www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 606 (2000) 169–175

Preparation and characterization of immobilized constrained-geometry hafnium complexes

Hannele Juvaste [a], Tuula T. Pakkanen [a,*], Eero I. Iiskola [b]

[a] Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland
[b] VTT Chemical Technology, P.O. Box 1401, Biologinkuja 7, FIN-02044 VTT, Finland

Received 18 April 2000; received in revised form 26 May 2000

Abstract

Heterogeneous constrained-geometry hafnium complexes were prepared by anchoring $Hf(NMe_2)_4$ on a heterogenized *ansa*-cyclopentadienylamino ligand of type $(RN)R'R''Si(C_5R'''_4)$, surface **1**: $R = –O–Me_2Si(CH_2)_3$; R', R'', $R''' = Me$; surface **2**: $R = –O–Me_2Si(CH_2)_3$; R', $R''' = Me$, $R'' = H$. Preparation of the constrained-geometry catalyst ligand on silica surface was carried out in two steps: functionalizing of the silica surface with aminopropyldimethylethoxysilane (APDMES) by using saturated gas–solid reactions and immobilizing of (tetramethylcyclopentadienyl)chlorosilanes, $Me_2Si(C_5Me_4H)Cl$ or $MeHSi(C_5Me_4H)Cl$, on the functionalized silica by utilizing *n*-butyllithium (*n*-BuLi). $Hf(NMe_2)_4$ was immobilized on the heterogeneous surfaces by the amine elimination route. The complexes were characterized by ^1H, ^{13}C, and ^{29}Si solid state NMR and FTIR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silica; Cyclopentadienyl; Hafnium; Amide; Constrained-geometry; Nuclear magnetic resonance

1. Introduction

Ever since Bercaw and co-workers [1,2] introduced the first *ansa*-cyclopentadienylamido complexes of scandium for the polymerization of α-olefins, intensive efforts have been devoted to the synthesis and study of corresponding Group 4 metal complexes [3–26]. Okuda [5] reported in 1990 on the synthesis of titanium constrained-geometry compounds and later Dow and Exxon [27,28] began to investigate their activity in olefin polymerization. Constrained-geometry catalysts differ from bis(cyclopentadienyl)metallocenes in their ability to readily incorporate α-olefins in copolymerizations with ethylene. This ability is due to the open nature of the catalyst active site.

The method initially used for preparation of these complexes involves the metathetical reaction of the dilithio salt of $[(C_5R_4)L(NR')]^{2-}$ with an appropriate metal halide. However, in some cases this route produces only low isolated yields or isomeric mixtures. A more efficient route is the amine elimination reaction developed by Lappert [29] for metallocene compounds. This reaction strategy was subsequently utilized for *ansa*-cyclopentadienyl and indenyl complexes [22,30–35], and recently for stereoselective syntheses of chiral *ansa*-metallocenes [36–40]. Carpenetti et al. [20] prepared *ansa*-monocyclopentadienylamido Group 4 complexes using a neat amine elimination reaction. Eisen et al. [41] synthesized a constrained-geometry titanium complex in toluene using an amine elimination reaction.

To date almost all *ansa*-monocyclopentadienylamido catalysts have been homogeneous. Only Exxon [42] and Vega et al. [43] in their patents and Eisen et al. in their paper [41] have tested heterogenization of these constrained-geometry catalysts.

We report the preparation and characterization of heterogeneous constrained-geometry hafnium complexes constructed in stepwise fashion. We have previously described the first two steps: the modification of the silica surface with aminopropyldimethylethoxysilane (APDMES) and immobilization of (tetramethylcyclopentadienyl)chlorosilanes, $Me_2Si(C_5Me_4H)Cl$ or $MeHSi(C_5Me_4H)Cl$, on the APDMES-modified surface [44]. Moreover, we have reported the anchoring of

---

* Corresponding author. Tel.: +358-13-2513340; fax: +358-13-2513344.

E-mail address: tuula.pakkanen@joensuu.fi (T.T. Pakkanen).

