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Tetrapyrrole bizirconium complexes as active catalysts for ethylene polymerization

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Abstract Ethylene polymerization was carried out by using a group of new dizirconium(IV) tetrapyrrole complexes as catalysts and *MAO* as co-catalyst under 1 atmosphere pressure of ethylene gas at 25 and 40°C. The highest value of catalyst activity was obtained at 40°C by using bizirconium complexes including one calix[4]pyrrole between two zirconium centers and two terminal chlorines, while zirconium(IV) complexes with coordinated *THF*, almost have not catalytic activity. The maximum catalytic activity mounted to $830\,\mathrm{kg/mol\cdot bar\cdot h}$ by $Zr_2(Cy_4\mathit{Pyr}_4)Cl_4$. The results show that the structure of the coordination sphere of zirconium(IV) has great influence on the rate of polymerization, molar masses of forming polymer, and its molecular mass distribution.

Keywords Ethylene; Polymerizations catalysts; Zirconium coordination; Calix[4]pyrrole complexes.

Introduction

An active area of research in the field of metal complexes containing chelating amido ligands has focused on the development of well-defined metal complexes as catalysts for olefin polymerization [1]. Chelating and multidentate amido ligands have emerged as a viable alternative to the traditionally used cyclopentadienide ligands in the chemistry of early transition metals [2].

Literature reviews on the catalytic polymerization of olefins show that catalytic performance improvement of high valance d^0 early transition metals [3] and more particularly, amido complexes of fourth group elements are still on important subject [4, 5].

Commonly, metal chloride derivatives are used as polymerization catalysts with the co-catalyst methylaluminoxane (*MAO*) [6]. Actually, high olefin polymerization activity of dichloro-diamido zirconium(IV) complexes [7] and dibenzyl derivatives [5] are valuable evidence for this opinion. But low stability of the coordination sphere has limited their application as robust catalyst. Although the elucidation of the structure of the active site and the polymerization mechanism are not completely understood yet but using of high valances early transition metals as strong *Lewis* acids and specific ligands including hard donor atoms as strong σ- and π-donors are appropriate. Our goal is the development of hydrocarbon polymerization under controlled and mild condition. For this purpose, we discuss the use of a group of new tetraamido pyrrole complexes (Fig. 1) of bizirconium(IV) and their use as ethylene polymerization catalysts when activated in the standard fashion with methylaluminoxane (*MAO*).

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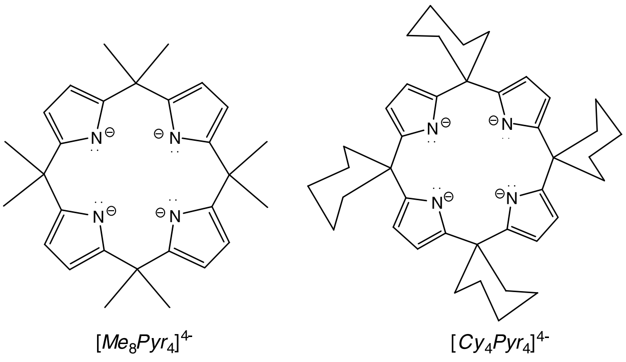

Fig. 1 Tetraamido calix[4]pyrrole ligand's systems

Results and discussion

Synthesis

New bizirconium complexes **3**–**6** using calix[4]pyrrole ligands that differ in the nature of their substituents (Fig. 1) were synthesized by reaction with $ZrCl_4$ and $ZrCl_4 \cdot 2THF$ (Fig. 2). All compounds are highly soluble in hydrocarbons. The calix[4]pyrrole ligands used in this study were prepared from the reaction of pyrrole with corresponding ketone derivatives using a standard condensation method [13, 14]. All ligands were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. Corresponding tetraamido ligands are obtained by the reaction of calix[4]pyrrole ligand with potassium hydride in 1:4 *M* ratio. Thermally robust tetrapyrrolidine zirconium(IV) complexes were successfully obtained from the reaction of 1 equiv of potassium tetrapyrrolidine salt with $ZrCl_4$ in toluene (Fig. 2). The complexes **1** and **2** were obtained from the reaction of 1 equiv potassium tetrapyrrolidine salt with $ZrCl_4 \cdot 2THF$ in *THF* [13, 14]. In the complexes **1** and **2** (Fig. 3c), it is assumed that these complexes are more likely a tetrapyrrole in which all four pyrroles are η^1 bound to the metal, with two *THF* ligands completing its pseudo-octahedral coordination sphere [14]. In monozirconium species **3** or **4**, zirconium bound with two η^5 pyrroles and two η^1 pyrroles (Fig. 3a).

