text{–}N}C^{N\text{–}Ph(CN)}$), 159.2 (*i*-Ph(CN)), 148.7 (dm, $^1J_{FC} \approx 246$ Hz, C_6F_5), 143.8 (*o*-Ar), 141.5 (*i*-Ar), 141.1 (dm, $^1J_{FC} \approx 241$ Hz, C_6F_5), 137.9 (dm, $^1J_{FC} \approx 254$ Hz, C_6F_5), 135.9 (*m*-Ph(CN)), 126.6 (*p*-Ar), 126.5 (*o*-Ph(CN)), 125.9 (br., *i*-C_6F_5), 124.2 (*m*-Ar), 116.3 (C≡N), 114.0 (Cp), 97.54 (*p*-Ph(CN)), 28.2 ($^HC^{iPr}$), 25.3 (Me^{iPr}), 24.7 ($Me^{iPr'}$), 18.0 (Me^C). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 298 K): δ/ppm = –3.3 ($\nu 1/2 \sim 500$ Hz). FT-IR (KBr) = 2310 cm^{-1} ($\tilde{\nu}$ (C≡N), s). Elemental analysis (%): $C_{44}H_{29}BCl_2F_{15}N_3Zr$ (M = 1057.64 g/mol): calculated C 49.97, H 2.76, N 3.97; found C 50.11, H 2.69, N 3.99%. For additional 2D NMR data see Supporting information.

2.3. Grafting of complexes **1** and **3**

The supported catalysts were prepared under an inert atmosphere using Schlenk techniques and a glove-box. A solution of the zirconium complexes **1** or **3** in toluene (30 mL), to give a theoretical level of 1% Zr/SiO_2, was added to partially dehydroxylated silica, $SiO_2(773)$, $\mathbf{S_1}$, (1 g), and the mixture was stirred at 298 K for 16 h. The slurry was filtered through fritted discs and washed three times with toluene (20 mL). The resultant solids were dried under vacuum at 343 K for 16 h. A similar procedure was followed for modified silicas $\mathbf{S_2}$ and $\mathbf{S_3}$. In the case of $\mathbf{S_2}$, $SiO_2(773)$ (1 g) was treated with an excess (5 mL) of the bis(trimethylsilyl)ether and the mixture was stirred at 333 K for 16 h. The solids were carefully washed with toluene, dried and the resulting materials were impregnated with a solution of **1** or **3** as described above. In the case of MAO-modified silica $\mathbf{S_3}$, $SiO_2(773)$ (1 g) was treated with 5 mL (to give a theoretical level of 15% Al/SiO_2) of the toluene solution of MAO. The mixture was stirred at 298 K for 1 h and dried in vacuo. The resulting materials were impregnated with the zirconium complexes **1** or **3** in toluene solutions, and the mixtures were stirred for 16 h at 298 K. The slurries were filtered through fritted discs and washed three times with toluene (20 mL). The resultant solids were dried under vacuum at 343 K for 16 h. Finally, in the case of $\mathbf{S_4}$, a solution of the zirconium complexes **1** or **3** in toluene (30 mL) (to give a theoretical level of 1% Zr/$MgCl_2$) was added to activated $MgCl_2$(523) [9] (1 g) and the mixture was stirred at 333 K for 16 h. The slurries were filtered through fritted discs and washed three times with toluene (20 mL). The resultant solids were dried under vacuum at 343 K for 16 h.

2.4. *Characterization*

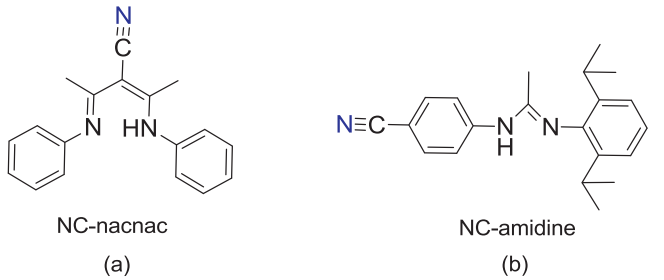
Infrared spectra were recorded on a Bruker Tensor-27 spectrophotometer using an infrared cell with CaF_2 or KBr windows; this set-up allowed *in situ* studies. A total of 32 scans were typically accumulated for each spectrum (resolution 2 cm^{-1}). The samples consisted of ca. 20 mg of silica pressed into a 1-cm diameter self-supported disc. The samples were dehydroxylated at the desired temperature for 16 h. MAO-modified samples were treated with a 10% solution of MAO in toluene and dried under vacuum. Zirconium complex grafting was performed using a 10^{-2} M solution of the zirconocene in toluene. The samples were heated at 333 K for 1 h, washed with toluene and dried under vacuum at 343 K until further changes were not observed (sublimation of a slight excess of complex was observed in some cases). The FT-IR analyses were repeated on three different samples in order to ensure reproducibility. NMR analyses were performed in $CDCl_3$ or CD_2Cl_2 using a Bruker Advance 400 NMR spectrometer. Most NMR assignments were supported by additional 2D experiments. UV-Vis analyses were performed using a Shimadzu UV-2501PC spectrophotometer. The soluble complexes were dissolved in dry toluene and placed in special cells under dry nitrogen (1.0 cm path length). The solid samples were suspended in Nujol to form a slurry. The absorption spectra were recorded between 190 and 900 nm and toluene or Nujol were used as a reference.