PII: S0022-328X(00)00342-9

Table 1
Elemental analyses of the modified surfaces and complexes

Modified support	Anal. C (w%)	Anal. N (w%)	N (nm^{-2})	Anal. Hf (w%)	Hf (nm^{-2})	N/Hf
SiO_2+APDMES	4.0	1.0	1.4			
Surface **1**	8.06	0.94	1.35			
Complex **1**	8.09	1.56	2.24	4.91	0.55	4.1
SiO_2+APDMES	4.0	1.0	1.4			
Surface **2**	7.71	0.93	1.33			
Complex **2**	8.28	2.06	2.95	5.48	0.62	4.8

zirconium complex ($Zr(NMe_2)_4$) onto these prepared surfaces [45]. In our present paper we report the immobilization of hafnium complex ($Hf(NMe_2)_4$) onto these bifunctional surfaces by amine elimination reaction. The prepared heterogeneous complexes were characterized by ^1H, ^{13}C, and ^{29}Si solid state NMR and FTIR spectroscopy.

2. Results and discussion

2.1. Preparation of bifunctional silica carriers

The pretreated silica surface (600°C) was modified first with APDMES in an atomic layer chemical vapor deposition (ALCVD) reactor utilizing saturated gas–solid reactions. The content of nitrogen after modification, corresponds to 1.4 N atoms (or APDMES molecules) nm^{-2} of SiO_2 (see Table 1).

In the next step, two (tetramethylcyclopentadienyl)methylchlorosilanes, $Me_2Si(C_5Me_4H)Cl$ (surface **1**) and $MeHSi(C_5Me_4H)Cl$ (surface **2**), were immobilized on the APDMES-functionalized silica by utilizing *n*-BuLi. The reaction of the amino group of the modified silica surface with *n*-BuLi in pentane produces a lithiated amido group, which reacts further with the chloride of the silane. A chemical bond is formed between nitrogen and silicon of the silane and lithium chloride (LiCl) is formed as a by-product. The modification and structural characterization of the catalyst carriers have been described in detail in our earlier report [44] and the elemental results are given in Table 1.

2.2. Preparation of heterogeneous catalysts

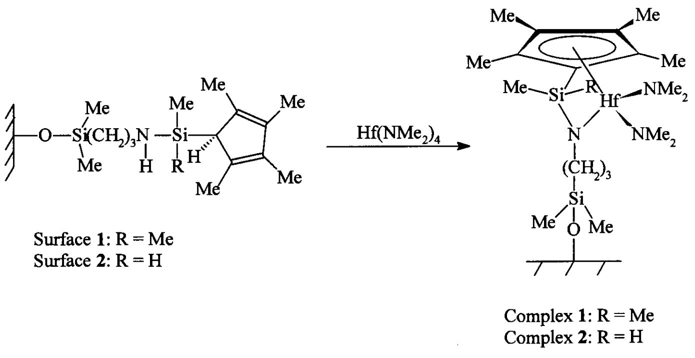
Tetrakis(dimethylamino)hafnium was attached to the heterogenized *ansa*-cyclopentadienylamino ligands with a liquid phase reaction in toluene (Scheme 1). $Hf(NMe_2)_4$ was expected to react with both the cyclopentadienyl ring and the amino group of surfaces **1** and **2**, with the evolution of NMe_2H. This amine elimination reaction does not require the use of an organolithium reagent, and one step in the synthetic route is thus eliminated.

*2.2.1. Reaction of $Hf(NMe_2)_4$ with surface **1***

After $Hf(NMe_2)_4$ treatment of surface **1** the hafnium content of the supported complex (complex **1**) was 4.91 w%, corresponding to ca. 0.55 Hf atoms nm^{-2} of support (Table 1), and the nitrogen content was 1.56 w%, corresponding to ca. 2.24 N atoms nm^{-2} of support. This represents a N/Hf ratio of 4.1. From these results and a comparison of the hafnium loading of complex **1** with the nitrogen loading of surface **1** (Table 1), we conclude that $Hf(NMe_2)_4$ has reacted with about 40% of the amino groups. This means that there are still some unreacted amino and cyclopentadienyl groups left on the surface. Metal loadings on surface **1** were higher for $Zr(NMe_2)_4$, corresponding to 0.9 Zr atoms nm^{-2} of support [45].

In the IR spectrum of complex **1** (Fig. 1(b)), a weak band typical of η-Cp group is observed at 3907 cm^{-1}. Two other new bands, at 2820 and 2768 cm^{-1}, can be assigned as CH stretchings of the CH_3N group bonded to hafnium.

