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Synthesis of $(C_5H_5)_2Zr(O_2C)CH_3$ and $(C_5H_5)_2Zr(O_2C)CH_2CH_3$ for olefin polymerization

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Summary

$(C_5H_5)_2Zr(O_2C)CH_3$ and $(C_5H_5)_2Zr(O_2C)CH_2CH_3$ complexes were synthesized, characterized and activated with MAO for ethylene polymerization. The highest catalytic activity was achieved at Al/Zr molar ratio of 3000 for both systems. The effects of the size of the R group in the carboxylate ligands, the Al/Zr molar ratio and reaction temperature on the catalytic activity and polymer properties were studied and discussed.

Introduction

Metallocenes have opened the way to produce polyolefins with defined properties. The aspects that determine the behavior of a metallocene complex as a catalyst in polymerization reactions are its structure and geometry [1]. Certain substitutes in specific positions in the molecule of the catalytic precursor can exert a drastic influence not only on the activity and stereo-selectivity of the catalyst, but also on the molar mass and molar mass distribution of the generated polymers [2,3]. The change of chlorine ligands, in classical metallocene complexes of group IV, by electro donor groups provides a way to modify the electronic and steric enviroment of the catalytic precursor. Thus, Mack et al. [4] observed a rise in the catalytic activity during the ethylene polymerization when chlorine ligands in Cp_2ZrCl_2 were substituted by a bidentate nitrogen ligand $(Me_3SiN\text{-}(CH_2)_2\text{-}NSiMe_3)\ Li_2$. The authors stated that new ligand could act either as a counterion or as a spectator group, during the polymerization reaction.

In the same way, Morillo et al. [5] reported that the catalytic activity in ethylene polymerization of a series of amide titanocenes was considerable lower in comparison with the starting complex, Cp_2TiCl_2, in the following order: $Cp_2Ti\ (NEt_2)_2$ > $CpTi\ (NEt_2)_3$ > $CpTi\ (N^nPr_2)_3$. This effect on the activity is possibly due to the great stability of the amide ligands, which reduce the formation of the catalytic active species. However, polyethylenes with higher molar masses were obtained with the amide substituted complexes. Probably, the propagation stage is favored by the electronic donation that nitrogen ligands exert over the metallic center. The same effect was found by Henderson et al. [6], who observed lower activities with zirconocene amide complexes [Cp_2Zr (Cl) N $(CH_2C_6H_5)_2$] and [Cp_2Zr (Me) N $(CH_2C_6H_5)_2$] during ethylene polymerization, than the ones obtained with Cp_2ZrCl_2. According to the authors, the reduction of the activities was a result of a higher difficulty to cleave Zr-N linkage compared to Zr-Cl, diminishing the generation of active species.

Dias et al. [7] reported the synthesis of a zirconium metallocene complex $Ind_2Zr(OC_{10}H_{17})Cl$ which show a lower activity than that of the corresponding dichloride, Ind_2ZrCl_2, for ethylene polymerization. In this case, the authors attributes the decrease in the activity to the more difficult alkylation of the transition metal core due to a presence of the voluminous and sterically shielding bridged ligand.

Benetollo et al. [3] published the synthesis of new complexes with oxygenated and nitrogen ligands, [$(C_5H_5)_2Zr\{2, 6\text{-}OC_6H_3\ (CH_3)_2\}_2$], [$(C_5H_5)_2Zr\{2, 4, 6\text{-}OC_6H_3\ (CH_3)_3\}_2$] and [$(C_5H_5)_2Zr\ (CH_3)\ \{CH\ (NC_6H_5)\}_2$], which were active for ethylene polymerization. The catalytic activities as well as molar mass of the polymers were strongly dependent on the electronic and steric effects of the ligands bounded to the zirconium center.

