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Olefin polymerisation with hafnocenes: A bridged alicyclic alcohol as a ligand and as the hafnocene modifier

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Abstract

Homogeneous ethylene and propylene polymerisation with new mixed-ligand chloroalcoholate of hafnocene was investigated. The catalytic activity of the complex was studied in comparison with Cp_2HfCl_2 pre-treated with 2-methyladamantan-2-ol in different molar ratios. The addition of the bridged alicyclic alcohol to the metallocene does not deactivate the catalytic system, but results similar to those obtained with the corresponding mixed-ligand hafnocenes were obtained. The voluminous alcoholato-moiety makes part of the [MAdO–MAO]$^-$ counter-ion where it promotes regioerrors in the growing polymer chain. The X-ray structure of new complex was determined.
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1. Introduction

Olefin polymerisation with homogeneous catalysts based on group 4 metallocenes activated by methylaluminoxane (MAO) was discovered over 25 years ago [1,2]. However, a detailed study of the catalytic system components continues to be actual, especially owing to vigorously growing output of the world plastic industry reaching 150 million tons per year [3]. From the academic point of view, investigation of structure–properties relationship for the metallocene/MAO catalysts opens a possibility to tune finely the polymer properties and to create tailor-made polymer microstructures.

A major part of research activities in the field of metallocene catalysis have mainly been focused on changes within η^5-bonded aromatic ligands [4–6] and the role of different co-catalysts [6,7], while the σ-bonded part of the metallocene complex has received a little attention.

Earlier, some examples of such influence of the σ-ligands in metallocene core on the catalyst performance were reported [8–13]. First, differences in polymerisation rate were shown by comparison of dimethylzirconocene and zirconocene dichloride behaviour [8]. The substitution of chloro-ligands by alcoholato-moieties also had a positive influence in the case of styrene polymerisation with half-metallocenes activated by methylaluminoxane (MAO). For instance, when $CpTiCl_2(OR)$/MAO (R=Me, Et, Pr^i) was used as the catalytic system, an increase was observed both in the activity and in syndiospecificity, when compared with the trichloride analogue [9,10]. Another example is the zirconocene binaphtholate that produces a significant fraction of non-cycled units in cyclopolymerisation of 1,5-hexadiene [11,12]. Finally, fluorinated half-sandwich complexes were reported to be more active than the chloro-analogues [13]. However, until now electronic and steric

effects arising from the η^5-ligand system are considered to be the main factors influencing the performance of the catalyst, while the role of different σ-ligands was still underestimated.

Previously, we have shown that bridged alicyclic alcoholato-ligands, σ-bonded to the transition metal central atom, markedly affect the catalytic system improving its thermal stability, solubility in non-polar media, and giving rise to polymers with higher molecular weights [14]. Unlike σ-bonded ligands of small dimensions having practically negligible influence on the polymerisation process, voluminous bridged alicyclic moieties, comparable with the rest of the metallocene core, start to be 'participants', and not only 'spectators' of the polymerisation. Nevertheless, their influence is not so pronounced, as those of π-bonded aromatic rings, the σ-ligands also have to be considered in a holistic approach to the metallocene-MAO catalytic system [15,16]. For example, asymmetric mixed-ligand Ind$_2$Zr(OFl)Cl (where –OFl corresponds to a deprotonated moiety of fenchyl alcohol: 1,3,3-trimethylbicyclo[2.2.1]-heptan-2-ol) gives rise to a copolymer containing up to 35.4% of ethylene units during one-monomer propylene polymerisation [16]. By that reason we decided to study the performance of similar bis-cyclopentadienylhafnium derivatives. According to the accepted reaction mechanism [2], the MAO will detach the alcoholato-moiety from the coordination centre. Therefore, it was interesting to compare the influence of the same sterically hindered fragments as alcoholato-ligands inside the complex with that of the free alcohol as the metallocene modifier, onto the catalytic behaviour of the system and final polymer properties.

2. Experimental

All reactions were carried out under purified nitrogen atmosphere using glove-box and Schlenk techniques.

2.1. Materials and syntheses

Research grade ethylene, propylene, and nitrogen were purified by passing through columns with molecular sieves 3 Å and Cu catalyst. MMAO was donated by Crompton GmbH as 10%wt solution in toluene and was used as received. Toluene was purified by reflux and distillation over Na/benzophenone. 2-methyladamantan-2-ol (MAdOH) (Aldrich) were purified from traces of O_2 and H_2O by repeated melting/cooling under dry nitrogen atmosphere. The chloroalcoholate of hafnocene was

synthesised similarly to our previously described procedures [16,17].