In the ^{13}C-NMR spectrum of surface **1** (Fig. 2(b)) the signals of the cyclopentadienyl *C*Me carbons are observed at about 132 and 135 ppm, but after coordination of the hafnium (complex **1**) the signals shift to about 127 ppm (Fig. 2(c)). Also, the signal of the bridgehead carbon of the ring shifts from 56 to 101 ppm, but it is very weak and difficult to observe. The methyl groups of the hafnium amide give signals at 38 and 42 ppm. In our earlier studies of $Zr(NMe_2)_4$ on surface **1**, we observed only one signal (42 ppm) [45].



Scheme 1.

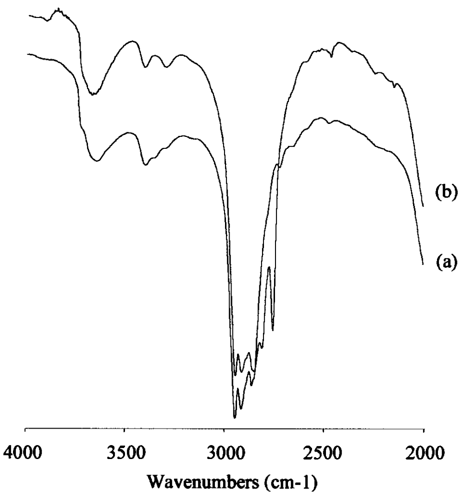


Fig. 1. IR spectra of (a) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5Me_4H)Cl$ (b) complex **1**, surface **1** after anchorage of $Hf(NMe_2)_4$.

Possibly in the case of $Zr(NMe_2)_4$ on surface **1** there is a signal at about 38 ppm, but it is overlapped by the more intense signal at 42 ppm. The extra signal at 38 ppm can be explained in terms of the ability of a molecule of NMe_2H to coordinate to hafnium. This coordination could also explain the high nitrogen content relative to hafnium content. Eisen et al. [41] have proposed that NEt_2H group coordinates to the titanium group in the amine elimination reaction and therefore there are two signals for CH_2- and two for CH_3-groups. Carpenetti et al. [20] found NMe_2H group to coordinate to zirconium when they converted $[(C_5H_4)SiMe_2$-(N-*t*-Bu)]$Zr(NMe_2)_2$ to chloride derivative. The signal of the coordinated NMe_2H group was found at the same chemical shift of 39 ppm that we observed.

The ^{29}Si-NMR spectrum of complex **1** (Fig. 3(c)) shows the same silica and APDMES resonances at −110 and 12.8 ppm as before anchorage of $Hf(NMe_2)_4$ (surface **1**, Fig. 3(b)), but the signal of the $Me_2Si(C_5Me_4)$ group is shifted from 1.2 to −22.2 ppm due to coordination of the hafnium. There is also a weak signal of the unreacted $Me_2Si(C_5Me_4H)$ groups at 1.2 ppm.

2.2.2. Reaction of $Hf(NMe_2)_4$ with surface 2

The nitrogen content of surface **2** was 0.93 w%, corresponding to ca. 1.33 N atom nm^{-2} of support (Table 1). The immobilization of $Hf(NMe_2)_4$ on surface **2** increased the nitrogen content to 2.1 w%, corresponding to 2.95 N atoms nm^{-2} of support. Complex **2** contained 5.48 w% of hafnium corresponding to Hf loading of ca. 0.62 Hf atoms nm^{-2} of support. From these results, and comparing the hafnium loading of complex **2** with the nitrogen loading on the surface **2** (Table 1), we conclude that about half of the amino groups reacted with hafnium molecules. This Hf loading is only slightly higher than the Zr loading (0.49 Zr atom nm^{-2}) we achieved with surface **2** in our earlier study [45].

