

Novel single-site catalysts containing a platinum group metal and a macrocyclic sulfur ligand for ethylene polymerization

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Abstract

The reactions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PtCl_4 with 1,4,7-trithiacyclononane in ethanol lead to the formation of $(\text{S}_3\text{-ethano-9})\text{RhCl}_3$ and $(\text{S}_3\text{-ethano-9})\text{PtCl}_4$, respectively. The complexes catalyzed polymerization of ethylene in pentane in the presence of methylalumoxane (MAO) at 70°C and at ethylene pressure of 10 bar. The obtained polyethylenes had an averaged molecular weight of $M_w = 272,000$ ($(\text{S}_3\text{-ethano-9})\text{RhCl}_3$) and 901,000 ($(\text{S}_3\text{-ethano-9})\text{PtCl}_4$) and narrow molecular weight distributions of $M_w/M_n = 2.95$ ($M_n = 92,000$) ($(\text{S}_3\text{-ethano-9})\text{RhCl}_3$) and $M_w/M_n = 4.0$ ($M_n = 226,000$) ($(\text{S}_3\text{-ethano-9})\text{PtCl}_4$). On the basis of the narrow molecular weight distribution the catalysts can be considered as single-site catalysts.

Keywords: Ethylene; Polymerization; Rhodium; Platinum; Homogeneous; Macrocyclic thioether

1. Introduction

The metallocene catalysts became of wider interest when Kaminsky and coworkers found that very high productivity for ethylene polymerization can be obtained with the group 4 metallocenes in the presence of oligomeric, partially hydrolyzed trimethylaluminum (methylalumoxane, MAO) [1]. The $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system exhibited very high activity but lacked selectivity. The catalysts based on chiral ansa-metallocene compounds, like racemic ethylene-bridged bis(indenyl)titanium dichloride [2] and ethylene-bridged

bis(tetrahydroindenyl)zirconium dichloride [3] used in combination with MAO, are capable of stereospecific polymerization of propylene. The catalytically active form of these ansa-metallocene catalysts is assumed to be an electrophilic Cp_2MR^+ moiety [4]. In this the bent framework of Cp_2M forces the vacant coordination site to be in a *cis* position towards the metal–alkyl bond thus promoting an intramolecular insertion reaction. Nowadays the interest is in the ancillary ligands which would have similar steric and electronic properties to those of cyclopentadienyl ligands but which are more easily modified than the Cp ligand.

Wang and Flood have reported a rhodium complex of facially-coordinating tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) which has catalytic activity toward ethy-

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lene [5,6]. C_nRhMeX_2 ($X = OTf, BF_4$) polymerize ethylene in any solvent in which the components are soluble at 15 atm ethylene pressure. The polymerization is rather slow with an average turnover number of 1 per day.

We report here our results of investigations on platinum group metal complexes of macrocyclic tri- and tetradentate sulfur ligands. The macrocyclic sulfur ligands coordinate readily to the metal centers producing stable complexes. In these complexes the macrocyclic ligand acts as a protecting group for the metal ion; this parallels with the role of cyclopentadienyl and aryl ligands in traditional metallocenes.

2. Experimental

2.1. Materials

Ethylene (99.95%, AGA) was used after passing through deoxygenation and drying columns. The commercial macrocyclic thioethers 1,4,7-trithiacyclononane (S_3 -ethano-9), 1,4,7,10-tetrathiacyclododecane (S_4 -ethano-12), 1,4,8,11-tetrathiacyclotetradecane (S_4 -ethano-propano-14) and 1,5,9,13-tetrathiacyclohexadecane (S_4 -propano-16) (Aldrich Chemie), metal chlorides $FeCl_3$ (Merck), $RuCl_3$, $RhCl_3$, $PtCl_2$ and $PtCl_4$ (Johnson and Matthey AB) and $IrCl_3$ (Ventron) were used without further purification. Methylalumoxane (MAO) was purchased from Schering AG (now Witco, Bergkamen, Germany) as a 30% (m/m) toluene solution. Toluene was deoxygenated and dried by distillation over sodium-benzophenone ketyl. The other solvents were dried over activated 4 Å molecular sieves and purged with nitrogen gas.