The analytical and spectroscopic data for Cp$_2$Hf(OMAd)Cl (C$_{21}$H$_{27}$ClHfO) are shown in the Table 1.

2.2. X-ray structure determination for [(Cp)$_2$Hf(OMAd)Cl]^2

A prismatic air sensitive (yellowish transparent) crystal of dimensions $0.20 \times 0.12 \times 0.28$ mm^3 was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 (Febo System) diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71069$ Å), following standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption, as described by North et al. [18].

The structure was solved by heavy atom method [19]. Refinement was carried out by full-matrix least-squares; the minimised function was $\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$, with weighting scheme $w = 1/[(\sigma^2(\text{Fo}^2) + (0.0166P)^2 + 2.95P]$, where $P = \max(\text{Fo}^2 + 2\text{Fc}^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 U$_{equiv}$ of the parent carbon atom). For a total of 285 parameters, $wRl = [\sum w(\text{Fo}^2 - \text{Fc}^2)^2/\sum w(\text{Fo}^2)^2]^{1/2} = 0.045$, $S = 1.067$, and conventional $R = 0.018$, based on the F values of 2986 reflections having $\text{Fo}^2 \geq 2\sigma(\text{Fo}^2)$. Structure refinement and final geometrical calculations were carried out with SHELX-97 program package [19], using atomic scattering enclosed therein, and PARST programs [20,21]. Drawings were produced using ORTEP II [22].
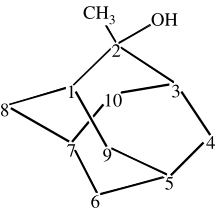
2.3. Polymerisation

The polymerisation was performed in a 300 ml autoclave equipped with mechanical stirrer and thermostated at 30 °C. Hundred millilitres of toluene and a required amount of MMAO ([Al]/[Hf] = 2000) were added to the reactor under nitrogen atmosphere. Subsequently, the reactor was saturated with ethylene or propylene at 200 kPa, and toluene solution of the catalyst or its mixture with the bridged alicyclic alcohol was injected. In the latter case, the hafnocene dichloride was brought in contact with the prescribed amount of the MAdOH in a separate Schlenk flask. The mixture was stirred at room temperature for 15 min and then injected into the reactor. The reaction was carried out for 1 h. The polymerisation was terminated by addition of ethanol acidified by HCl. The polymer was washed up with plenty of ethanol and vacuum dried at 60 °C.

2.4. NMR spectra

NMR spectra of the complex were recorded on Brucker

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[2] CCDC 188476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1
Analytical data, properties, and NMR spectra of Cp$_2$Hf(OMAd)Cl

Compound	Formula	% Hf (found/calcd)	M_w[a] (Da)	T_{decomp} (°C)	Yield (%)
Cp$_2$Hf(OMAd)Cl	C$_{21}$H$_{27}$ClHfO	34.90/35.04	508	159–161	91

NMR data

Compound	Position	^{1}H (ppm)	Δ[b] (ppm)	^{13}C (ppm)	Δ[b] (ppm)
	2	–	–	83.82	10.77
	–CH$_3$	1.52	0.39	28.92	1.25
	1; 3	1.73	0.01	40.21	1.72
	4; 9 ax.	2.49; 2.43	0.13; 0.13	32.94	−0.26
	4; 9 eq.	1.49; 1.43	0.01; 0.01		
	5	1.57	0.04	28.02	0.05
	6	0.85	0.01	38.83	0.69
	7	1.57	0.04	27.52	−0.07
	8; 10 ax.	1.68	0.03	35.57	0.25
	8; 10 eq.	1.64	0.04		
	Cp	5.91	0.10	112.31	−2.07

[a] Mass-spectrometric data were obtained on VG ZAB 2F instrument (VG Analytical, Manchester, UK) and referred to ^{178}Hf isotope.
[b] The difference of chemical shifts is shown in comparison with the corresponding signals in the MAdOH and Cp$_2$HfCl$_2$, positive values of Δ correspond to downfield shifts.

AC-200 NMR-spectrometer at 293 K in C$_6$D$_6$ vs TMS as internal standard. The samples were prepared in a dry-box, the ^{1}H and ^{13}C spectra were recorded at 200.13 and 50.33 MHz, respectively. ^{13}C NMR spectra of polypropylenes were obtained on Varian Mercury 300 MHz instrument at 353 K in trichlorobenzene containing C$_6$D$_6$ vs TMS as internal standard at 75.45 MHz.

2.5. Polymer characterisation

The melting temperature (T_m) and the crystallinity degree (χ_c) of the polymers were determined by differential scanning calorimetry (DSC) technique in the temperature range of 50–250 °C and the heating rate of 10 °C/min. The χ_c was calculated using $\Delta H_{0ethylene} = 292$ J/mol value.