We have previously reported the synthesis of a Ti metallocene complex with benzoate ligands, $Cp_2Ti\ (O_2CC_6H_5)_2$, which showed a high activity during ethylene polymerization and produced ultra high molar mass polyethylene. We presumed that the carboxylate ligands stripped during the formation of the active species could still in close proximity to the catalyst, leading to a stabilization of the propagating species [8].

In this work we reported the synthesis of two new zirconocene complexes with carboxylate ligands, $Cp_2Zr\ (O_2C)\ CH_2CH_3$ y $Cp_2Zr\ (O_2C)\ CH_3$. The influence of polymerization parameters on activity and polymers properties are discussed.

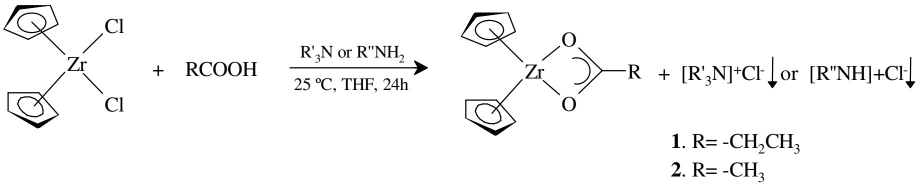
Experimental

General

All experiments were carried out under a high purity nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled prior use and stored over molecular sieves. Acetic acid (Riedel de Haën) and propanoic acid (Merck) were purified by reaction with acetic anhydride and benzoic anhydride, respectively, using chrome trioxide as catalyst. N-butylamine and triethylamine (Riedel de Haën) were distilled from sodium/benzophenone alloy; biscyclopentadienyl zirconium dichloride Cp_2ZrCl_2, (Aldrich) and methylaluminoxane (MAO, Albermale) were used without further purification. Nitrogen (99.99 %, PRAXAIR) was passed through columns with adequate drying agents, while ethylene (PRAXAIR, polymerization grade) was passed through columns packed with an activated BASF R3-11 catalyst. ^1H- NMR were carried out in $CDCl_3$, using a 400 MHz BRUKER spectrometer. Chemical displacements were reported in ppm relative to TMS. IR spectra were recorded using a FTIR Nicolet, Nexus 470. Zirconium content present in the dissolutions of the complexes was determined using a UV-Visible Perkin – Elmer Lambda 2S, by the colorimetric revelation method [9].

To synthesize $Cp_2\ Zr\ (OCOCH_2CH_3)$, 1 g (3.4 mmol) of Cp_2ZrCl_2 was weighted in a Schlenk and suspended in tetrahydrofuran (THF); then, 6.8 mmol of propanoic acid were added dropwise to the mixture, and was stirred at room temperature for 20 min. After that, 6.8 mmol of triethylamine were added obtaining triethylamine chlorhydrate as a white precipitated, which was separated by filtration. Finally, the solvent was removed under reduced pressure to yield the title compound as a yellow solid (Scheme 1).

Cp_2 Zr ($OCOCH_3$) was prepared following the procedure described before, but using acetic acid and n-butylamine, obtaining the compound as an orange solid.



Scheme 1. Synthesis of oxygenated complexes.

Product characterization, **1**: IR(KBr): 3092(ν C-H_{olefin}); 2980, 2874 (ν_{asym} ,ν_{sym} CH_3); 2933 (ν_{asym} CH_2); 1558, 1441 (ν_{asym}, ν_{sym} OCO); ^1H RMN ($CDCl_3$): δ = 1.35 (t, 3H, CH_3); 3.06 (q, 2H, -CH_2-); 6.65 (s, 10H $(C_5H_5)_2$). **2**: IR (KBr): 3098 (ν C-H_{olefin}); 2958, 2872 (ν_{asym}, ν_{sym} CH_3); 2927 (ν_{asym} CH_2); 1553, 1450 (ν_{asym}, ν_{sym} OCO); ^1H RMN ($CDCl_3$): δ = 2.47 (s, 3H, CH_3); 7.02 (s, 10H $(C_5H_5)_2$).

