

Phenoxy substituted zirconocenes in ethylene polymerization¹

Timo Repo^{*}, Gerhard Jany, Mia Salo, Mika Polamo², Markku Leskelä

University of Helsinki, Department of Chemistry, Laboratory of Inorganic Chemistry, P.O. Box 55, FIN-00014 Helsinki, Finland

Received 10 January 1997; accepted 19 January 1997

Abstract

Zirconocene dichloride was reacted with either 2,6-di-*tert*-butyl- or 2,6-diisopropyl phenol to form bis(η^5 -cyclopentadienyl) zirconium(IV) monochloride complexes **1** and **2** respectively. A bisphenoxy derivative of Cp_2ZrCl_2 , **3**, was formed, when sterically less demanding 2,6-dimethyl phenol was utilized. The ability of the complexes **1**, **2** and **3** in ethylene polymerization with MAO as cocatalyst was examined. Polymer analysis indicates that, regardless of which complex was used, only one kind of catalytically active metal center is formed and polymer properties resemble those obtained with the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system. The solid state structure of bis(η^5 -cyclopentadienyl) zirconium(IV) 2,6-di-*tert*-butyl-phenoxy monochloride (**1**) is reported. © 1997 Elsevier Science S.A.

Keywords: Zirconocene; Phenoxide; Aryloxides; Polymerization

1. Introduction

After the discovery of methylalumoxane (MAO) as an effective activator for Group 4 metallocene complexes, a lot of work has been directed to these compounds (see reviews in Refs. [1,2]). The cocatalyst MAO forms a cationic metal center which is responsible for catalytic activity. Depending on variations in the ligand environment, different kinds of polymer microstructures and polymers with different properties can be achieved.

In the last years renewed attention has been focused on complexes bearing metal amine or metal alkoxide bondings, which could also be used as polymerization catalysts and have a comparable coordination geometry to traditional metal η^5 -Cp complexes [2,3]. When metal alkoxide coordination complexes are activated with MAO, they often produce polymers with broad molecular weight distribution. To better understand such Group 4 metal and alkoxo ligand interactions in the presence of MAO, we chose zirconocenes with different types of phenoxy substituents as model compounds and studied their polymerization behavior when activated with MAO. Zirconium aryloxides have been widely investi-

gated and characterized [4,5]. Synthesis of the complexes **1**, **2** and structural analogues for the complex **3** have been presented previously [5,6] (Fig. 1).

2. Experimental

All preparative reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Hydrocarbons and ethers were purified by distillation from LiAlH_4 . ^1H NMR was recorded on a Varian Gemini 200 MHz spectrometer and MS(EI) and HRMS on a JEOL JMS-SX102 mass spectrometer.

Complexes **1** and **2** were prepared using modified literature procedures [6]. Either 2,6-di-*tert*-butyl phenol or 2,6-diisopropyl phenol (6 mmol) were dissolved in 20 ml of dry tetrahydrofuran (THF). The solution was cooled to -78°C and 1.6 M *n*-butyl lithium (3.6 ml, 6 mmol) was added dropwise. After addition was complete, the reaction mixture was allowed to come to ambient temperature to complete the reaction and further cooled down again to -78°C . Cp_2ZrCl_2 (1.7 g, 6 mmol) was added to the reaction mixture and slowly heated up to the boiling point of THF and refluxed for 20 h. THF was removed and the white solid powder was extracted with *n*-hexane.

1: (1.16 g, 2.5 mmol) was isolated after vaporization of *n*-hexane with 42% yield. Colorless crystals suitable for X-ray measurements were formed via slow vaporiza-

^{*} Corresponding author. E-mail: timo.repo@helsinki.fi.

¹ Dedicated to Professor Dr. G. Huttner on the occasion of his 60th birthday.

² X-ray diffraction studies.