2.2. Measurements

Elemental analyses for carbon, hydrogen and sulfur were determined by Carlo Erba CHN + O/S 1106 analyzer. The IR spectra were mea-

sured on a Nicolet Magna-IR 750 IR spectrometer with a spectral resolution of 2 cm^{-1} . 1H NMR spectra were recorded by Bruker AM 250 NMR spectrometer with TMS as reference. The molar-mass distribution of the polymer was measured at 135°C by gel-permeation chromatography (HTGPC Waters 150C ALC) using 1,2,4-trichlorobenzene as a solvent.

2.3. Preparation of catalysts

All reactions were carried out under nitrogen atmosphere using the Schlenk technique except the filtrations which were carried out in air.

2.3.1. (S_3 -ethano-9) $RuCl_3$

$RuCl_3 \cdot 3H_2O$ (0.25 g, 1.0 mmol) and S_3 -ethano-9 (0.17 g, 1.0 mmol) were placed into the reaction flask with 20 ml dry ethanol. The reaction mixture was stirred at 60°C for 2 h and at room temperature for 12 h. The dark brown precipitate was filtered, washed with ethanol and diethylether and dried in vacuum. The yield was nearly 100%. The material was insoluble in any common organic solvent. Elemental analysis: found: C 17.99, H 3.40, S 23.21; calculated for (S_3 -ethano-9) $RuCl_3$: C 18.58, H 3.12, S 24.80. Infrared spectrum: 2979.9, 2933.8, 1444.4, 1411.5, 1268.7, 1176.7, 1128.0, 1014.0, 908.0, 824.1, 677.9 cm^{-1} .

2.3.2. (S_3 -ethano-9) $RhCl_3$

A mixture of $RhCl_3 \cdot 3H_2O$ (0.24 g, 1.0 mmol) and 1,4,7-trithiacyclononane (0.2 g, 1.1 mmol) in 20 ml ethanol was stirred first at 60°C for two hours and then at room temperature overnight. The precipitate was collected on a sintered glass funnel in air, washed with ethanol and diethylether and dried in vacuum. The yield of the yellow powdery product was 84%. The 1H NMR spectrum (DMSO- d_6 250 MHz, 293 K) showed one singlet at δ 3.3 ppm, relative to TMS. Elemental analysis: found: C 18.43, H 3.07, S 25.82; calculated for (S_3 -ethano-9) $RhCl_3$: C 18.50, H 3.10, S 24.69. Infrared spectrum: 2987.6, 2923.4, 2874.6, 2807.1,

1449.8, 1404.9, 1283.6, 1266.0, 1171.3, 1123.7, 1016.2, 940.0, 908.0, 828.9, 680.6, 663.1 cm^{-1} .

2.3.3. (*S*₃-ethano-9)IrCl₃

A mixture of IrCl₃ · 3H₂O (0.4 g, 1.1 mmol) and 1,4,7-trithiacyclononane (0.2 g, 1.1 mmol) was refluxed in acetonitrile/dichloromethane (3/1). After refluxing overnight the yellow solid was filtered and dried in vacuum. The yield of insoluble yellow material was 51%. Elemental analysis: found: C 15.5, H 2.57; calculated for (*S*₃-ethano-9)IrCl₃: C 15.05, H 2.53. Infrared spectrum: 2967.5, 2919.8, 1411.6, 1263.2, 1103.4, 1028.1, 804.3, 669.6 cm^{-1} .

2.3.4. (*S*₃-ethano-9)PtCl₄

PtCl₄ (0.07 g, 0.2 mmol) and *S*₃-ethano-9 (0.04 g, 0.2 mmol) were mixed together in 20 ml ethanol. The temperature was maintained at 60°C for 2 h and at room temperature for 12 h. The brownish yellow solid was filtered, washed with ethanol and ether and dried in vacuum. The yield was 69%. The material was weakly soluble in DMSO, but insoluble in any other common organic solvent. Elemental analysis: found: C 13.69, H 2.13; calculated for (*S*₃-ethano-9)PtCl₄: C 13.93, H 2.34. Infrared spectrum: 2993.1, 2973.1, 2927.2, 2894.3, 2835.1, 2813.2, 1443.0, 1398.1, 1260.4, 1177.3, 1117.6, 946.5, 913.3, 834.4, 657.1 cm^{-1} . ¹H NMR was recorded in DMSO-*d*₆ and showed two broad singlets at 3.83 ppm and 4.01 ppm (250 MHz, 293 K).