The crystallization of **5** and **6** attempts were unsuccessful. Suggested structures for **5** and **6** (Fig. 3b) are confirmed by ^1H, ^{13}C NMR, IR spectroscopy, and elemental analysis data. Elemental analyzes show a 2:1:4 *M* ratio of Zr:calix[4]pyrrole:Cl for **5** and **6**. In the ^1H NMR spectra of the complexes **5** and **6**, two singlets assigned to the pyrrole rings were observed at $\delta = 5.85$ and 5.88 ppm. The ^{13}C NMR spectra of these complexes show two resonances for the pyrrole rings. In fact, the same chemical shifts (δ, ppm) of all four pyrrole rings in ^1H and ^{13}C spectra are precious reason for establishment of the purposed structure. These details show

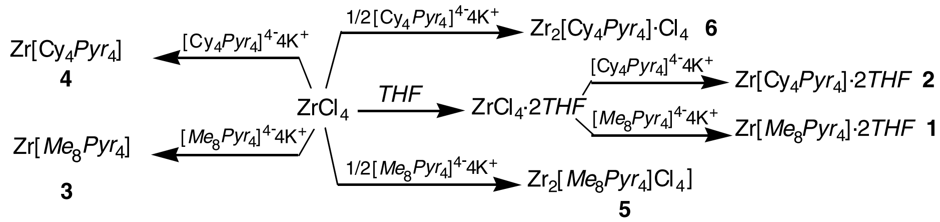

Fig. 2 Syntheses of zirconium(IV) calix[4]pyrrole complexes **1**–**6**

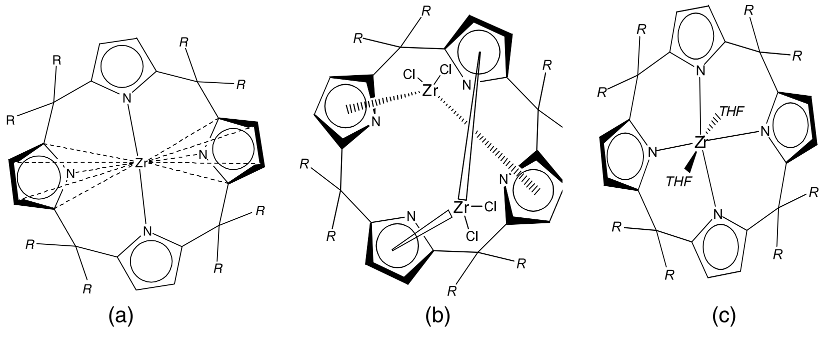

Fig. 3 Structures of zirconium(IV) calix[4]pyrrole complexes, (a) Zr(Me_8Pyr_4) (**3**), (b) Zr_2(Me_8Pyr_4)Cl_4 (**5**), (c) Zr(Me_8Pyr_4) · 2*THF* (**1**)

that all pyrroles of tetrapyrrole ligands in the high symmetry complexes **5** and **6** have same electronic condition and same coordination mode. In addition, the C=N stretching vibration frequency of pyrrole rings is only observed of $\bar{\nu} = 1441$ and $1455\,\mathrm{cm}^{-1}$ for **5** and **6**, as expected for η^5-pyrrole fashion. We would guess that dizirconium complexes **5** and **6** (Fig. 3b) are most likely akin to a pair of $(cp)_2ZrCl_2$ species in which two of the four pyrrole rings are interacting with each zirconium in an η^5 fashion and two chlorides are bound to the metal in an η^1 mode. Thus, in this suggested structure, one available orbital should remain. Because, for similar electronic skeleton $(cp)_2Zr$ fragments, it has been well established that there remain 3 orbitals available after the two η^5 interactions [14, 15].

Polymerization

The reactivity of complexes toward ethylene in the presence of methylalumoxane (*MAO*) in 1/500 *M* ratio of Zr/Al was studied under 1 bar of ethylene pressure 25 and 40°C. The results are shown in Table 1.

Complexes **1** and **2** with coordinated *THF* displayed no activity, while polyethylene was produced in the absence of coordinated *THF*. But, **3** and **4** have displayed very low ethylene polymerization activities. Due to one available orbital on the zirconium center, these polymerization rates were in spite of expectation. Low catalytic efficiency of **3** and **4** should be related to strong ligand field and a high constrain effect of the tetrapyrrole ligand about the zirconium center.

In contrast, **5** and **6** with two terminal chlorines at each side (Fig. 3b) have made ethylene polymerization with high activities of more than 830 kg-polymer/mol-Zr h bar in the presence of *MAO* which are comparable to those found for titanium complexes with pyrrolide-imine ligands under the same polymerization conditions [16]. Multimodal polyethylene is produced by the zirconium catalyst with broad molecular weight distributions, possibly caused by the gradual generation of the active species and/or isomerization of the active species in the polymerization conditions [17].