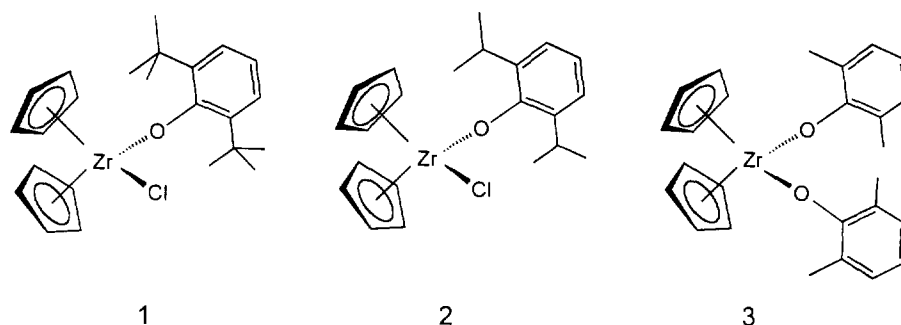


Fig. 1. The schematic structures of zirconocenes with different types of phenoxy substituents used in ethylene polymerization.

tion of *n*-hexane. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.44$ (d, 18H, $J = 7.3$ Hz, (*tert*-butyl)), 6.34 (s, 10H, Cp), 6.73–7.19 (m, 3H). MS (EI, 70 eV): 460.1 (M^+), 254.9 ($\text{M}^+ - 2,6$ -*tert*-butyl-phenoxy). HRMS (EI, 70 eV): calculated for $\text{C}_{24}\text{H}_{31}\text{OZrCl}$ 460.1110, found 460.1123.

2: The procedure described above gave a white solid powder (0.96 g, 2.2 mmol) with 37% yield. $^1\text{H NMR}$ (CDCl_3): $\delta = 1.22$ (d, 12H, isopropyl), 3.16 (t, 1H, isopropyl) 6.39 (s, 10H, Cp), 6.87–7.08 (m, 3H). MS (EI, 70 eV): 432.1 (M^+), 397.1 ($\text{M}^+ - 2,6$ -diisopropyl-phenoxy). HRMS (EI, 70 eV): calculated for $\text{C}_{22}\text{H}_{27}\text{OZrCl}$ 432.0797, found 432.0795.

Complex **3** was prepared using a slightly different procedure from that described above. 2,6-Dimethyl-phenol (0.6 g, 5 mmol) was dissolved in 10 ml of diethyl ether. The solution was cooled to -20°C and *n*-butyl lithium (3.0 ml, 1.6 M, 5.0 mmol) was added. After stirring for 1 h at room temperature, 30 ml of toluene was included and lithiosalt of phenoxide was cooled again to -20°C . After addition of Cp_2ZrCl_2 (0.7 g, 2.5 mmol), the reaction mixture was stirred overnight at room temperature and then filtered through Celite and the solvent was removed. The yellow oily residue was dissolved in 20 ml *n*-hexane and the white solid powder (0.28 g, 0.6 mmol) was isolated with 24% yield after crystallization at -20°C .

3: $^1\text{H NMR}$ (CDCl_3): $\delta = 2.28$ (s, 12H, (methyl)), 6.23 (s, 10H, Cp), 6.76–7.08 (m, 6H). MS (EI, 70 eV): 462.0 (M^+), 341.0 ($\text{M}^+ - 2,6$ -dimethyl-phenoxy). HRMS (EI, 70 eV): calculated for $\text{C}_{26}\text{H}_{28}\text{O}_2\text{Zr}$ 462.1137, found 462.1150.

Lower pressure polymerizations were performed in 300 ml toluene in a 1 l glass reactor equipped with a propeller-like stirrer. The stirring speed was 800 rpm, temperature 30°C ($\pm 0.2^\circ\text{C}$) and ethylene overpressure 2.0 bar (± 0.05 bar). During polymerization the partial pressure of ethylene was maintained constant with an electronic pressure controller and ethylene flow was followed with a calibrated mass flow meter. To stop the polymerization the reactor was degassed and the product quantitatively dropped out with 600 ml of acidified methanol, further washed several times with methanol

and dried overnight at 70°C . The Al/Zr ratio used in polymerizations was 6000:1.

The polymerization experiments at higher pressure were carried out as follows: a 2 l steel autoclave was filled with 1.7 l pentane. The ethylene pressure was 10 bar and kept constant during polymerization experiments. The polymerization temperature was 80°C . The consumption of ethylene was followed by an on-line mass flow meter. The Al/Zr ratio was 1500:1.