Polymerizations

Polymerization reactions were carried out in a 350 ml stainless steel reactor using toluene as solvent (150 mL). Methylaluminoxane (MAO) was used as the cocatalyst in Al/Zr molar ratios between 1000 and 5000. For each experiment, 2 μmol of Zr were added into the reactor. The polymerizations were performed at 5 bar of ethylene at different temperatures, for 30 min.

The reagents were introduced into the reactor in the following order: solvent, cocatalyst, ethylene and catalyst. Acidified (HCl) methanol was added to quench the process, and reactions products were separated by filtration, washed with methanol and hexane, and finally dried until constant weight.

Polymers thermal properties were determined using a differential scanner calorimeter (DSC), Rheometric Scientific DSC PLUS-E. The samples were heated until 170°C at a heating rate of 10°C/min under nitrogen flow and kept at that temperature for 10 min. Temperature fusion peaks (Tf) and the heat of fusion (ΔH_f) were obtained by reheating the samples at rate of 10 °C/min. Intrinsic viscosities, [η], of polymer solutions in decaline at 135 ± 0.01°C, were determined using a LAUDA PVS1 viscometer and the viscosimetric molar masses were calculated using the Mark-Houwink equation.

Results and discussion

Characterization of metallocene complexes with carboxylate ligands

The difference between the ν_{asym} (COO) and ν_{sym} (COO) infrared frequencies were 110 cm^{-1} and 108 cm^{-1} for complexes **1** and **2**, respectively. According to Coutts et al [10], this is the expected result for a bidentate simetrically bounded carboxylate ligand.

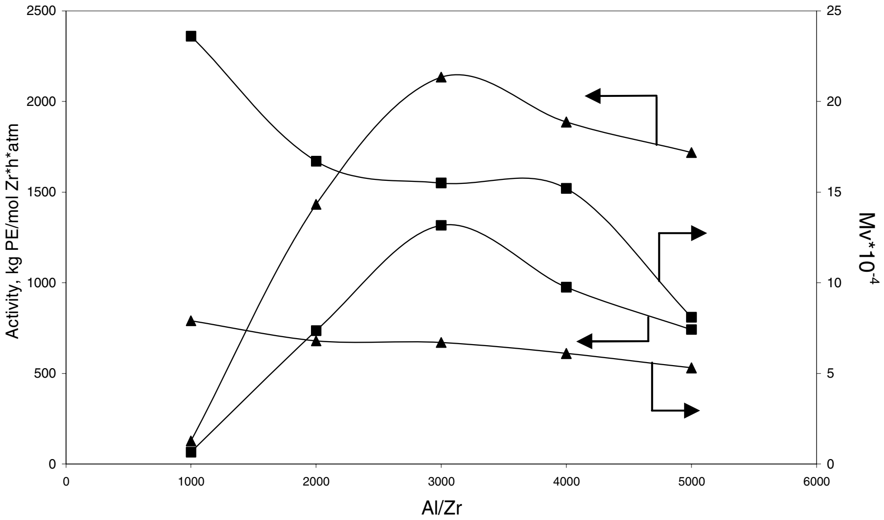


Figure 1. Catalytic activity and molar mass in the polymerization of ethylene with 1: $Cp_2Zr(OCOCH_2CH_3)$ (■) and 2: $Cp_2Zr(OCOCH_3)$ (▲) as the function of Al/Zr molar ratio.

Ethylene polymerization

Figure 1 shows the catalytic behavior of the complexes **1** and **2** versus the Al/Zr molar ratio in the polymerization of ethylene at 70 °C, using MAO as cocatalyst. Both catalysts showed a maximum of activity at an Al/Zr molar of 3000.

Below this optimum ratio, the MAO concentration could be insufficient to convert all the bis-Cp-Zr-carboxylate species into the active cationic complexes and/or to eliminate catalyst poisons present in the polymerization medium. On the other hand, higher concentrations lead to a lower activity, because of the poisoning effect of MAO [11, 12].