The polymers were characterized by gel permeation chromatography (GPC) on a Waters Alliance GPC 2000 system equipped with a refractive index detector. Samples were run at 150 °C in spectrophotometric grade 1,2,4-trichlorobenzene (TCB) stabilized with BHT (0.5 g BHT/4 L solvent). Molecular weights were calculated using a universal calibration from narrow polystyrene standards in the molecular weight range from 580 to 7.5 million g/mol. Mark–Houwink parameters of $a = 0.7$ and $k = 47.7$ were used to correct for polyethylene.

Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 2920) at a rate of 10 °C/min for two cycles in the temperature range 25–200 °C.

2.5. *Polymerization tests*

Polymerizations were carried out in a *Parr* autoclave reactor (100 mL), loaded inside a glove-box with the appropriate amount of the pre-catalyst (**1**, **2**, **3** and $\mathbf{3\text{-}S_4}$) and the corresponding MAO with toluene, such that the final volume of the toluene solution was 30 mL. The reactor was sealed inside the glove-box and was attached to an ethylene line. Ethylene was fed continuously into the reactor to a pressure of 12.5 bar. The pressurized reaction mixture was stirred at the appropriate temperatures. After 10 min, the ethylene was vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried overnight.



NC-nacnac
(a)

NC-amidine
(b)

Fig. 1. *N,N* ligands used to stabilize metal centers.

3. Results and discussion

3.1. *Synthesis and characterization of compounds **1** and **2***

The nacnac class of ligands (see Fig. 1a) has been extensively used in organometallic chemistry as bidentate *N,N* ligands for the stabilization of both early and late transition metal complexes [13]. In this paper we will focus our interest on a related NC-amidine ligand family (see Fig. 1b) that allows the use of a common ligand framework, while at the same time introducing groups that can affect the steric and electronic properties of the ligand [14].

Compound **1** was synthesized by the reaction of the deep-red ligand solution obtained by deprotonation of the NC-amidine ligand, previously reported by our group [12], with KH and with $Zr(\eta^5\text{-}C_5H_5)Cl_3$ (THF, rt, 4 h) (see Scheme 1).

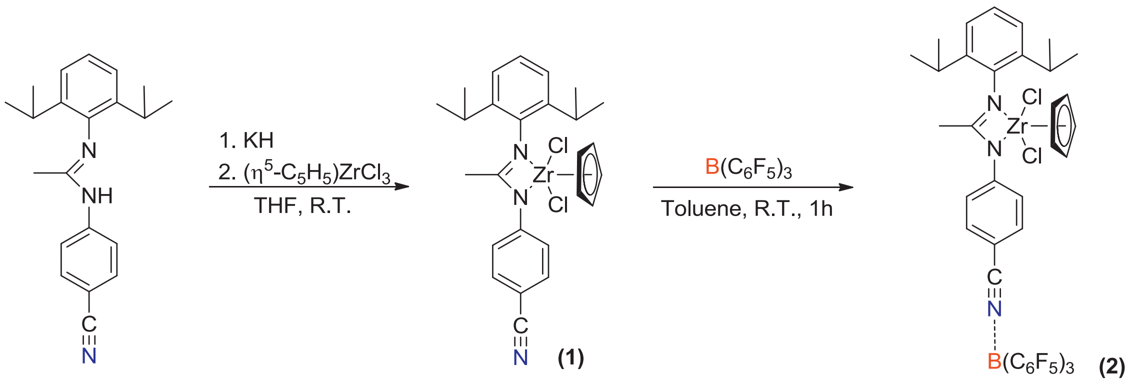
The ^1H NMR characterization of complex **1** is summarized in the Supporting Information file. The NMR spectrum contains a singlet at 1.55 ppm (3*H*-Me) and a singlet at 6.20 (5*H*-Cp ring). In the ^{13}C NMR spectrum, the Cp signal appears at 113.8 ppm and the cyano carbon (CN) signal at 119.5 ppm. The signal at 107.5 ppm can be assigned to the carbon that contains the CN group and the imine carbon signal appears at 172.7 ppm. All of these resonances, especially the last one, are strongly shielded compared to those of the free ligand. Similar behavior was previously observed for another series of zirconium complexes including the (NC-nacnac) ligand [14].