Table 1 The catalytic test result of ethylene polymerization by using zirconium(IV) calix[4]pyrrole complexes as catalysts and *MAO* as co-catalyst at 25 and 40°C[a]

Complexes	Activity (25°C)/ kg $\mathrm{mol}^{-1}\,\mathrm{bar}^{-1}\,\mathrm{h}^{-1}$	Activity (40°C)/ kg $\mathrm{mol}^{-1}\,\mathrm{bar}^{-1}\,\mathrm{h}^{-1}$
1, $Zr(Me_8Pyr_4)\cdot 2THF$	0.5	1.0
2, $Zr(Cy_4Pyr_4)\cdot 2THF$	0.6	0.9
3, $Zr(Me_8Pyr_4)$	4.1	5.8
4, $Zr(Cy_4Pyr_4)$	5.2	6.0
5, $Zr_2(Me_8Pyr_4)Cl_4$	470	620
6, $Zr_2(Cy_4Pyr_4)Cl_4$	540	830

[a] Pressure = 1 atmosphere of ethylene gas, time = 4 h

The molecular weight distribution (M_w/M_n) values of the polymer obtained are 1.8–2.4, as expected for a polymer produced by a single-site catalyst, with values for M_w of 1.7×10^4 to 9.6×10^4. It is noteworthy that the complexes **5** and **6** exhibit activities that are almost three orders of magnitude larger (830 kg-polymer/mol-Zr · h-bar) and give polymers with narrow molecular weight distribution values (M_w/M_n) *ca.* 2. Our finding is comparable with metallocene-based systems. Therefore, electrophility, coordinating ability, and bulkiness of the catalyst have affected the activity of the catalyst [18]. In all cases the polymerization rate and activity slow down at lower temperature. However, zirconium(IV) calix[4]pyrrole complexes containing specifically η^1 and η^5 interaction and low constrain ligands promise to be highly efficient olefin polymerization catalysts and bizirconium calix[4]pyrrole complexes **5** and **6** could polymerize ethylene with highest activity.

Conclusion

Zirconium tetraamido compounds behave as active catalysts for the polymerization of ethylene when activated by *MAO*. This group of new bizirconium(IV) tetrapyrrolide complexes has shown good potential for ethylene polymerization. Our study was carried out by using zirconium(IV) amido pyrrole complexes in toluene in presence of *MAO* in 1/500 *M* ratio of Zr/Al as co-catalyst. The results revealed that monozirconium compounds exhibit moderate catalytic activities toward ethylene polymerization while bizirconium complexes **5** and **6** with four terminal chlorines show the highest activities. In the suggested structure, two of the four pyrrole rings interact with each zirconium in an η^5 fashion and one orbital should be available after two η^1 coordinated chlorides. These facts indicate that the structure of the coordination sphere of zirconium strongly affects the polymerization activity.

Experimental

Materials and instruments

All experiments were carried out under an inert atmosphere in a Vacuum Atmosphere dry box or by *Schlenk* techniques. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Solvents (*Et*$_2$O, C_6H_6, $C_6H_5CH_3$, and *THF*) were refluxed over an appropriate dehydrating agent [9] and distilled under dry nitrogen.

Polymerization studies were carried out in classical glassware connected to an ethylene line and its monomer pressure was controlled and monitored with use of a mercury column. Polymerization runs were quenched by addition of methanol. The polymers were filtered off, washed with acetone, and dried under vacuum.

NMR spectra were recorded on a Bruker AC-300 spectrometer at ambient temperature and in $CDCl_3$ or C_6D_6. Chemical shifts are given in ppm, with tetramethylsilane as internal reference. IR spectra were recorded with a Mattson Infinity 60 MI FTIR spectrometer as KBr pellets. Elemental analyzes were carried out with a Heraeus elemental analyzer CHN–O-Rapid and obtained results agreed favorably with calculated values.

$ZrCl_4$(*THF*)$_2$ was prepared according to Ref. [10], tetracyclohexyl calix[4]pyrrole and octamethyl calix[4]pyrrole [12], and their zirconium complexes **1**–**4** were prepared by literature methods [13, 14].