The syntheses of (*S*₃-ethano-9)FeCl₃ [7], (*S*₃-ethano-9)PtCl₂ [8], (*S*₄-ethano-12)RhCl₃ [9], (*S*₄-ethano-propano-14)RhCl₃ [9] and (*S*₄-propano-16)RhCl₂ [9] were performed according to literature.

2.4. Polymerization of ethylene

2.4.1. Method 1

The glass parts of the polymerization apparatus were dried in an oven at 110°C and assembled in the glove box while still warm. Solid catalyst, cocatalyst and toluene were placed into

the 0.1 dm³ glass reaction flask in the glove box. The metal complexes were not soluble in toluene but after addition of MAO the complexes dissolved producing yellow solutions. The activity of the catalysts were tested by using Al/M ratio of 500. The mixture was stirred and ethylene was led into the reactor at 1 bar pressure for one hour while the temperature was raised to 80°C with a water bath. The resulting polymer was poured into acidic methanol to remove the residual catalyst, filtered and dried in an oven at 70°C.

2.4.2. Method 2

The polymerization was carried out in a two liter pressure reactor under an anhydrous atmosphere. The solid catalyst, cocatalyst (MAO) and *n*-pentane (1.3 l) were kept at 10 bar ethylene pressure and at 70°C for one hour. The ratio of Al/M was 500. The experimental conditions were held constant during the polymerization test.

3. Results and discussion

3.1. Syntheses and characterization

The reaction of MCl_{*x*} (M = Fe, Ru, Rh, Ir, Pt; *x* = 2–4) with macrocyclic thioethers, (*S*₃-ethano-9, *S*₄-ethano-12, *S*₄-ethano-propano-14, *S*₄-propano-16), in an 1:1 mole ratio in a suitable solvent (at 60°C or in reflux) leads to a formation of complex LMCl_{*x*} (L = macrocycle). The color of the products was usually yellow except for the (*S*₃-ethano-9)RuCl₃, which was brown. The products were stored in a glove box although they seem to endure the exposure of the air at least for short periods. The complexes were insoluble in common organic solvents except six compounds, (*S*₃-ethano-9)RhCl₃, (*S*₃-ethano-9)PtCl₂, (*S*₃-ethano-9)PtCl₄, (*S*₄-ethano-12)RhCl₃, (*S*₄-ethano-propano-14)RhCl₃, (*S*₄-propano-16)RhCl₂, which were slightly soluble in DMSO. Mostly the observed and calculated percentages of carbon, hydrogen and sulfur of

the chemical analyses agreed well, only in a few cases the difference was substantial and was probably caused by solvent residues.

The IR spectra of the materials are rather complicated due to lack of specific IR active groups easy to recognize. IR bands of the complexes in the range of $1460\text{--}1411\text{ cm}^{-1}$ are slightly shifted to a lower wavenumber with respect to the free ligand indicating complex formation.

In ^1H NMR spectra of $(\text{S}_3\text{-ethano-9})\text{RhCl}_3$ ($\text{DMSO-}d_6$ 250 MHz, 293 K) and $(\text{S}_3\text{-ethano-9})\text{PtCl}_2$ there was one singlet at δ 3.3 ppm and δ 3.35 ppm, respectively. The ligand in a complex gives a singlet at a lower field with respect to the free ligand ($\text{S}_3\text{-ethano-9}$, δ 3.07 ppm). The thioether ligand is coordinated to the metal center facially with all the three sulfur atoms. In the ^1H NMR spectrum of $(\text{S}_3\text{-ethano-9})\text{PtCl}_4$ there were two broad singlets at δ 3.83 ppm and δ 4.01 ppm. The thioether ligand is probably coordinated to the metal with the two sulfur atoms instead of all three.

The structures of the synthesized 1,4,7-trithiacyclononane metal ($\text{M} = \text{Fe}, \text{Ru}, \text{Rh}, \text{Ir}, \text{Pt}$) tri- and dichloride complexes (Fig. 1) are supposed to be similar to those given in literature for $(\text{S}_3\text{-ethano-9})\text{Mo}(\text{CO})_3$ [10] or $(\text{S}_3\text{-ethano-9})\text{RuCl}_2(\text{PPh}_3)$ [11]. The metal has a slightly distorted octahedral coordination, and the thioether acts as a facial tridentate ligand, ex-

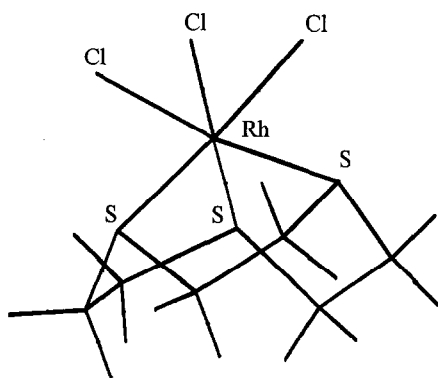


Fig. 1. The supposed structure of $(\text{S}_3\text{-ethano-9})\text{RhCl}_3$.