The reaction between one equivalent of $B(C_6F_5)_3$ and compound **1** produced the adduct $[Zr\{(C_6F_5)_3B\text{-NC-amidine}\}(\eta^5\text{-}C_5H_5)Cl_2]$ (**2**) in 95% yield (see Scheme 1). ^1H NMR characterization of the adduct revealed the characteristic singlets associated with the Cp ring (6.21 ppm) and the methyl group (1.69 ppm), both of which were shifted slightly downfield compared to the signals for complex **1**. The ^{13}C NMR spectrum contained the expected signal for the imine carbon (C═N) at 173.8 ppm, the Cp ring at 114.0 ppm, and the C^{CN} at 97.5 ppm. The C^{CN} resonance is strongly shielded compared to that for complex **1** (107.5 ppm). We attribute this change to the inductive effects resulting from the intermolecular coordination of the Lewis acid $B(C_6F_5)_3$ with the C≡N group.

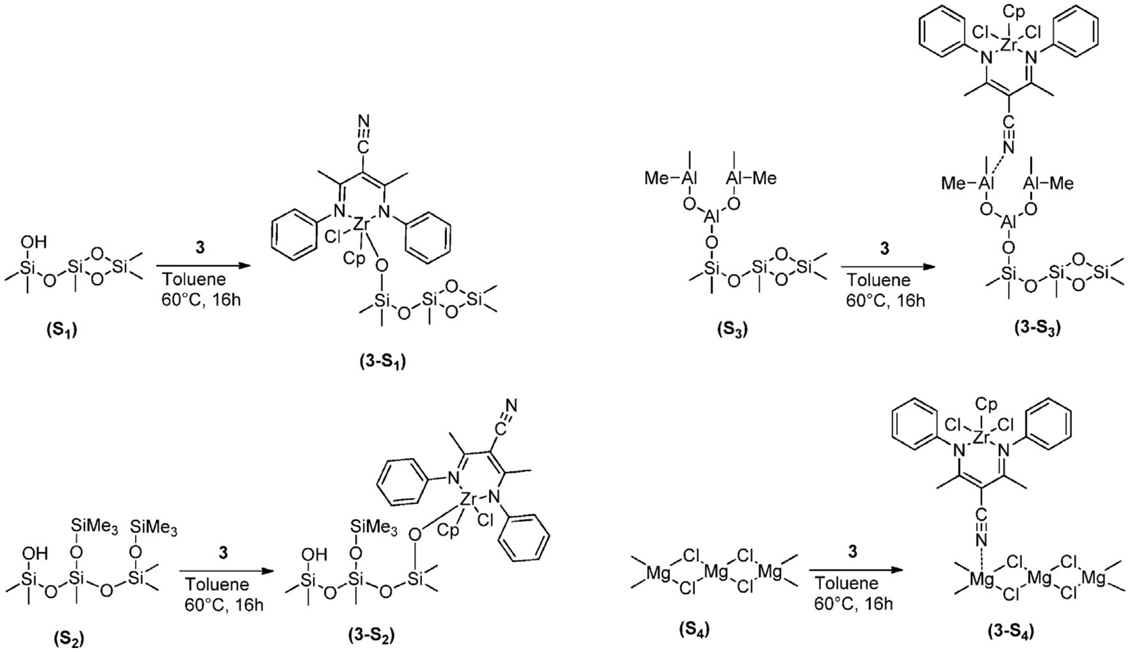
The IR spectrum of the borane adduct **2** shows a sharp C≡N stretching band at $\tilde{\nu} = 2310\ cm^{-1}$ and this is shifted by $\Delta\tilde{\nu} = 88\ cm^{-1}$ to higher wavenumbers compared to the corresponding band of complex **1**. This shift in wavenumber is expected from the simple addition of a nitrile to a strong Lewis acid: sharing the nitrogen lone pair with the boron atom effectively reduces the electronic repulsion between nitrogen and carbon to make the C≡N triple bond in **2** slightly stronger [5].

3.2. *Grafting of complexes **1** and **3***

In this study we used four modified inorganic supports, namely $^tSiO_2$ ($\mathbf{S_1}$), $^tSiO_2/O(SiMe_3)_2$ ($\mathbf{S_2}$), $^tSiO_2$/MAO ($\mathbf{S_3}$), and $MgCl_2$ ($\mathbf{S_4}$), for the grafting complexes **1** and **3** (Fig. 2, previously reported by our



Scheme 1. Synthesis of compounds **1** and **2**.



Scheme 2. Grafting of complex **3** onto the prepared supports.

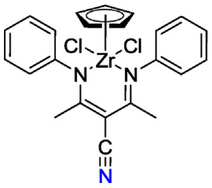


Fig. 2. Complex 3.

Table 1
FT-IR bands assigned to the $\tilde{\nu}$ (CN) group of complexes of **1-S$_x$** and **3-S$_x$**.