The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) on Waters 150CV Plus instrument at 135 °C using a set of μ-Styragel HT6E, HT3, HT4 columns (Waters), monodisperse polystyrene calibration standard, and trichlorobenzene solvent.

The pentad distribution was found according to [23] and percent of ethylene units was calculated following the scheme proposed by De Pooter et al. [24].

3. Results and discussion

The synthesis of hafnocene chloroalcoholate from the Cp$_2$HfCl$_2$ and lithium 2-methyladamantan-2olate (MAdOLi) was realised according to the procedure, analogous to our previously described one [17]. The difference consists in a necessity to maintain an excess of the metallocene dichloride in the reaction solution; hence, inverse order of the reagent addition was used. The reaction

proceeds smoothly and a final product could be recrystallised from benzene. The resulting complex reveals a considerable tolerance vs exposure to room atmosphere with respect to the hafnocene dichloride, and it is much more soluble in non-polar media. It was characterised by mass-spectrometry, ^{1}H and ^{13}C NMR spectroscopy and X-ray structure analysis. Assignment for both ^{1}H and ^{13}C resonances were made on the basis of the relative chemical shifts in comparison with the NMR spectra of the nearest analogue, adamantan-2-ol, previously studied by us in detail using a suitable combination of ^{1}H–^{1}H and ^{1}H–^{13}C correlation experiments [25]. The analytical data and interpretation of the NMR spectra are shown in the Table 1.

The formation of the complex was confirmed by a pronounced downfield shift of ^{13}C NMR signal of the C2 carbon, directly bonded to the oxygen atom.

A suitable crystal of chloro-(2-methyladamantan-2-olato)-bis-(cyclopentadienyl) hafnium (IV) was used for X-ray structure determination. The compound crystallises in a monoclinic system in a space group $P2_1/c$ with the following elementary cell parameters: $a = 15.353(3)$ Å; $b = 7.9423(2)$ Å; $c = 16.025(4)$ Å; $\beta = 103.03(3)°$. A volume of the elementary cell is 1903.9(8) Å^3, and the cell contains four formula units of the complex Cp$_2$Hf(OMAd)Cl (Fig. 1). The density calculated from XRD data $d_c = 1.777$ g/cm^3.

The molecular structure of the complex is shown on the Fig. 2, average values of the bond lengths and bonding angles are present in the Table 2. Nevertheless, the structure of Cp$_2$Hf(OMAd)Cl is similar to that of 'traditional' hafnocenes, i.e. those containing aliphatic or alicyclic ligands without bridges [26–29]; it is evident from the Fig. 2 and the Table 2 that molecular geometry of the complex in question deviates considerably from ideal tetrahedral configuration. The presence of voluminous tricyclic moiety of 2-methyladamantyl bonded to oxygen
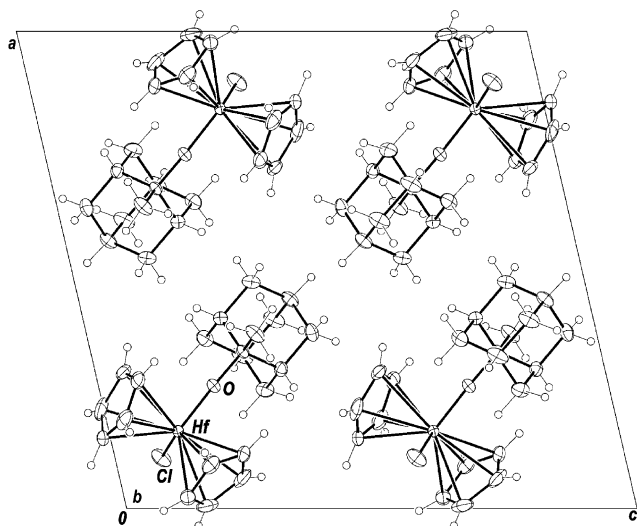
Fig. 1. Elementary cell of chloro-2-methyladamantan-2-olato-bis-(cyclo-pentadienyl) hafnium (IV).