The table 1 shows the results of ethylene polymerization with complexes **1** and **2** as a function of Al/Zr molar ratio where also, for comparison, the results obtained with Cp_2ZrCl_2 are included.

Table 1. Al/Zr molar ratio influence on ethylene polymerizations with complexes **1** and **2** activated with MAO[a].

Al/Zr	Activity [b]		Tm_1 °C		ΔHf_1 J/g		Tm_2 °C		ΔHf_2 J/g		$Mv x 10^{-4}$ g/mol	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
1000	65	127	135	135	213.2	207.6	136	137	204.2	221.7	23.6	6.1
2000	735	1433	135	135	199.2	217.5	137	137	194.5	208.2	16.7	6.8
3000	1316	2134	137	134	205.9	224.4	138	136	190.3	206.5	15.5	6.7
4000	976	1887	136	134	188.9	211.4	138	137	155.3	202.1	15.2	6.9
5000	741	1719	135	134	205.2	211.9	137	136	173.9	199.1	8.1	5.3
3000†	**5680**		**136**		**194.3**		**139**		**180.3**		**8.2**	

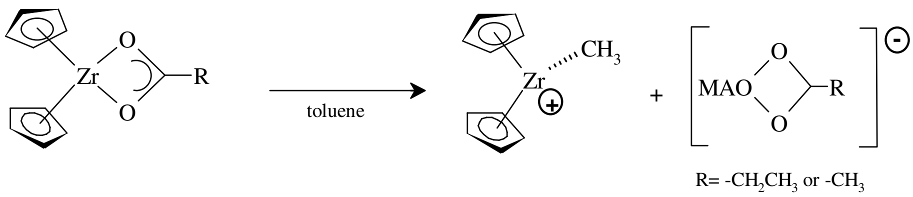
[a] : experimental conditions: 150 mL toluene, 2μmol of Zr, 5 bar of C2, 70°C.

[b] : kgPE/mol Zr atm h.

†: results for Cp_2ZrCl_2 under the same experimental conditions

The carboxylate complexes gave lower activities than the one obtained with the model catalyst. This could be explained taken into account that the bidentate carboxylate ligand is more strongly bounded to zirconium than chlorine groups and then removal of oxygenated ligands by cocatalyst, to produce the active specie, should result quite difficult [3], as seen in scheme 2.

On the other hand, polymerization activity of Cp_2 Zr ($OCOCH_3$) was higher, by a factor of 2, than that of its analogue Cp_2Zr ($OCOCH_2CH_3$). This difference indicates that the nature of the counterion formed in each case affect the catalyst behavior.



Scheme 2. Proposed formation of the active cationic complexes.

In $[Cp_2Zr^+CH_3]$•$[MAO•OCOR]^-$, the ethyl group does exerts a donor effect slightly higher than methyl group. This, combined with the higher size of the ethyl group, probably causes a reduction in its propagation speed and, as a result, a lower activity in the ethylene polymerization.

The melting temperatures of the nascent polyethylenes (Tm_1) were slightly lower (closed to 2 °C) than that of melt-crystallized ones (Tm_2); while the melting enthalpies of nascent state polyethylenes were higher than that of melt-crystallized ones. These findings are in according to the reported by Loos et al [13], for polymerization temperatures up to 60 °C. In the first heating, the disordered polymer chains start melting at a temperature range according to their size; then, they cool freely allowing the chains to pack. After melting and recrystalization the entanglement density of the polymer may be increased. Therefore, the chain mobility will be reduced, which hinders crystallization, resulting in a differently organized morphology having lower crystallinity.