	$\tilde{\nu}$ (CN)	MAO addition
1*	2222	2310**
1-S$_1$	2222	2230
1-S$_2$	2222	2230
1-S$_3$	2234	2234
1-S$_4$	2243	2243
3*	2209	2261**
3-S$_1$	2209	2216
3-S$_2$	2209	2216
3-S$_3$	2216	2216
3-S$_4$	2229	2229

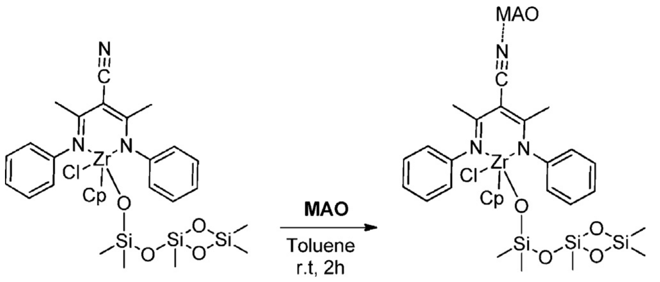
Values in cm^{-1}.
* Complexes **1** and **3** as references.
** Adduct formed by the reaction of **1 or 3** and B(C$_6$F$_5$)$_3$.

group [5]). The grafting of complex **3** is summarized in Scheme 2, being analogous to grafting of complex **1**.

The resulting systems were characterized by FT-IR spectroscopy. The $\tilde{\nu}$ (CN) band was used to verify the grafting and identify the interaction mode of the complex on the surface.

The wavenumbers corresponding to the nitrile stretching bands for **3-S$_x$** and **1-S$_x$** are shown in Table 1 and the bands assigned to the $\tilde{\nu}$ (CN) group of complexes **1** and **3** are included as references. The compounds supported on **S$_1$** and **S$_3$** were treated with MAO according to a reported procedure [10] (for more details see Supporting Information). The wavenumbers of the stretching bands of these systems are also shown in Table 1.

Comparison of the displacement of the corresponding C≡N band for the isolated complexes and the **S$_1$**-supported complexes did not show any changes, indicating that the coordination does not occur through this group. Based on results obtained with the same support and metallocene compounds [10], it can be stated that the coordination of complexes to **S$_1$** may be taking place through a Zr–O bond after reaction with terminal OH groups and elimination of HCl.



(3-S_1) **(3-S_1-MAO)**

Scheme 3. Formation of the **3-S_1-MAO** system.

Similar behavior was observed after impregnation of complexes **1** and **3** on **S_2**, with the cyanide band appearing at 2209 cm^{-1}, i.e., in a similar position to those of the **S_1** systems. The $ClSiMe_3$ elimination reaction is thermodynamically favoured and leads to the formation of strong Zr—O bonds. The coordination mode leaves the C≡N group free in the complexes and this is available to coordinate with another incoming Lewis acid group. Addition of MAO to the complexes supported on **S_1** led to a shift of the cyanide bands to higher wavenumbers (from 2209 to 2216 cm^{-1}), thus confirming the hypothesis outlined above (Scheme 3).

After the addition of complexes to the MAO-modified support (**S_3**, Scheme 2) the $\tilde{\nu}$ (CN) frequency appeared at 2216 cm^{-1}, which is quite different to that in the S_1 systems but identical to that found for the S_1-MAO systems. This finding indicates that the complexes are coordinated through the nitrile to acidic sites derived from MAO. The addition of further quantities of MAO did not lead to changes in the frequency or intensity of this characteristic band. (see Supporting information Fig. 3).

In an effort to make this approach feasible for a larger-scale industrial process by reducing the required amounts of MAO or other molecular Lewis acids ($B(C_6F_5)_3$), $MgCl_2$ was used as a support (**S_4**) [10]. $MgCl_2$ is readily available, has a low-cost and contains intrinsic Lewis acid sites on its surface to which compounds with a Lewis base functionality could coordinate [15].

As indicated above, the addition of a solution of complexes **1** or **3** to a suspension of $MgCl_2$ in toluene led to the formation of the supported systems **1-S_4** and **3-S_4**.

FT-IR characterization of these systems (Table 1) showed that the $\tilde{\nu}$(CN) bands were shifted by about 20 cm^{-1} to higher wavenumbers in relation to the bands in the free complexes, thus confirming the coordination of the complex through the nitrile fragment to the magnesium cation centers. The more marked displacement of the IR band of the $\tilde{\nu}$ (CN) fragment with respect to that observed for **S_3** systems may be due to the more effective coordination of the complexes, which is aided by the absence of bulky groups around the magnesium centers on the surface and in the MAO.

3.3. UV–vis spectrophotometric study

Qualitative ethylene polymerization reactions were carried out using **3-S_x**, **1-S_x** and ethylene at a pressure of 1 bar. The results of these experiments indicated that the most active heterogeneous systems in the presence of MAO are **3-S_3** and **3-S_4** and a UV–vis spectrophotometric study of these complexes was therefore carried out.

As mentioned above, one of the main reasons for carrying out research into homogeneous and supported catalytic systems is the reduction or elimination of the use of MAO as cocatalyst.

UV–vis spectroscopy was employed, in conjunction with our previous results on metallocenes [11b,c], to identify the minimum Al/Zr ratio needed to generate the active species for complex **3** (homogeneous phase) and for supported systems **3-S_3** and **3-S_4** (heterogeneous phase). The presence of chromophoric aromatic ligands directly attached to the metal enables the study of these systems by UV–vis spectroscopy. The formation of various species upon the incremental addition of MAO was identified by this technique.