[μ-[(1,2,3,4,11,12,13,14-η:6,7,8,9,16,17,18,19-η)-5,10,15,20,22,24-hexahydro-5,5,10,10,15,15,20,20-octamethyl-21H,23H-porphinato(4-)-κN21,κN23:κN22,κN24]]dizirconium tetrachloride
(**5**, $C_{28}H_{32}Cl_4N_4Zr_2$)

Step one: K$_4$*[Me*$_8$*Pyr*$_4$*]:* Octamethyl calix[4]pyrrole (1.85 g, 2 mmol) was dissolved in 25 cm^3 of toluene, the solution was cooled to −15°C, and 8.5 equivalents of potassium hydride were added with vigorous stirring for 1 h. The solution turned cloudy and gradually changed to yellow. After removal of the H_2 gas and filtration, the solution was used for the next step immediately.

Step two: To a fresh stirred solution of K$_4$[*Me*$_8$*Pyr*$_4$] (1 mmol in 25 cm^3 toluene) was added $ZrCl_4$ (0.47 g, 2 mmol) at −15°C. After the mixture was stirred at room temperature overnight, the solvent was removed in vacuum and the resulting product dissolved in 50 cm^3 toluene. The residual insoluble KCl was separated by centrifugation and decantation of the solution. The volatile material was removed and 0.51 g oily yellow-brown product **5** were obtained (68%). ^{1}H NMR (C_6D_6); $\delta = 5.88$ (s, 8H), 1.85 (s, 24H) ppm; ^{13}C NMR (C_6D_6); $\delta = 30.1$, 43.5, 114.5, 133.4 ppm; IR $\bar{\nu} = 3310$, 2973, 1441, 1361, 1113, 973, 758 cm^{-1}.

[μ-[(1,2,3,4,11,12,13,14-η:6,7,8,9,16,17,18,19-η)-tetraspiro[21H,23H-porphine-5(15H),1′:10(22H),1″:15,1‴:20(24H),1⁗-tetrakiscyclohexanato](4-)-κN21,κN23:κN22,κN24]-dizirconium tetrachloride (**6**, $C_{40}H_{48}Cl_4N_4Zr_2$)

Step one: K$_4$*[Cy*$_4$*Pyr*$_4$*]:* Tetracyclohexyl calix[4]pyrrole (1.08 g, 2 mmol) was dissolved in 25 cm^3 of toluene, the solution was cooled to −15°C, and 8.5 equivalents of potassium hydride were added with vigorous stirring for 1 h. The solution turned cloudy and gradually changed to bright yellow. After removal of the H_2 gas and filtration, the solution was used for next step immediately.

Step two: To a fresh stirred solution of K$_4$[Cy$_4$*Pyr*$_4$] (1 mmol in 25 cm^3 toluene) was added $ZrCl_4$ (0.47 g, 2 mmol) at −15°C. After the mixture was stirred at room temperature overnight, the solvent was removed in vacuum and the resulting product dissolved in 50 cm^3 toluene. The residual insoluble KCl was separated by centrifugation and decantation of the solution. The volatile material was removed and 0.69 g solid yellow-brown **6** were obtained (76%). ^{1}H NMR (C_6D_6); $\delta = 1.61$ (q, 8H), 1.76 (m, 16H), 2.08 (t, 16H), 5.85 (s, 8) ppm; ^{13}C NMR (C_6D_6); $\delta = 22.2$, 29.2, 42.0, 45.2, 110.5, 136.8 ppm; IR $\bar{\nu} = 3270$, 2951, 1455, 1389, 1171, 1023, 942, 745 cm^{-1}.

Ethylene polymerization

A sample of the zirconium complex (approximately 0.03 mmol) and a 500-fold excess of *MAO* (approximately 15 mmol) was dissolved in 20 cm^3 toluene under N_2 counter-flow to the reactor *via* cannula tubing from a measuring cylinder at 25°C (or 40°C). The reactor was pressurized to 1 bar ethylene pressure. The ethylene concentration in the reaction medium was kept constant in the polymerization medium through continuous ethylene feeding under vigorous stirring. The reaction was stopped by venting the ethylene gas and degassing the reactor to the atmosphere and pouring the solution into a mixture of 10 cm^3 methanol, 10 cm^3 distilled water, and 5 cm^3 concentrated HCl. After separation of polyethylene by filtration, it was washed with methanol several times until no longer acidic, and then with acetone to remove all of the unreacted co-monomer. Finally, the polymer was transferred to a rotary evaporator and dried at 50°C under reduced pressure to constant mass. ^{1}H NMR ($CDCl_3$); $\delta = 1.32$ (m), 1.14 (m), 1.08 (m), 0.89 (m), olefin signals at 4.92, 4.44 ppm; ^{13}C NMR ($CDCl_3$); $\delta = 39.8$, 33.4, 28.8, 23.3, 11.3, olefin signals at 124.3, 126.2, 128.0 ppm.

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