Table 2
Selected average bond distances (Å) and angles (°) for $Cp_2Hf(OC_{11}H_{17})Cl$

Bond distances		Bond angles	
M–Cp1	2.519(5)	Cp–M–Cp	129.9(2)
M–Cp2	2.502(5)	Cl–Hf–Cp	101.2(3)
M–O	1.900(2)	O–Hf–Cp	107.9(2)
M–Cl	2.455(1)	Hf–O–C	172.1(2)
O–C	1.429(4)	O–Hf–Cl	95.7(1)

generates a certain contraction of the angle γ (Cp–Hf–Cp). The value of 129.9° is an intermediate one between 132.1° for dimethylhafnocene [29] and 127.9° for $Cp_2Hf(OSiPh_3)$-Cl [30]. The steric hindrance is also responsible for a little increase of the distance between the first Cp ring (C1–C5 on the Fig. 2) and the central atom, when compared to that of the second one (C6–C10 on the Fig. 2). A mutual repulsion of the σ-bonded ligands in a bisector plane of the bent metallocene leads to a slight increase of the angle O–Hf–Cl between them −95.7°, when compared to 94.8° in $Cp_2Hf(CH_3)_2$. The angle Hf–O–C (Hf–O–C11 on the Fig. 2) unbends to nearly linear value of 172.1° due to effective p_π–d_π bonding [30,31] promoted by a hard chloro-ligand and by an inductive effect of the methyladamantyl moiety. Similarly to other group 4 metallocenes with bridged alicyclic alcoholato-ligands synthesised by us [16,17], new compound was tested for catalytic performance in homogeneous ethylene and propylene polymerisation.

Previously, we demonstrated [14–16] that the presence of bulky σ-bonded moiety in metallocene complex influences
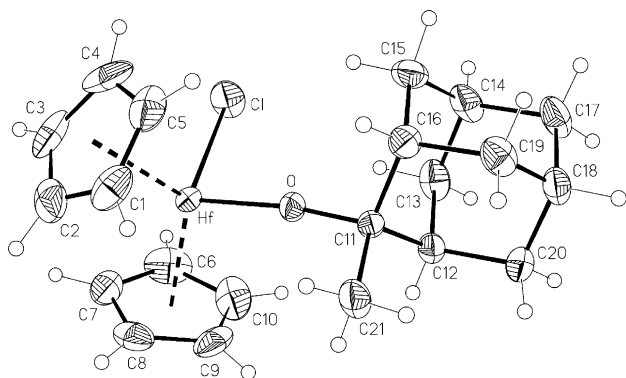

Fig. 2. Molecular structure of chloro-(2-methyladamantan-2-olato)-bis-(cyclopentadienyl) hafnium (IV) (the numeration of atoms corresponds to that of the CIF file deposited at the CCDC).

both the catalytic activity of the system and final polymer properties. Therefore, it was also interesting to study the catalytic properties of similar, but different systems composed from the hafnocene dichloride and free alicyclic alcohol additive. The solutions of MAdOH and Cp_2HfCl_2 were combined in a separate Schlenk flask and the mixture was injected into the reactor after stirring for 15 min.

Alcohols are usually referred to as poisons of homogeneous metallocene catalytic systems that deactivate the cationic transition metal active site. This is exactly the case of lower alcohols: methanol, ethanol, propanols, etc. The addition of an equimolar amount of isopropanol passivates completely the systems (Tables 3 and 4). Due to relatively low pKa values, and consequently, quite high activity of the hydroxyl proton in the lower alcohols, they react readily with dialkyls or dichlorides of metallocenes producing catalytically inactive species. At the same time, owing to steric and polarisation effects of the bridged alicyclic moiety, the hydroxyl proton in 2-methyladamantan-2-ol is rather inactive and does not react with Cp_2HfCl_2 catalyst. Such behaviour is in agreement with particularities of formation of bridged alicyclic alcoholates of metallocenes previously studied by us [17]. If the lower alcohols react easily with metallocene dichlorides in the presence of HCl scavengers (e.g. amines) giving rise to corresponding mono-or dialcoholates and their adducts [32,33], the derivatives of bridged alicyclic alcohols may be obtained only through an organolithium route [17,34]. These alcohols do not react directly with Cp_2MCl_2 both in polar and non-polar media.

In the present work, we studied two new catalytic systems: mixed ligand hafnocene alcoholate-chloride and the hafnocene dichloride modified by bridged alicyclic alcohol additive in different molar ratios in comparison with the Cp_2HfCl_2.