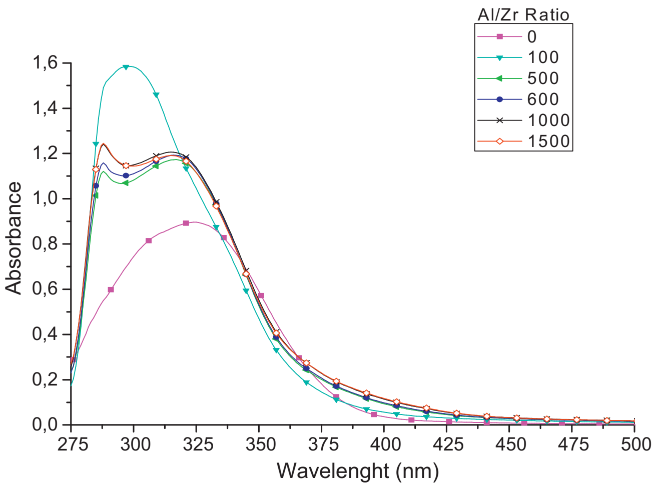


Fig. 3. UV–vis absorption spectrum of 3 at room temperature in toluene.

The most interesting absorptions were ligand-to-metal charge transfer transitions (LMCT), which occur because the ligands are electron rich and the metal is electron poor. For the same reason, neither metal-to-ligand charge transfer (MLCT) nor d–d transitions occur, meaning that the interpretation of the spectra is relatively straightforward.

These experiments were carried out in a special cell under dry nitrogen (1.0 cm path length) using dry toluene for the homogeneous experiment and Nujol as the dispersant for the heterogeneous experiments (see Supporting information).

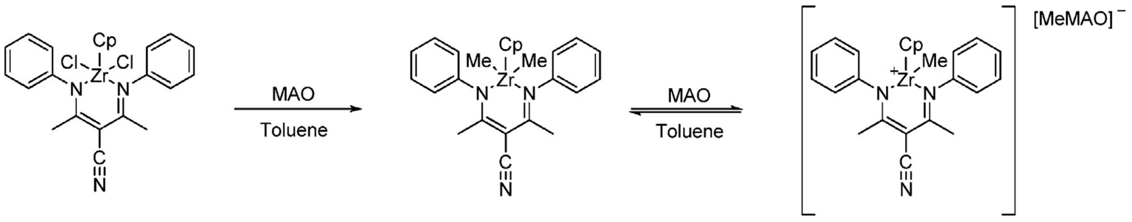
The UV–vis spectra of complex **3** in toluene (Al/Zr = 0 ratio used as reference with $[\mathbf{3}]_i = 1.2 \times 10^{-6}$ M) and those resulting from the successive additions of MAO in the studied range (100–1500) are shown in Fig. 3.

The results of this study suggest that the addition of a small amount of MAO (Al/Zr = 100) leads to the appearance of a new species with an absorption maximum shifted to lower wavelength (λ_{max} = 297 nm) in comparison to the band of the free complex (λ_{max} = 321 nm). A further increase in the Al/Zr ratio brings about the appearance of an additional band (λ_{max} = 315 nm). Based on the study of metallocenes [14], the absorption band at 297 nm would correspond to the dimethylated Zr compound (Scheme 4) and the band at 315 nm is due to the catalytically active cationic species. The combined form in which both bands appear accounts for the balance between the two species (see Scheme 4). Finally, there is an increase in the intensity of the band at 315 nm and this reaches a maximum at Al/Zr = 600. This ratio corresponds to the minimum MAO concentration required to achieve the maximum concentration of active species in solution.

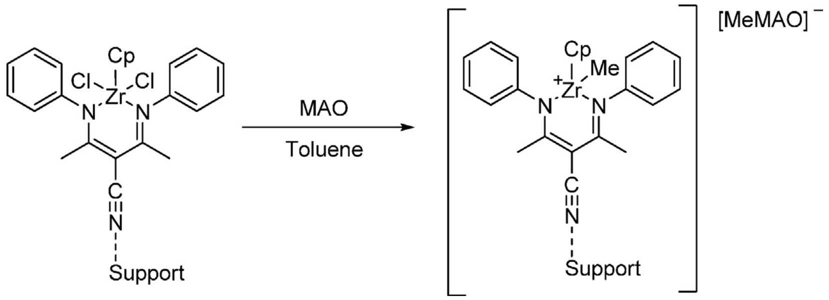
In the UV-Vis studies of the supported systems **3-S_3** and **3-S_4** a variable range of Al/Zr ratios were investigated with Nujol as the dispersant. The results are shown in Figs. 4 and 5, respectively.

It can be seen that the generation of cationic species in heterogeneous systems does not include the dimethylated intermediates (absence of an absorption at lower wavelengths) (Scheme 5).

The UV–vis spectra of the **3-S_3** and **3-S_4** systems show that the addition of a very small amount of MAO (Al/Zr = 50) does not lead to the formation of the cationic species. However, at Al/Zr = 100 a shoulder appears at higher wavelengths and this increases in



Scheme 4. Generation of cationic species for complex **3**.



