

Ethylene Polymerization Catalyzed by Diamide Complexes of Ti(IV) and Zr(IV)

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ABSTRACT: In this research, we describe the application of the complexes *o*-C₆H₄(NSiMe₃)₂ZrCl₂ (**1**), *o*-C₆H₄(NSiMe₃)₂TiBr₂ (**2**), *o*-C₆H₄(NSiMe₃)₂TiCl₂ (**3**), C₂H₄(NSiMe₃)₂ZrCl₂ (**4**), in the ethylene polymerization with different Al/M ratios and temperatures. These complexes presented significant catalytic activities in the presence of methylaluminoxane (MAO) as cocatalyst and toluene as solvent, producing high molecular weight linear polyethylenes. Zirconium complexes were more active at 60°C and

titanium complexes at 40°C. Zirconium complex (**1**) showed the best values of activity (347 kg PE/mol Zr h atm) for Al/Zr ratio of 340 and 60°C of temperature. In ethylene-1-hexene copolymerization, the best result was also reached with catalyst **1**, at the same conditions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 270–275, 2008

Key words: catalysts; copolymerization; diamide complexes; polyethylene (PE); polyolefins

INTRODUCTION

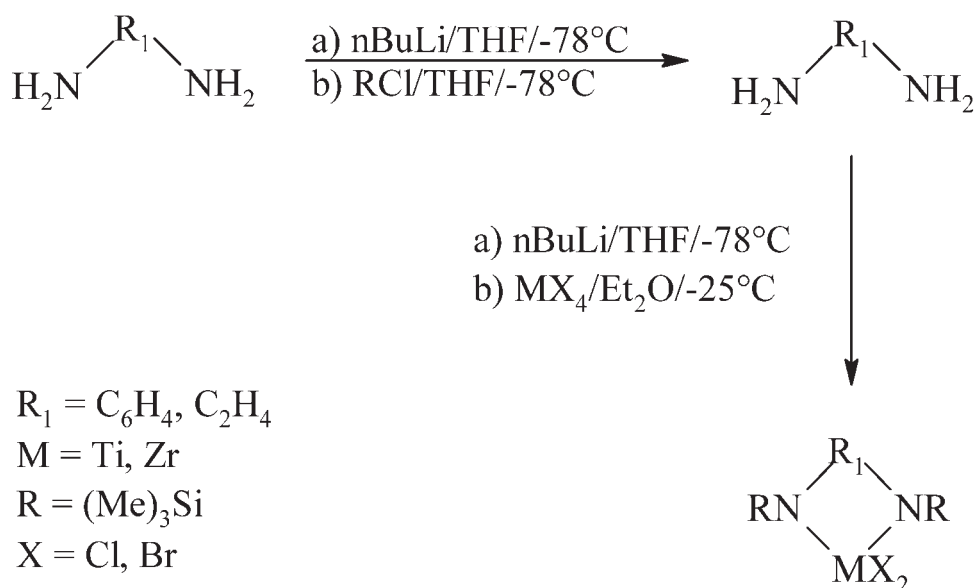
Olefin polymerization by homogeneous transition metal catalysis attracts particular attention in the field of organometallic chemistry, catalysis, and polymer chemistry.^{1–3} The organometallic chemistry of zirconium in the +4 oxidation state has been dominated by complexes formed by cyclopentadienyl ligands. Within this class of compounds, cationic metallocene derivatives of the type [Cp₂ZrR]⁺ exhibit high activity in the polymerization of ethylene and α -olefins. The bent Cp₂Zr framework restricts coordination of olefins to a site cis to the Zr-R bond, whereas the formally 14-electron count results in a highly electrophilic metal center. Studies in this area have been concerned with the way in which the stereoregularity, catalytic activity, and comonomer incorporation can be altered with changes to the Cp ligands.^{4,5} However, in an effort to create electron-deficient group 4 transition metal centers for catalytic transformations, linked diamides have been considered by many researchers as alternatives to the ubiquitous metallocenes. A variety of diamide ligands based on naphthalene, propylene, and substituted propylene diamines have been stud-

ied. The success of these ligands can be attributed to the hard nature of the N donor atoms, the diversity and relative easy manipulation of ligand topology, chirality, and coordination number, as well as the “tunability” of the associated steric factors.^{6,7}