3. Solid state structure

The structure of zirconocene 2,6-di-*tert*-butyl phenoxy monochloride (**1**) (Fig. 2) in the solid state reveals that the Zr–O bond length (2.008(2) Å) is comparable to the value found in the zirconocene complex bearing

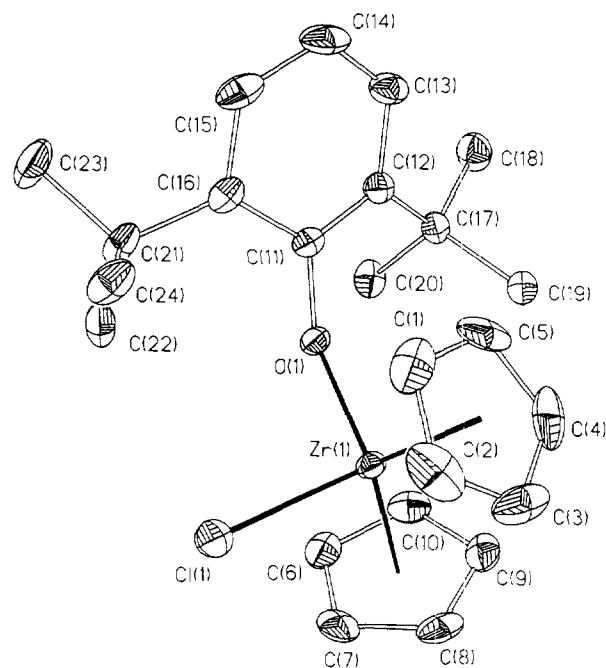


Fig. 2. View of $\text{Cp}_2\text{ZrClOC}_6\text{H}_3\text{Bu}^{1,2,6}$ with the atom labels and displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.

Table 1
Structural comparison of bis(cyclopentadienyl)zirconium(IV) aryloxides to bis(cyclopentadienyl)zirconium(IV) dichloride

	1	Cp ₂ ZrClOAr [8]	Cp ₂ ZrCl ₂ [7]
Zr–O (Å)	2.008(2)	1.98(2)	—
Zr–Cl (Å)	2.4642(11)	2.45(2)	2.445
Zr–Cen ^a (Å)	2.227	n.g.	2.198
Zr–O–C (°)	144.1(2)	150(1)	—

Ar = 2,6-Bu₂-4-MeC₆H₂.

^a Average value, if both are given; n.g., not given.

phenoxy ligands without 2,6-substituents [5]. The Zr–O distance in these complexes is shorter than its respective covalent radii, and this has been attributed to the fact that in this kind of bonding ionic contribution is also taking place [5]. The centeroids of the cyclopentadienyl rings are transferred slightly further away from the metal center than in the case of Cp₂ZrCl₂ [7]. The Zr–Cl bond length is slightly longer than those found in Cp₂ZrCl₂ (Table 1).

Crystal data for **1**: C₂₄H₃₁ClOZr, 426.16 g mol⁻¹, colorless prism, 0.4 × 0.3 × 0.1 mm, monoclinic, space group *P*2₁/*c*, *a* = 13.278(7), *b* = 10.005(6), *c* = 16.767(7) Å, β = 101.40(4)°, *V* = 2183(2) Å³, *Z* = 4, *D*_{calc} = 1.406 g cm⁻³, *F*(000) = 960, μ = 0.637 mm⁻¹, Rigaku AFC7S diffractometer, Mo Kα radiation (λ = 0.71069 Å), ω/2θ scans, *T* = -80°C. The structure was solved by direct methods (SHELXTL-PC vers. 4.1) and refined by full-matrix least-squares on *F*² using all collected reflections (SHELXL-93). ψ-Scans were used for absorption correction (range 0.9287–1.000). The data set was compressed to reflection files with TEXSAN single crystal structure analysis software. All non-hydrogen atoms were allowed to refine anisotropically. Hydrogen atoms were attached to calculated positions with thermal parameter 1.3 times that to host atoms. Final *R* = 0.040, *wR*(*F*²) = 0.101 for 2997 reflections with *I* > 2.0σ(*I*), *R* = 0.050, *wR*(*F*²) = 0.107 for all 3547 reflections.

In metallocene complexes where only one chlorine is replaced by a different kind of phenoxy ligand, which are δ-bonded to zirconium, the phenoxy and chloro ligands are in *cis*-position to each other and the metal center remains coordinatively unsaturated. Phenoxy substituted metallocenes **1–3** are relatively volatile and thus it might be possible to use them as starting materials for heterogenisation of metallocenes on ceramic supports via chemical vapor deposition methods.

Table 2
Polymerization results of the zirconocene **1** at 80°C and 10 bar

	Activity ^a	Zr (μmol)	<i>M</i> _w	<i>M</i> _w / <i>M</i> _n
Cp ₂ ZrCl ₂	7500	2.5	201 000	3.0
1	9700	5.0	225 000	2.7

^a kg PE/(mol Zrh).