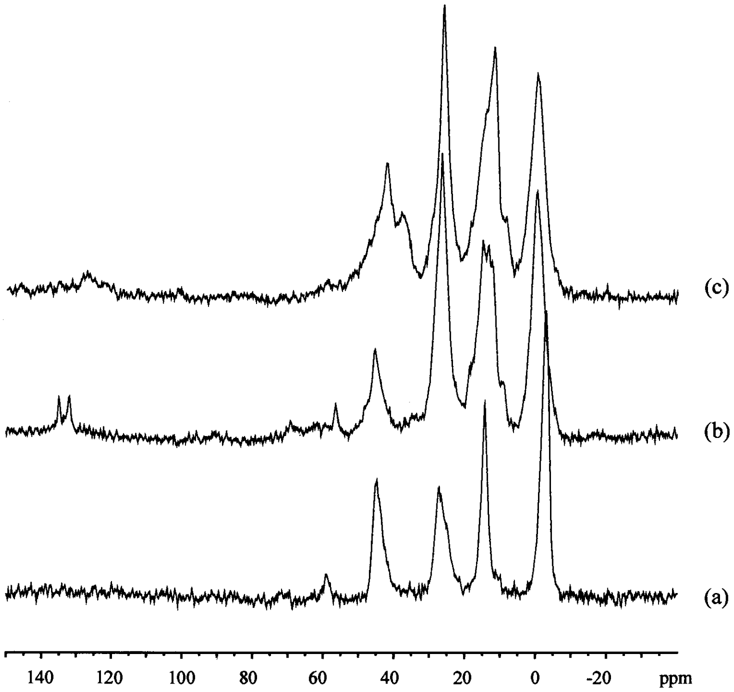


Fig. 2. CP/MAS ^{13}C-NMR spectra of (a) APDMES-modified silica (b) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5Me_4H)Cl$ (c) complex **1**, surface **1** after anchorage of $Hf(NMe_2)_4$.

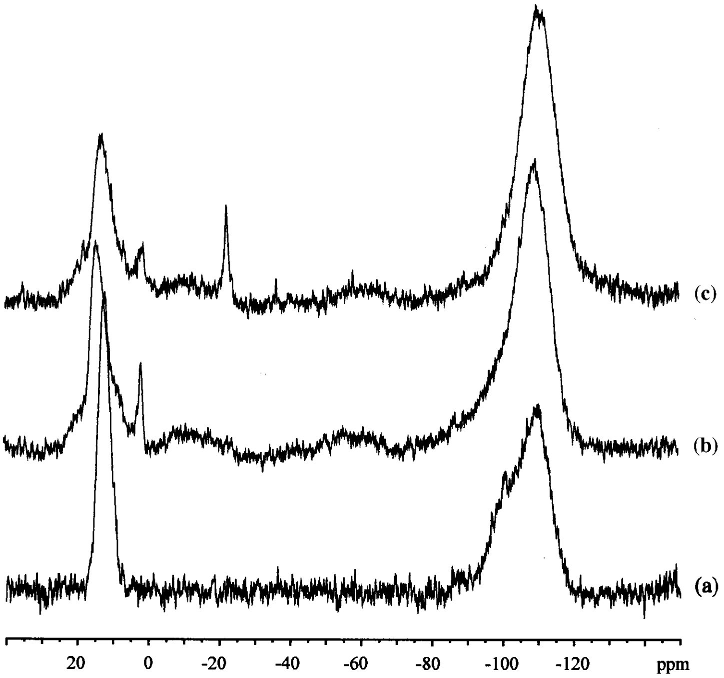


Fig. 3. CP/MAS ^{29}Si-NMR spectra of (a) APDMES-modified silica (b) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5Me_4H)Cl$ (c) complex **1**, surface **1** after anchorage of $Hf(NMe_2)_4$.

We have earlier suggested that there are two differently bound cyclopentadienyl groups on surface **2** [44]. As in the case of $Zr(NMe_2)_4$, we deduce that, for steric reasons, $Hf(NMe_2)_4$ preferably reacts with $MeHSi(C_5Me_4H)$ groups that are bonded to the amino groups. This claim is supported by the IR results. In the spectrum of surface **2** (Fig. 4(a)) the Si–H band at about 2100 cm^{-1} is quite broad, and in fact there are two bands: the band at 2113 cm^{-1}, assigned to $MeHSi(C_5Me_4H)$ groups bonded to the amino groups, and the band at 2159 cm^{-1}, assigned to $MeHSi(C_5Me_4H)$ groups bonded directly to the surface. In the spectrum of complex **2** (Fig. 4(b)), the band at 2113 cm^{-1} has disappeared and there is a new band at 2081 cm^{-1}. We can assume that the 2113 cm^{-1} band has shifted because hafnium amide has coordinated to the adjacent atoms of the SiMeH group. The band at 2159 cm^{-1} is still at the same wavenumber, but its intensity is weaker compared to the intensity of the band at 2081 cm^{-1}. There is also a weak band at 3907 cm^{-1} in the spectrum of complex **2**, which is typical for a η^5-Cp group. The new bands at 2860 and 2765 cm^{-1} are assigned as CH stretchings of CH_3N group bonded to hafnium.