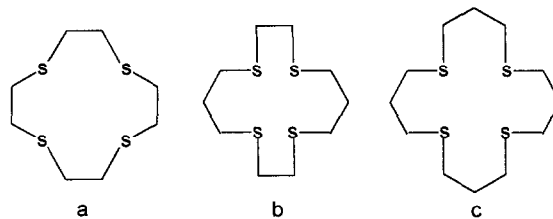


Fig. 2. (a) $\text{S}_4\text{-ethano-12}$, (b) $\text{S}_4\text{-ethano-propano-14}$, (c) $\text{S}_4\text{-propano-16}$.

cept for $(\text{S}_3\text{-ethano-9})\text{PtCl}_4$ where the ligand is bidentate. The stability of the complexes has been attributed to the fact that only a small change in the endodentate conformation of the free ligand is required for coordination.

The structures of the tetradentate thioether rhodium complexes have been determined in the literature [9], and only the 16 membered ring is big enough to encompass the metal. The 12 and 14 membered rings have to form *cis*-complexes (Fig. 2) [9].

3.2. Polymerization of ethylene

The activities of the complexes $[(\text{S}_3\text{-ethano-9})\text{MCl}_3]$ were tested in the polymerization of ethylene in the presence of the cocatalyst MAO ($\text{Al}/\text{M} = 500$) at normal pressure and at 80°C temperature. The resulting activities were determined in units of kg polyethylene (PE)/(mol metal h) and they varied between 0.3 and 7.1 kg/(mol M h). The polymerization started at room temperature but the activity increased markedly with temperature. The platinum and rhodium complexes, $(\text{S}_3\text{-ethano-9})\text{PtCl}_4$ and $(\text{S}_3\text{-ethano-9})\text{RhCl}_3$, activated with MAO showed a moderate activity towards ethylene (Fig. 3). The other metal chlorides such as PtCl_2 and IrCl_3 have also been found to act as starting materials for the active catalyst. The melting point of the polymers were in the range $129\text{--}132^\circ\text{C}$. In the IR-spectra of polyethylenes six strong bands at wavenumbers 2920.5, 2851.0, 1473.3, 1463.1, 731.0 and 719.6 cm^{-1} were observed.

Activity as a function of a metal

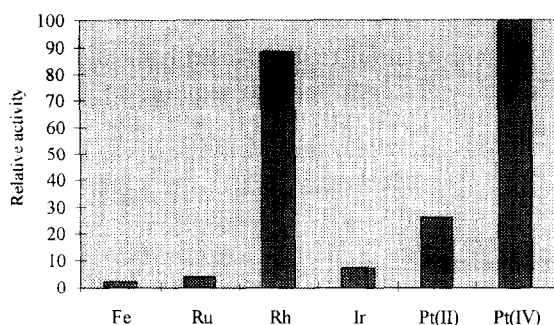


Fig. 3. The polymerization activity as a function of a metal for LMCl_x ($L = \text{S}_3$ -ethano-9, $M = \text{Fe, Ru, Rh, Ir, Pt}$, $x = 2-4$) complexes. The polymerization were conducted with $\text{Al}/M = 500$ at 1 bar ethylene pressure and at 80°C for 1 h.