Scheme 5. Generation of cationic species for supported systems.

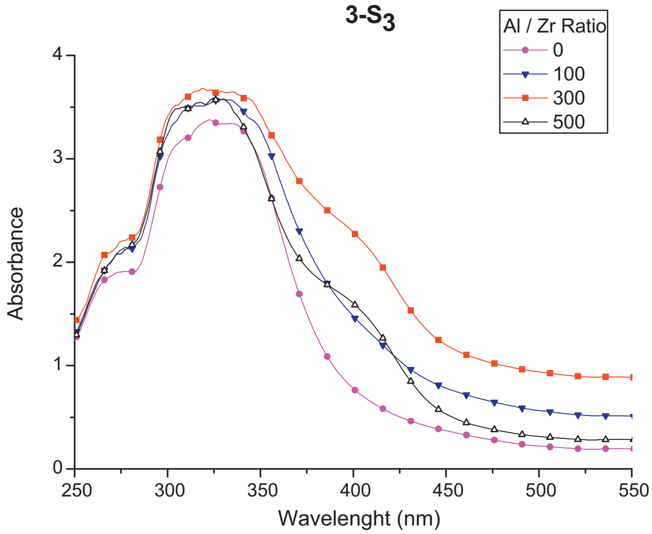


Fig. 4. UV–vis absorption spectrum of **3-S**$_3$ at room temperature in Nujol.

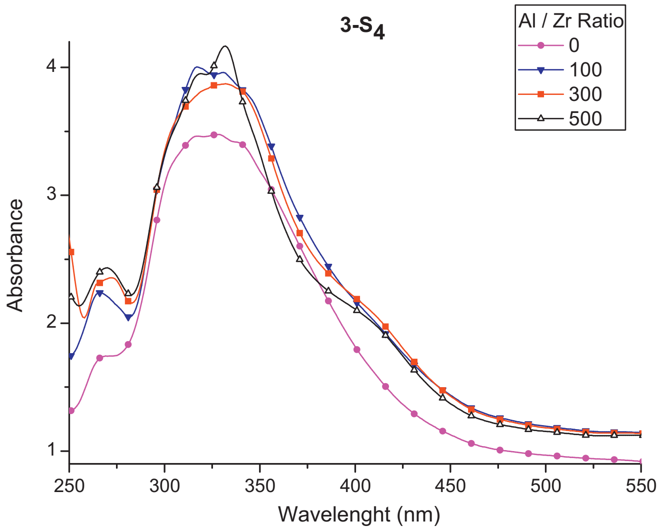


Fig. 5. UV–vis absorption spectrum of **3-S**$_4$ at room temperature in Nujol.

intensity before reaching its maximum absorption at Al/Zr = 300. This absorption band at ~403 nm is associated with the active cationic species.

Comparison of the UV–vis spectra for the homogeneous and heterogeneous phases shows that the MAO concentration required to generate the active species in the heterogeneous phase is half that required for the homogeneous phase. These results are consistent with the situation generally observed in heterogeneous catalyst systems [8].

*3.4. Homogeneous ethylene polymerization using compounds **1** and **2***

A series of homogeneous ethylene reactions were carried out using compounds **1** and **2** under various reaction conditions with MAO as the cocatalyst. The results are summarized in Table 2.

The effect of reaction temperature on complex **1** is shown by the results in entries 1–3. It can be seen that a significant increase in activity occurs and this is consistent with an increase in the propagation rate. Furthermore, the molecular weight decrease observed on increasing the reaction temperature is due to an increase in the chain termination process. The effect of MAO concentration is shown by the results in entries 3–5 and it can be seen

Table 2
Selected homogeneous ethylene polymerization reactions.[a]

Entry	Precatalyst	[Al]/[Zr] ratio	T[b]	A[c]	M_w[d]	PDI
1	**1**	250	40	5210	183	2.3
2	**1**	250	60	8005	108	2.1
3	**1**	250	75	9782	88	2.1
4	**1**	500	75	10047	48	3.5
5	**1**	125	75	26	186	1.7
6	**2**	250	75	10112	67	2.9
7	**2**	125	75	6819	76	1.9

[a] Ethylene polymerizations test were carried out in a 100 mL autoclave reactor. The conditions are as follows: $P = 12.5$ bar; 6×10^{-6} mol of complex in 30 mL of toluene .The cocatalyst was MAO. Reaction time 10 min.

[b] Reaction temperature in °C.

[c] Activity (kgPE[mol(Zr)h]$^{-1}$).

[d] $\times 10^3$ g/mol.

that the molecular weight decreases and the PDI increases as the MAO concentration is increased. These changes can be explained by an increase in the cocatalyst transfer rate. MAO also appears to have a small effect on the polymerization activity, which increases slightly on increasing the MAO concentration. It is worth noting that complex **1** has a very low activity at low MAO concentrations (Al/Zr = 125, entry 5), probably due to the inability of the coactivator to activate the metal center.