The ^{13}C-NMR spectrum of complex **2** (Fig. 5(c)) shows signals for the methyl groups of the hafnium amide at 37 and 42 ppm, as for complex **1**. The signals of four cyclopentadienyl *C*Me carbons have shifted from 132 and 135 ppm to about 122 and 128 ppm owing to coordination of hafnium compound. The signals at 125 and 135 ppm can be assigned to solvent (toluene) or to unreacted cyclopentadienyl groups. The signal of the bridgehead carbon of the ring is seen at about 103 ppm but it is very weak.

The only change in the ^{29}Si-NMR spectrum of complex **2** relative to the spectrum of surface **2** is the shift in the signal of the $MeHSi(C_5Me_4)$ group from -9 to -39.5 ppm due to coordination of the hafnium (Fig. 6).

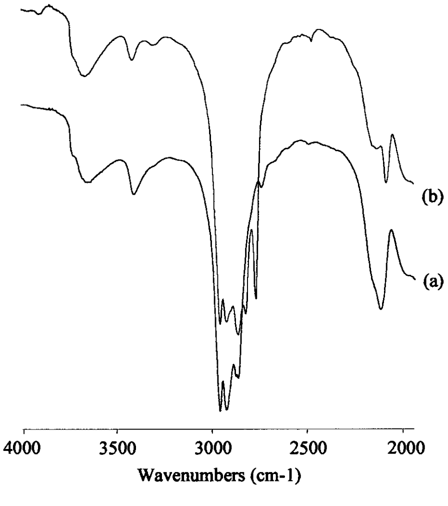


Fig. 4. IR spectra of (a) surface **2**, APDMES-modified silica after immobilization of $MeHSi(C_5Me_4H)Cl$ (b) complex **2**, surface **2** after anchorage of $Hf(NMe_2)_4$.

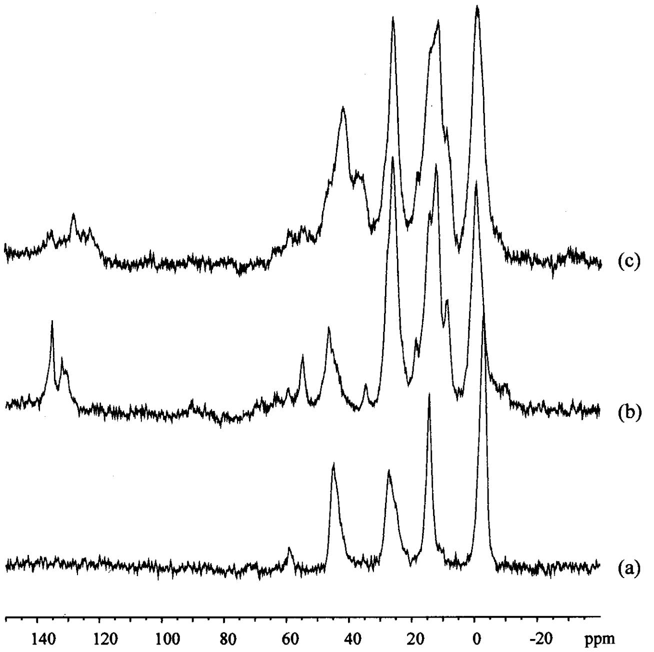


Fig. 5. CP/MAS ^{13}C-NMR spectra of (a) APDMES-modified silica (b) surface **2**, APDMES-modified silica after immobilization of MeHSi(C_5Me_4H)Cl (c) complex **2**, surface **2** after anchorage of Hf(NMe_2)$_4$.

2.3. Polymerization of ethylene

Both hafnium complexes were tested for polymerization of ethylene in the presence of cocatalyst MAO. Polymerizations were performed in the same reactor and with use of the same polymerization conditions (ethylene pressure 2.5 bar, temperature 80°C, reaction time 30 min, Al/Hf ratio 5000 and toluene as reaction media) as in our earlier study with zirconium catalysts [45]. The hafnium complexes showed only weak activity for ethylene polymerization (complex **1**: 12 kg of PE/(mol of Hf·h), complex **2**: 11 kg of PE/(mol of Hf·h)). In comparison with the activities obtained with zirconium catalysts (about 200 kg of PE/(mol of Zr·h)) [45], the present results are thus poor. However, we fully expected that the activity would be poorer. In tests of homogeneous constrained-geometry catalysts of type [M(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)$R_2$, M=Zr, Hf; R=Me, ^{n}Bu] for ethylene polymerization in the presence of MAO, Okuda et al. [13] found the zirconium catalysts to be 5–15 times more active than the corresponding hafnium catalysts when polymerizations were performed at 70°C. Activities were not different when polymerizations were performed at 25°C.