4. Polymerizations

Phenoxy substituted zirconocenes **1–3** were used as catalyst precursors for ethylene polymerization. According to preliminary ethylene polymerization results, the activity and polymer properties of phenoxy substituted zirconocenes **2** and **3** do not significantly differ from the activity of zirconocene dichloride under the same conditions. At 30°C and 2 bar ethylene pressure the complexes **2** and **3** produce polyethylene with an activity of 1,910 and 1,740 kg PE/(mol Zrh) respectively (the activity of Cp₂ZrCl₂ under identical conditions was 2,200 kg PE/(mol Zrh). Zirconocene **1** instead shows reduced activity, 400 kg PE/(mol Zrh), and we attribute this to steric reasons. When the polymerization temperature and pressure are increased (80°C, 10 bar), complex **1** shows similar polymerization properties as Cp₂ZrCl₂/MAO (Table 2). Molecular weights and molecular weight distributions do not differ significantly from the values obtained for polymer produced by Cp₂ZrCl₂/MAO.

The observed polymerization behavior might be explained by the formation of only one catalytically active species with MAO. According to earlier studies on interactions between MAO and zirconocene dichloride, and later on with studies of cationic zirconocenes, it is obvious that both Cl and phenoxy ligands were removed and replaced by an alkyl group and a vacant coordination site.

The slightly higher activity of phenoxy substituted zirconocene **1** compared to zirconocene dichloride might be caused by the higher solubility of the complex to the polymerization medium (pentane). Another possible explanation for such behavior might be the ease of activation of complex **1**, since its Zr–Cl bond is longer and should undergo methyl transformation faster than the chloride in the Cp₂ZrCl₂/MAO systems. Further polymerization studies of phenoxy substituted zirconocene monochlorides are underway.

5. Conclusions

The phenoxy substituted zirconocenes **1–3** along with MAO show comparable polymerization behavior to the non-substituted Cp₂ZrCl₂/MAO system, as expected. This can be regarded as proof that during the polymerization process similar kinds of active centers are formed for all compounds.

6. Supplementary material available

Tables of non-H atomic coordinates, bond lengths and angles, anisotropic displacement parameters, H-atom

coordinates and isotropic displacement parameters and structure factors (15 pages). Ordering information is given on any current masthead page.

Acknowledgements

The financial support of the Academy of Finland is gratefully acknowledged.

References

- [1] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1143.
- [2] M. Bochmann, *J. Chem. Soc., Dalton Trans.* (1996) 255.
- [3] S. Tinkler, R.J. Deeth, D.J. Duncalf, A. McCamley, *J. Chem. Soc., Chem. Commun.* (1996) 2623; L. Matilainen, M. Klinga, M. Leskelä, *J. Chem. Soc., Dalton Trans.* (1996) 219; A. Van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A. Orpen, *J. Am. Chem. Soc.* 117 (1995) 3008; P. Aaltonen, J. Seppälä, L. Matilainen, M. Leskelä, *Macromolecules* 27 (1994) 3136; E.B. Tjaden, R.F. Jordan, *Macromol. Symp.* 89 (1995) 231; T. Repo, M. Klinga, P. Pietikäinen, M. Leskelä, A.-M. Uusitalo, T. Pakkanen, K. Hakala, P. Aaltonen, B. Löfgren, *Macromolecules* 30 (1997) 171.
- [4] E. Hey-Hawkins, *Chem. Rev.* 94 (1994) 1661.
- [5] W.A. Howard, T.M. Trnka, G. Parkin, *Inorg. Chem.* 34 (1995) 5900.
- [6] A.W. Duff, R.A. Kamarudin, M.F. Lappert, R.J. Norton, *J. Chem. Soc., Dalton Trans.* (1986) 489.
- [7] T. Repo, M. Klinga, I. Mutikainen, Y. Su, M. Leskelä, M. Polamo, *Acta Chem. Scand.* 50 (1996) 1116; G.L. Soloveichik, T.M. Arkhireva, V.K. Bel'skii, B.M. Bulychev, *Metalloorg. Khim.* 1 (1988) 226.
- [8] A. Antiñolo, G.S. Bristow, G.K. Campbell, A.W. Duff, P.B. Hitchcock, R.A. Kamarudin, M.F. Lappert, R.J. Norton, N. Sarjudeen, D.J.W. Winterborn, J.L. Atwood, W.E. Hunter, H. Zhang, *Polyhedron* 8 (1989) 1601.