The data on ethylene polymerisation are present in the Table 3. The table clearly demonstrates that addition of an equimolar amount of isopropanol deactivates completely the catalytic system, while in the remaining cases the activity difference is less significant. It is slightly higher for a mixed ligand metallocene, and lower for the equimolar mixture of Cp_2HfCl_2 with MAdOH, when compared to the reference system Cp_2HfCl_2/MMAO. Some polyethylene properties like T_m and χ_c are practically unchanged, while the M_w is higher for the systems under investigation with respect to the reference one. It is interesting to note that the highest value of the M_w was achieved in polymerisation with the hafnocene dichloride—bridged alicyclic alcohol

Table 3
Ethylene polymerisation data

Catalyst	Activity (kgPE/[Hf]×h)	$M_w \times 10^{-5}$ (Da)	T_m (°C)	χ_c (%)
Cp$_2$HfCl$_2$	620.2	8.39	136	51.6
Cp$_2$HfCl$_2$+i-PrOH (1:1)	0	–	–	–
Cp$_2$HfCl$_2$+MAdOH (1:1)	501.4	8.74	nd	nd
Cp$_2$Hf(OMAd)Cl	724.6	8.55	135	53.3

mixture. This behaviour may be attributed to a decrease of the β-hydrogen elimination rate caused by the presence of a voluminous alcoholato-ligand in the anionic MAO fragment [14,15].

The activity of hafnocenes towards propylene polymerisation was lower (Table 4). However, it is interesting to point out, the activity of Cp$_2$HfCl$_2$ was practically unaffected by addition of the bridged alicyclic alcohol. This behaviour is evidently due to the fact that MAdOH may react with MAO giving rise to modified co-catalyst species. Indeed, when the MAdOH is present in the polymerisation medium it can react with alkylaluminums always present in MAO, with the metallocenium cation, and with MAO; but only [MAO–OR]$^-$ species are able to influence the behaviour of the active site. Results in the Table 4 suggest that [MAO–OR]$^-$ anion may favour the 2,1-insertion rather than the 1,2-insertion, which is more common in olefin polymerisation with group 4 metallocenes.

Analysis of the ^{13}C NMR spectra of the polypropylenes obtained gave a pentad distribution and a possibility to estimate a percent of ethylene units that appear due to 2,1-insertions. All polymers were atactic and had nearly the same microstructure. However, the 2,1-insertions became more probable both in the system containing the alcoholato-ligand and the system containing the alcohol additive in equimolar and higher ratios, i.e. with the presence of the sterically hindered moiety bonded to the MAO counter-ion [16]. Under these conditions one may note a complete disappearance of *mrrr* pentads as well as a significant increase of *mrrm* and *rrrr* pentads. The presence of the *mrrr*

pentads at lower [MAdOH]/[Hf] ratios may be attributed to unmodified MAO species.

4. Conclusions

New mixed-ligand alcoholato-chloride of hafnocene was synthesised and characterised. The complex in question is a bent metallocene with a Hf–O–C angle of 172.1°, owing to the effective p$_\pi$–d$_\pi$ bonding. Catalytic activity of the complex was studied in comparison with Cp$_2$HfCl$_2$ pre-treated with 2-methyladamantan-2-ol in different molar ratios. Addition of the bridged alicyclic alcohol to the metallocene does not deactivate the catalytic system, but the results were similar to those obtained with the corresponding mixed-ligand hafnocene. Nevertheless the additive slightly diminishes the catalytic activity, reaction of the metallocene with the monomer producing a growing polymer chain is more favoured with respect to its interaction with the sterically hindered alcohol. In the case of mixed-ligand complex the voluminous alcoholato moiety makes part of the [MAdO–MAO]$^-$ counter-ion [16], where it promotes regioerrors in the growing chain. The same conclusion is also valid for the system containing Cp$_2$HfCl$_2$ modified by MAdOH, taking into a consideration the similarity of their catalytic performances.

Table 4
Propylene polymerisation results and pentad distribution in polypropylenes obtained with pure, modified and substituted hafnocene catalysts

[MAdOH]/ [Hf]	Activity (kgPP/ [Hf]×h)	–CH$_2$–CH$_2$– (mol%)	Pentad distribution								
			mmmm	*mmmr*	*rmmr*	*mmrr*	*mrrm*	*mrmr*	*mmrm*+ *rmrr*	*mrrr*	*rrrr*
Cp$_2$HfCl$_2$											
*i*PrOH (1:1)	–	–	–	–	–	–	–	–	–	–	–
Not added	93.2	2.67	16.89	20.31	6.10	9.45	2.33	11.52	26.06	1.83	2.67
0.5	91.8	2.73	17.08	20.50	6.17	9.42	2.58	12.08	26.35	1.80	4.02
1	83.8	3.90	17.17	20.71	6.27	9.40	4.47	11.29	26.39	0	4.28
2	79.8	2.54	17.40	20.24	6.67	9.91	4.25	10.95	26.13	0	4.47
Cp$_2$Hf(OMAd)Cl											
–	129.0[a]	3.93	16.87	20.50	6.54	9.66	4.22	10.77	26.26	0	5.17

[a] $P=300$ kPa.

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