The polymerization mechanism of the constrained-geometry catalysts (η^5-$C_5H_4SiH_2NH$)TiMe and (η^5-

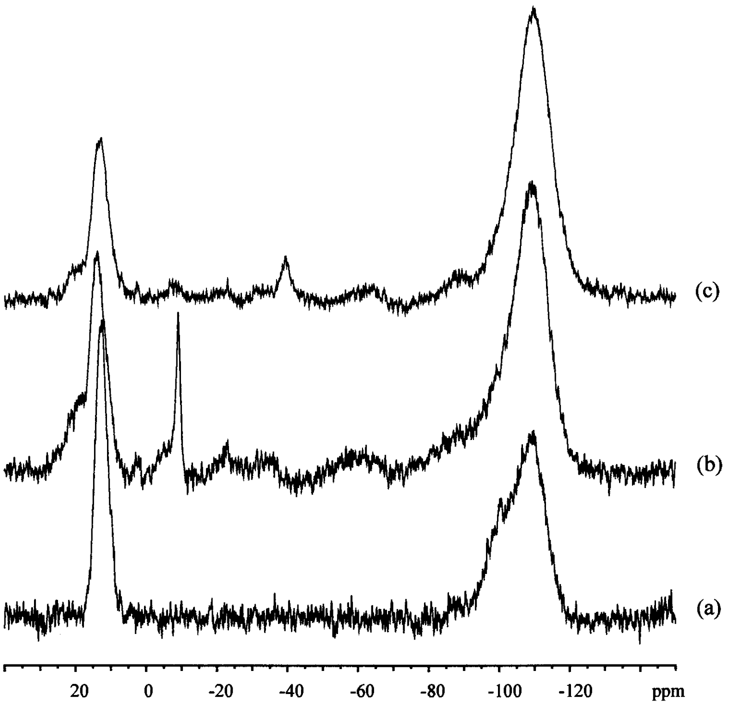


Fig. 6. CP/MAS ^{29}Si-NMR spectra of (a) APDMES-modified silica (b) surface **2**, APDMES-modified silica after immobilization of MeHSi(C_5Me_4H)Cl (c) complex **2**, surface **2** after anchorage of Hf(NMe_2)$_4$.

$C_5H_4SiH_2NH)MMe^+$ (M=Ti, Zr, Hf) has been studied theoretically by density functional theory and molecular mechanics [46]. Examination of the insertion process of the Ti(IV)- Zr(IV)- and Hf(IV)-based constrained-geometry catalysts, showed the insertion barriers to increase in the order $Ti < Zr \approx Hf$. The calculated insertion barriers for Zr and Hf are fairly similar (5.1 kcal mol^{-1} and 5.8 kcal mol^{-1}), but the higher barrier for Hf could reduce the activity.

3. Conclusion

Heterogeneous constrained-geometry hafnium complexes were prepared by attaching tetrakis(dimethylamino)hafnium ($Hf(NMe_2)_4$) to bifunctional silica surfaces. The bifunctional carrier, containing amino and tetramethylcyclopentadienyl groups in the same coupling agent molecule, was prepared in two stages. The reaction of the hafnium compound with tetramethylcyclopentadienyl and amino groups proceeded via elimination of amines, yielding a constrained-geometry structure according to IR and ^{13}C and ^{29}Si CP/MAS NMR results.

Both complexes were tested for polymerization of ethylene in the presence of cocatalyst, MAO. In the conditions employed, the polymerization results for both complexes showed only moderate activity towards ethylene (about 11 kg of PE/(mol of Hf·h)).