Park and coworkers⁸ reported titanium(IV) and zirconium(IV) complexes containing rigid diamide ligands derived from *N,N*-disilylated 1,8-diaminonaphthalene. When the lithiated diamide was reacted with titanium or zirconium tetrachloride, a bis(diamide) titanium(IV) or zirconium(IV) complex, [1,8-C₁₀H₆(NSiMe₃)₂]₂M (M = Ti, Zr), and a mono(diamide) titanium(IV) or zirconium(IV) dichloride, [1,8-C₁₀H₆(NSi(*i*-Pr)₃)₂]₂MCl₂ (M = Ti, Zr), were obtained. The dichloride titanium complex showed moderate activity in ethylene polymerization, but the zirconium complex was not active. The same author reported later,⁹ an amine elimination reaction leading to the less bulky mono(diamide) complex [1,8-C₁₀H₆(NSiMe₃)₂]₂ZrCl₂ and this complex presented a moderate catalytic activity (90 kg PE/mol_{Cat} h atm at 60°C) in ethylene polymerization. They have also prepared zirconium(IV) complexes bearing a *flexible* propylene diamide ligand ([RN(CH₂)₃NR]₂; R = SiMe₃, Si(*i*-Pr)₃) which showed to be less active than the rigid linkage.

Nomura et al.^{10–12} reported that the complex [1,8-C₁₀H₆(NR)₂]₂TiCl₂ (R = Si^{*i*}Pr₃, Si^{*t*}BuMe₂, SiMe₃) showed remarkable catalytic activities in ethylene polymerization and in ethylene-1-hexene copolymerization in the presence of cocatalysts such as methylaluminoxane (MAO), methylisobutylaluminoxane

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Scheme 1 Synthesis of the titanium(IV) and zirconium(IV) diamide complexes.

(MMAO), and Al^iBu_3 - or AlEt_3 - or $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$. They observed that the solvent as well as the cocatalyst is very important to have high catalytic activities. The catalytic activities performed in heptane (cocatalyst MMAO) were higher than those carried out in toluene (cocatalyst MAO). The catalytic activity increased with R in the following order: $\text{Si}^i\text{BuMe}_2 > \text{SiMe}_3 > \text{Si}^i\text{Pr}_3$. They also tested the catalyst system ($\text{R} = \text{Si}^i\text{BuMe}_2$) and cocatalyst MMAO in copolymerization reactions of ethylene and 1-hexene, 1-octene, and 1-decene. The resultant copolymers gave relatively broad molecular weight distributions, consisting of high and low molecular weight copolymers.

Scollard and McConville^{13,14} reported that the chelating diamide complex $[\text{ArN}(\text{CH}_2)_3\text{NAr}] \text{TiMe}_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) serves as a precursor for highly active living polymerization of α -olefins. In contrast, the analogous zirconium compounds ($[\text{ArN}(\text{CH}_2)_3\text{NAr}]\text{ZrX}_2$, $\text{X} = \text{Me}, \text{Cl}$) showed little or any activity in the polymerization of α -olefins under the same conditions. Strong binding of the cocatalyst to the electrophilic, low-coordinate zirconium metal center may preclude formation of a cationic alkyl complex, as has been observed for other chelating diamides of Ti and Zr.¹⁵

Kim and coworkers¹⁶ showed that titanium and zirconium complexes with a new ancillary ligand, *N,N*-bis(trimethylsilyl)aminobenzylamine activated by modified methylaluminoxane (MMAO) and $\text{B}(\text{C}_6\text{F}_5)_3$ had moderate activities in the polymerization of olefins.