Adduct **2** was used with lower amounts of MAO (entries 6–7, Al/Zr = 250 and 125, respectively) in order to confirm the previously reported observation that the activity remains constant as the amount of MAO is decreased. On lowering the Al/Zr ratio to 125 it was found that the adduct had a very high activity (entry 7)—a situation in contrast to that found for complex **1**, which is practically inactive (entry 5) under the same reaction conditions, probably because now the coactivator useful activates the metal centre of the catalyst once the CN group of the ligand is blocked by the $B(C_6F_5)_3$ group.

In all cases a linear polyethylene was obtained with a small decrease in melting point (137 ± 2 °C).

3.5. Heterogeneous ethylene polymerization

The heterogenized systems **3-S$_x$** were tested as catalysts for ethylene polymerization under a pressure of 1 bar. The most efficient system was **3-S$_4$** and this was subsequently studied in greater depth. In this sense **3** and **3-S$_4$** were studied under the same conditions as previously reported [5] using MAO as cocatalyst. The new results are presented in Table 3. The behavior of complex **3** and its adducts **3** + $B(C_6F_5)_3$ as catalysts has been reported previously by our group [5].

Table 3
Selected ethylene polymerization reactions.[a]

Entry	Precatalyst	Al/Zr ratio	A[b]	M_w[c]	PDI
1	**3**	500	1910	147	1.8
2	**3**	250	1689	147	1.8
3	**3** + $B(C_6F_5)_3$	250	1944	190	5.6[*]
4	**3-S$_4$**	250	4830	72	4
5	**1-S$_4$**	250	3240	189	1.8
6	**1-S$_4$**	125	1227	194	2.1

[a] Ethylene polymerizations test were carried out in a 100 mL autoclave reactor. The conditions are as follows: $P = 12.5$ bar; 1.86×10^{-6} mol of complex or 100 mg of supported catalyst in 30 mL of toluene .The cocatalyst was MAO. Reaction time 10 min.

[b] Activity (kgPE[mol(Zr)h]$^{-1}$).

[c] $\times 10^3$ g/mol.

[*] Bimodal distribution.

The heterogeneous system with $MgCl_2$ as support was used to optimize the olefin polymerization process as this material has intrinsic Lewis acid sites that are capable of interacting with the nitrile group of the ligand and enhancing the activity, in a similar manner similar to that seen in entry 3, where complex **3** was coordinated with the borane derivative. However, in this case the support is cheaper and is easy to prepare.

Entries 1 and 2 correspond to the behavior of complex **3** as catalyst in the ethylene polymerization in the homogeneous phase on varying the concentration of MAO. In fact, on decreasing the amount of MAO to 50%, the activity decreased by 13% but the properties of the polymer obtained in both cases are the same (M_w, PDI and T_f). Entry 3 corresponds to the behavior as catalyst in the homogeneous phase of the interaction product between **3** + $B(C_6F_5)_3$. In this case the use of Al/Zr = 250 led to the same activity as previously found for complex **3**, but in that case a higher