4. Experimental

All manipulations were performed under nitrogen using a vacuum line and Schlenk techniques. SiO_2 (EP 10, Crosfield Ltd.) was heat treated in air for 16 h at 600°C. The pretreated silica was functionalized with APDMES (aminopropyldimethylethoxysilane) in a commercial F-120 ALCVD (Atomic Layer Chemical Vapor Deposition) reactor manufactured by Microchemistry Ltd., Finland, according to published procedures [44]. $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$ were prepared and immobilized on the APDMES-functionalized silica according to published procedures [44]. The solvents were distilled from sodium benzophenone ketyl under nitrogen atmosphere. $Hf(NMe_2)_4$ (Strem Chem.) was used as received. Methylaluminoxane (30%) was purchased from Witco GmbH. Ethylene was passed through a purification system containing molecular sieves and activated Cu just before feeding to the reactor.

IR spectra of the solid samples were recorded on a Nicolet Impact 400D FTIR spectrometer equipped with DRIFT (Diffuse Reflectance Infrared-Fourier Transform) and connected airtightly to a glovebox. The solid-state ^1H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer equipped with a magic angle spinning probehead using the parameters described in reference [47]. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with a Carlo Erba Instruments EA 1110 CHNS-O analyzer. Zirconium analyses were carried out with an inductively coupled plasma atomic emission spectrometer (ICP).

*4.1. Anchoring of tetrakis(dimethylamino)zirconium ($Hf(NMe_2)_4$) on the $Me_2Si(C_5Me_4H)Cl$ modified surface (surface **1**)*

Modified silica (surface **1**, 0.5 g) was packed into a flask in the glove box, and toluene (15 ml) was added with a syringe. $Hf(NMe_2)_4$ (0.15 g, 0.42 mmol) was diluted with toluene (5 ml) and both mixtures were cooled to − 60°C. The solution of $Hf(NMe_2)_4$ in toluene was added to the flask dropwise, with a double-ended needle, while stirring. After the reaction mixture had warmed to room temperature, it was refluxed for an hour. A light yellow solid was produced. The solution was filtered off and the resulting solid was washed three times with toluene and twice with pentane. Finally the solvent was evaporated under reduced pressure.

Complex **1**: ^1H-NMR (400 MHz) δ − 0.05 (Si–CH_3), 0.6 (CH_2Si and CH_2), 1.2 (ring CH_3), 2.6 (CH_2N, NCH_3) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ − 0.4 (Si–CH_3), 11.7 (ring CH_3), 26 (CH_2), 38 (NMe_2), 42 (NMe_2), 101 (ring C), 122 (ring C), 127 (ring C) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ 12.8 (silica–Si–CH_3), − 22.2 (Si–CH_3), − 110 (silica) ppm.

*4.2. Anchoring of tetrakis(dimethylamino)zirconium ($Hf(NMe_2)_4$) on the $MeHSi(C_5Me_4H)Cl$ modified surface (surface **2**)*

Anchorage of $Hf(NMe_2)_4$ was done by the same procedure as for surface **1** except that the reflux time was half an hour (0.5 g of modified silica and 0.15 g (0.42 mmol) of $Hf(NMe_2)_4$). The product was light yellow.

Complex **2**: ^1H-NMR (400 MHz) δ − 0.08 (Si–CH_3), 0.6 (CH_2Si and CH_2), 2.1 (ring CH_3), 2.6 (CH_2N, NCH_3) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ − 0.5 (Si–CH_3), 11.8 (ring CH_3), 26.1 (CH_2), 37 (NMe_2), 42 (NMe_2), 103 (ring C), 122 (ring C), 128 (ring C) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ 12.8 (silica–Si–CH_3), − 39.5 (Si–CH_3), − 110 (silica) ppm.

4.3. Ethylene polymerization

Ethylene polymerization was carried out in toluene in a 0.5 dm^3 stainless steel autoclave. Toluene (250 ml) and the MAO (30%) used as cocatalysts were introduced into the evacuated and nitrogen purged reactor under nitrogen flow. The heterogeneous catalyst was rinsed into the reactor with toluene under a nitrogen flow. MAO and the catalyst were allowed to prereact for 15 min while the temperature of the reactor was raised to the polymerization temperature. The feeding of ethylene was begun and the ethylene pressure was regulated to 2.5 bar. The consumption of ethylene was regulated with a mass flow controller. The polymerization time was 30 min. After polymerization, the reactor was degassed and then allowed to cool down to room temperature. The polymerization product was stirred with a mixture of ethanol and a small amount of concentrated hydrochloric acid, and filtered. Finally the polymer was washed with ethanol and dried in an oven at 60°C.