Activity as a function of a ligand

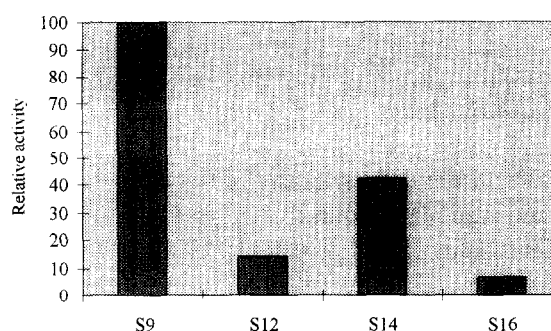


Fig. 4. The polymerization activity as a function of a macrocyclic thioether for LRhCl_x ($L = \text{S}_3$ -ethano-9 (S9), S_4 -ethano-12 (S12), S_4 -ethano-propano-14 (S14), S_4 -propano-16 (S16), $x = 2-3$). The polymerizations were carried out by method 1. The polymerization were conducted with $\text{Al}/M = 500$ at 1 bar ethylene pressure and at 80°C for 1 h.

Other macrocyclic thioethers, S_4 -ethano-12, S_4 -ethano-propano-14 or S_4 -propano-16, can also act as an ancillary ligands in syntheses of ethylene polymerization catalysts, in addition to S_3 -ethano-9 (Fig. 4). These tetradentate thioethers form the active rhodium catalysts for ethylene polymerization but even with the S_4 -ethano-propano-14 ligand which forms the most active catalyst of the afore-mentioned ligands the activity is less than half of that observed for the $(\text{S}_3$ -ethano-9) RhCl_3 . The activity of the $(\text{S}_4$ -propano-16) RhCl_2 is low which is reasonable since the 16 membered ring forms the *cis*-complex with rhodiumchloride, thus preventing the formation of the active center where a free coordination place and a metal alkyl bond are in a *cis*-position to each other.

For ethylene polymerization by method 2 the activity of the complexes $(\text{S}_3$ -ethano-9) PtCl_4 and $(\text{S}_3$ -ethano-9) RhCl_3 was tested at higher ethylene pressure. The activity of the $(\text{S}_3$ -

ethano-9) PtCl_4 was $232 \text{ g PE/g catalyst h}^{-1}$ ($120 \text{ kg PE/mol Pt h}^{-1}$) and with GPC (gel-permeation chromatography) characterization the product was relatively high molecular weight polyethylene with $M_w = 901,000$ and had a narrow molecular weight distribution $M_w/M_n = 4.0$ ($M_n = 226,000$). The activity of the $(\text{S}_3$ -ethano-9) RhCl_3 was $171 \text{ g PE/g catalyst h}^{-1}$ ($66.8 \text{ kg PE/mol Rh h}^{-1}$) and the molecular weight and the molecular weight distribution of the polyethylene were $M_w = 270,000$ and $M_w/M_n = 2.95$ ($M_n = 92,000$) (Table 1). On the basis of the narrow molecular weight distribution it may be said that the catalysts act as single-site catalysts.

The catalytic properties of these complexes in ethylene polymerization are better than those of C_nRhMe_3 , $\text{C}_n\text{RhMe}_2(\text{OTf})$ or $\text{C}_n\text{RhMe}(\text{OTf})_2$. The cyclic thioether containing catalysts show activities a couple of orders of

Table 1

Catalytic activity of cyclic thioether complexes of rhodium and platinum in ethylene polymerization^a

Catalyst	Al/M	PE yield (g)	Activity (kg PE/(mol h))	M_n	M_w	M_w/M_n
$(\text{S}_3$ -ethano-9) RhCl_3	500	1.8	67	92,000	272,000	2.95
$(\text{S}_3$ -ethano-9) PtCl_4	500	3.0	120	226,000	901,000	4.0

^a Conditions: solvent = pentane, $T = 70^\circ\text{C}$, $p(\text{ethylene}) = 10 \text{ bar}$, polymerization time = 1 h.

magnitude higher than those of afore-mentioned catalysts at low ethylene pressure.

4. Conclusions

The tridentate macrocyclic thioether 1,4,7-trithiacyclononane coordinates readily to the platinum metal center producing a stable complex. The macrocycle occupies one side of the metal leaving the other side available for the polymerization, which parallels the role of cyclopentadienyl ligands in the traditional metallocenes.

The reactions of platinum chloride and rhodium chloride with the S₃-ethano-9 ligand form yellow air-stable complexes, which are slightly soluble in DMSO. These complexes catalyze polymerization of ethylene in the solution in the presence of a cocatalyst methylalumoxane, MAO.

The relatively simple synthesis of the complex and the stability of the complex in air makes the system worth studying. As far as we know, the trithiacyclononane rhodium and platinum complexes are the first single-site olefin polymerization catalysts containing a late transition metal and a chalcogen ligand.

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