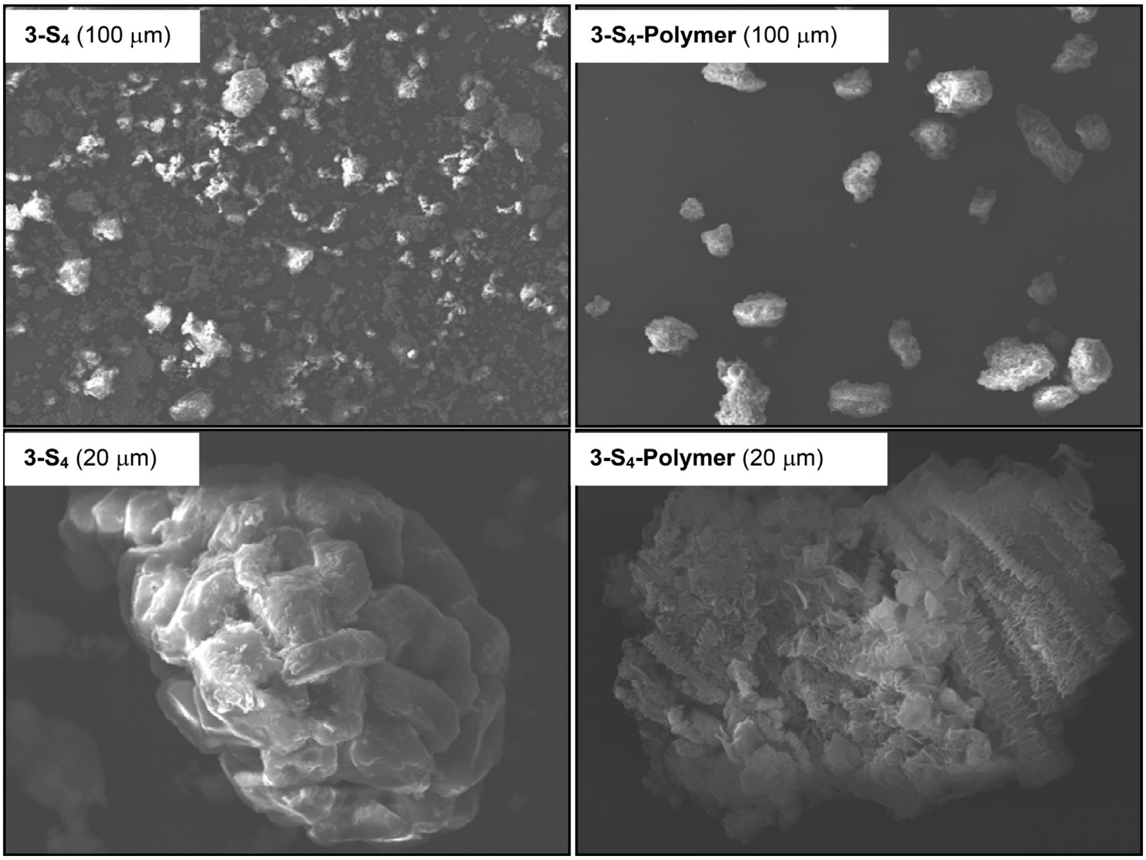


Fig. 6. SEM images for systems **3-S$_4$** and **3-S$_4$-Polymer**.

Al/Zr of 500 was required–a phenomenon that has been observed in a previous study [5]. This system also led to a polymer with higher molecular weight, probably due to the more marked steric influence around the metallic center caused by the coordination of tris(pentafluorophenyl)borane.

The results for the heterogeneous system **3-S$_4$** (entry 4) show a significant increase in activity from 1689 for complex **3** to 1944 for [**3** + B(C_6F_5)$_3$] and 4830 for the heterogeneous system, i.e. more than twice the activity of compound **3**, but in both cases(entries 3 an 4) the polymers have large PDI values in agreement with the results previously reported [5e]. However, on using the system **1-S$_4$** (entry 5) the opposite effect to that shown by **3-S$_4$** was observed, with the activity being practically reduced to 30% of the activity of adduct **2** (entry 6, Table 2) under the same conditions. This difference is attributed to the structures of the complexes used. Complex **3** has a more hindered steric environment than complex **1** and this helps to protect the metal center, whereas in the case of system **3-S$_4$** possible interactions with the acid sites on the support may lead to catalyst activation. It should be noted that although the activity at a low Al/Zr ratio (125, entry 6, Table 3) is lower than that shown by compound **2** under the same conditions, it is still higher than that shown by compound **1**, which is almost inactive. The most interesting result is the difference in the molecular weights of the polymers obtained [see entries 6 (Table 2) and 5 (Table 3) or entries 3 and 4(Table 3)]. In these cases a marked difference is observed on using a boron compound or an inorganic support as the remote activator for complex **1** (67 kg/mol and 189 kg/mol, respectively) and for complex **3**(190 kg/mol and 72 kg/mol, respectively), a result that highlights the importance of the support and its effect on the metal center.

SEM studies were carried out in order to determine the morphology of the **3-S$_4$** system as well as that of the polymer formed on using this system. It can be seen in Fig. 6 that at 100 μm magnification the **3-S$_4$** system corresponds to a solid with irregular size and shape but at a magnification of 20 μm the system consists of aggregates of smaller particles with a regular morphology that give rise to a compact solid. After the polymerization process (**3-S$_4$-Polymer**), the 100 μm magnification shows that these particles have a more regular size than in the case of **3-S$_4$**, which is close to 30 μm. Finally, at the 20 μm magnification it is evident that these particles correspond to a spongy material that is consistent with the formation of the polymer on the agglomerated particles of the **3-S$_4$** system.

4. Conclusion

The synthesis and characterization of two new zirconium compounds (complex **1** and adduct **2**) is reported. Both of these compounds are active in the polymerization of ethylene and yield linear, semicrystalline polyethylene of moderate molecular weight. It is interesting to note that at low MAO concentrations (Al/Zr = 125 ratio) the adduct is at least two orders of magnitude more active than the complex. Moreover, comparison of complexes **1** and **3** shows that a four-membered metallocycle (**1**) is five times more active in olefin polymerization than the six-membered metallocycle (**3**).

Complexes **1** and **3** were successfully heterogenized on different inorganic supports and, due to the presence of the nitrile group, there were two different interaction modes with the support. In cases where the support has Lewis acid sites on its surface, the complex participates in a Lewis acid-base interaction. However, if the support does not have such sites, the complex is linked through a Si—O—Zr bond. The results of a UV–vis study carried out to determine the smallest amount of MAO needed to activate the complex showed an optimum Al/Zr = 600 ratio for the homogeneous system, while for the heterogeneous system it was 200, i.e., a 66% decrease in the required Al/Zr ratio.

Finally, it was shown that the activity of **3-S$_4$** is twice as high in the polymerization of ethylene and it requires only half the cocatalyst in comparison to complex **3**. This is the most significant result because the use of $MgCl_2$ as support not only activates the system better than the Lewis acid B(C_6F_5)$_3$, but leads to a reduction in cost per gram in the synthesis of around 200 times.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.04.017.

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