In relation to the fusion enthalpies of recrystallized polyethylenes (ΔH_2), it can be noted that the higher the Al/Zr ratio was, the lower was ΔH_2. It could indicate that the increase in aluminum concentration affects the way the polyethylene chains crystallize. This is possibly due to the fact that the induction period (time necessary for the formation of the catalytically active species) becomes longer as the aluminum concentration in the systems gets higher, according to the reports done by Kim and Sik-Ha [14]. This could influence not only polymers crystallinity, but also their molar mass and reaction productivity.

Polyethylenes showed moderate molar masses, ranging from $5.3x10^4$ to $23.6x10^4$ g/mol. It was found that the higher the MAO concentration was, the lower was the molar mass (Figure 1). This result could be associated to a “deviation” of the single-site behavior of the catalysts, because the nature of the predominant active species in the reaction is different under different conditions of reaction. This tendency may be attributed to the formation of complexes between the active species and the cocatalyst, which leads to a reduction in the number of active centers that take part in the reaction and, as a consequence, to a decrease in the molar mass [11, 15].

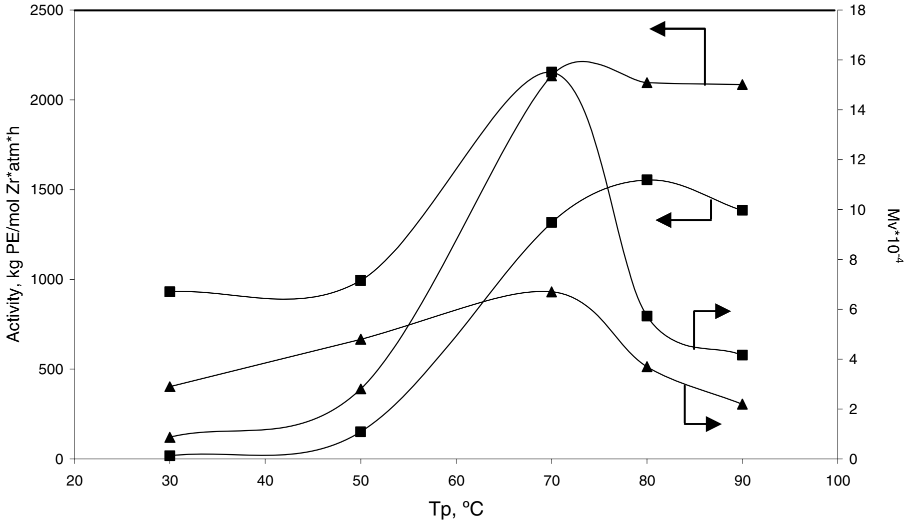


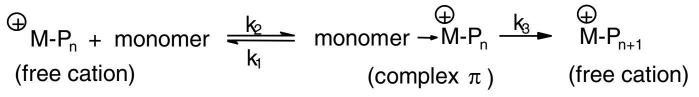
Figure 2. Dependence of catalytic activity and viscosimetric molar mass with polymerization temperature for **1**:$Cp_2Zr(OCOCH_2CH_3)$/MAO(■) and **2**:$Cp_2Zr(OCOCH_3)$/MAO(▲). Al/Zr molar ratio = 3000.

The average molar masses of the polyethylenes obtained with the complex **1** were higher than that of the complex **2**. This effect may be due to the influence of the size of the alkyl group, as it determines the kind of counterion produced with the cocatalyst which remains around the active species and could influence its stability and mobility. Probably, in the case of the specie $[Cp_2Zr^+CH_3]\bullet[MAO\bullet OCOCH_2CH_3]^-$ with a relatively higher steric hindrance, propagation predominates over transference, leading to the formation of longer chains.

Figure 2 shows the influence of polymerization temperature on the catalyst activity. Again, catalyst activity depended on the size of carboxylate group. Increasing the temperature from 30 to 90 °C increases catalyst activity until reach a maximum around 70°C. Above this value, the activity decreases.