References

[1] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.

[2] J.M. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.

[3] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[4] J. Okuda, T. Eberle, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, vol. 1, Wiley-VCH, Weinheim, 1998, pp. 415–453.

[5] J. Okuda, Chem. Ber. 123 (1990) 1649.

[6] K.E. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, Organometallics 14 (1995) 3129.

[7] J. Okuda, K.E. du Plooy, W. Massa, H.-C. Kang, U. Rose, Chem. Ber. 129 (1996) 275.

[8] F. Amor, J. Okuda, J. Organomet. Chem. 520 (1996) 245.

[9] J. Okuda, S. Verch, T.P. Spaniol, R. Stumer, Chem. Ber. 129 (1996) 1429.

[10] J. Okuda, T. Eberle, T.P. Spaniol, Chem. Ber. 130 (1997) 209.

[11] F. Amor, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4765.

[12] F. Amor, K.E. du Plooy, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 558 (1998) 139.

[13] F. Amor, A. Butt, K.E. du Plooy, T.P. Spaniol, J. Okuda, Organometallics 17 (1998) 5836.

[14] T. Eberle, T.P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. (1998) 237.

[15] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, Organometallics 14 (1995) 3132.

[16] Y.-X. Chen, C.L. Stern, S. Yang, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 12 451.

[17] L. Jia, X. Yang, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 842.

[18] Y.-X. Chen, T.J. Marks, Organometallics 16 (1997) 3649.

[19] L. Kloppenburg, J.L. Petersen, Organometallics 15 (1996) 7.

[20] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.

[21] L. Kloppenburg, J.L. Petersen, Organometallics 16 (1997) 3548.

[22] W.A. Herrmann, M.J.A. Morawietz, J. Organomet. Chem. 482 (1994) 169.

[23] J.C. Stevens, Stud. Surf. Sci. Catal. 89 (1994) 277.

[24] T.K. Woo, P.M. Margl, J.C.W. Lohrenz, P.E. Blöchl, T. Ziegler, J. Am. Chem. Soc. 118 (1996) 13021.

[25] S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 15 (1996) 5577.

[26] H.V.R. Dias, Z. Wang, S.G. Bott, J. Organomet. Chem. 508 (1996) 91.

[27] J.A.M. Canich (Exxon), Eur. Patent Appl. EP 420 436-A1.

[28] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S.-y. Lai (Dow), Eur. Patent Appl. EP 416 815-A2.

[29] G. Chandra, M.F. Lappert, J. Chem. Soc. A (1968) 1940.

[30] A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936.

[31] P.-J. Sinnema, K. Liekelema, O.K.B. Staal, B. Hessen, J.H. Teuben, J. Mol. Catal. A 128 (1998) 143.

[32] W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, Angew. Chem. Int. Ed. Engl. 33 (1994) 1946.

[33] W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, J. Organomet. Chem. 506 (1996) 351.

[34] W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, F. Küber, J. Organomet. Chem. 509 (1996) 115.

[35] W.J. Gauthier, J.F. Corrigan, N.J. Taylor, S. Collins, Macromolecules 28 (1995) 3771.

[36] G.M. Diamond, S. Rodewald, R.F. Jordan, Organometallics 14 (1995) 5.

[37] G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4030.

[38] J.N. Christopher, G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4038.

[39] G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4045.

[40] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024.

[41] M. Galan-Fereres, T. Koch, E. Hey-Hawkins, M.S. Eisen, J. Organomet. Chem. 580 (1999) 145.

[42] J.A.M. Canich (Exxon), US Patent. 5 057 475, 1991.

[43] W.M. Vega, P.L. Cañas, A.M.-E. Lafuente, G.H. Llinas, J.S. Royo, L.M. Llatas, US Patent. 5 824 620, 1998.

[44] H. Juvaste, E.I. Iiskola, T.T. Pakkanen, J. Organomet. Chem. 587 (1999) 38.

[45] H. Juvaste, E.I. Iiskola, T.T. Pakkanen, Organometallics 19 (2000) 1729.

[46] L. Fan, D. Harrison, T.K. Woo, T. Ziegler, Organometallics 14 (1995) 2018.

[47] E.I. Iiskola, S. Timonen, T.T. Pakkanen, O. Härkki, P. Lehmus, J.V. Seppälä, Macromolecules 30 (1997) 2853.