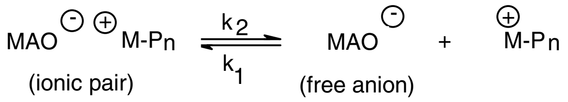
It is possible that the catalytically active species in these zirconocene complexes are unstable at high temperatures and proceeds to its decomposition. This factor, combined with the ethylene solubility reduction in the reaction means, could cause the reduction of the reaction productivity.

In order to explain the influence of the polymerization temperature on the active species, it is possible to use the mechanisms stated by Cosse-Arlman [16] and Qian [17]. The mechanism of Cosse-Arlman involves the following reaction:



$$\underset{\text{(free cation)}}{\overset{\oplus}{\text{M-P}_n}} + \text{monomer} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(complex } \pi\text{)}}{\text{monomer} \rightarrow \overset{\oplus}{\text{M-P}_n}} \xrightarrow{k_3} \underset{\text{(free cation)}}{\overset{\oplus}{\text{M-P}_{n+1}}} \qquad (\mathbf{1})$$

While Qian proposes that polymerization mechanism involves the formation of a ionic pair $[\text{catalyst}]^+$-$[\text{MAO}]^-$ whose association grade strongly influences the catalytic activity of metallocene complexes:



$$\underset{\text{(ionic pair)}}{MAO^{\ominus}\;{}^{\oplus}M\text{-}P_n} \;\underset{k_1}{\overset{k_2}{\rightleftharpoons}}\; \underset{\text{(free anion)}}{MAO^{\ominus}} + {}^{\oplus}M\text{-}P_n \qquad (\mathbf{2})$$

Where $M^+ = [Cp_2Zr^+Me]$ and P_n = growing polymer chain.

At low temperatures, both, ionic pair and complex π, are stable and catalytic activity is low. When polymerization temperature rises, ionic pair and complex π dissociation begin, producing the growing of k_3, with a rise in the activity. At high polymerization temperatures, both, complex π and ionic pair are completely dissociated and the activity falls, due to the decomposition of the active species.

The table 2 shows the results of ethylene polymerization with complexes **1** and **2**, as a function of the temperature of polymerization.

Enthalpies of fusion of nascent state polyethylenes were higher than the ones of melt-crystallized ones. This is probably due to the reorganization of the crystal formed during polymerization before melting during the first heat, which requires higher energy. Likewise, the rise of the enthalpy of fusion when polymerization temperature is increased indicates that the rise of temperature in the system favors packing of the chains.

According to Wunderlich [18] while at low temperatures, just formed molecules or molecules parts spontaneously crystallize, above a certain polymerization temperature molecule creation and crystallization proceed separately. According to this view, it is possible to assume that an increase of polymerization temperature will lead to a diminishing in the entanglement of the polyethylene molecules, which lead to higher cristallinity.

Table 2. Results of ethylene polymerization with **1**/MAO and **2**/MAO systems as a function of polymerization temperature[a].

Tp °C	Activity[b]		Tm_1 °C		ΔHf_1 J/g		Tm_2 °C		ΔHf_2 J/g		$Mv*10^{-4}$ g/mol	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
30	18	121	135	133	81.2	70.2	137	135	68.8	68.7	6.7	2.9
50	152	391	138	134	212.1	160.8	137	136	119.1	153.7	7.2	4.8
70	1316	2134	137	134	205.9	224.4	138	136	190.3	206.5	15.5	6.7
80	1554	2096	135	134	225.3	207.9	138	136	216.6	215.7	5.7	3.7
90	1384	2084	134	134	221.9	207.4	136	136	222.8	226.3	4.2	2.2

[a] : experimental conditions: 150 mL toluene, 2μmol of Zr, 5 bar of C2, 70°C.

[b] : kgPE/mol Zr atm h.

Al/Zr molar ratio = 3000

The molar mass of polyethylenes increases with polymerization temperature until reaching the highest value on 70°C (Figure 2). Above this point, the molar mass begins to diminish maybe due to the temperature rises favor the process of chain transference (through a β-H mechanism) over propagation.

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