Danièle et al.¹⁷ polymerized ethylene using the complex $o\text{-C}_6\text{H}_4(\text{NSiMe}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$, having a dimethylvinylsilyl group. For the polymerization reac-

tion, they used 6.4×10^{-4} mol of catalyst, MAO as cocatalyst, 500 of Al/Zr ratio and 2.4 bar of ethylene pressure for 15 min. They obtained a moderate activity ($14.2 \text{ kg/mol}_{\text{cat}} \text{ h bar}$).

In this article, we describe the use of the complexes $o\text{-C}_6\text{H}_4(\text{NSiMe}_3)_2\text{ZrCl}_2$ (**1**), $o\text{-C}_6\text{H}_4(\text{NSiMe}_3)_2\text{TiBr}_2$ (**2**), $o\text{-C}_6\text{H}_4(\text{NSiMe}_3)_2\text{TiCl}_2$ (**3**), and $\text{C}_2\text{H}_4(\text{NSiMe}_3)_2\text{ZrCl}_2$ (**4**), in the ethylene polymerization, at different Al/M ratios and temperatures. Complexes **1** and **4** were also copolymerized with 1-hexene.

EXPERIMENTAL

Synthesis of the complexes

All reactions were done as it is shown at Scheme 1. The ligands 1,2-phenylenediamine (31.75 mmol) and ethylenediamine (31.75 mmol) were reacted at -78°C with nBuLi (63.5 mmol), which was added in several portions during 30 min. The stirred reaction mixture was warmed to room temperature and stirred for more 6 h. The reaction mixture was then cooled to -78°C and Me_3SiCl (64.8 mmol) was added in several portions by using an addition funnel during 30 min. The mixture was warmed slowly to room temperature and stirred for 12 h. The solution was then warmed to 50°C and stirred for an additional 2 h to complete the reaction. Then, the solution was cooled to -78°C and added nBuLi (63.5 mmol) to remove the two remaining hydrogens, then the solution was warmed to room temperature and stirred for at least 10 h. The solvent was eliminated under vacuum. MCl_4 ($\text{M} = \text{Ti}$ or Zr) (10.54 mmol) was added drop wisely to a chilled

TABLE I
Ethylene Polymerizations at 60°C

Entry	C	Al/M	Rend. (g)	Catalytic activity	T_m (°C)	X_c (%)	M_w (g/mol)	M_w/M_n
1	1	80	0.31	38.5	133.3	77	863,000	6.3
2	1	170	2.10	263.0	133.9	49	973,000	4.0
3	1	340	2.78	347.0	133.6	46	1,038,000	3.7
4	1	670	2.46	307.2	133.3	41	935,000	5.6
5	1	1340	2.05	255.8	128.8	10	1,264,000	3.0
6	2	80	0.07	8.4	130.9	35	–	–
7	2	170	0.06	7.4	132.5	70	–	–
8	2	340	0.05	6.5	132.4	50	–	–
9	2	500	0.06	8.0	132.5	50	–	–
10	2	670	0.04	5.3	131.4	33	–	–
11	2	1340	1.58	197.3	133.2	19	–	–
12	3	80	0.02	2.6	132.3	44	–	–
13	3	170	0.03	4.3	133.4	62	–	–
14	3	340	0.02	3.2	133.3	54	–	–
15	3	500	0.03	3.8	132.7	43	–	–
16	3	670	0.02	2.4	133.6	66	–	–
17	3	1340	0.06	7.8	131.8	20	–	–
18	4	2000	0.78	324.4	134.2	43	320,300	1.9
20	4	3000	0.45	187.2	131.1	36	375,800	2.1
21	4	4000	4.05	1685.8	134.1	47	340,400	1.8

Al/M, cocatalyst/catalyst; catalytic activity (kg/mol_M h atm); T_m , melting temperature; X_c , crystallinity; M_w , weight-average molecular weight; polymerization conditions: time = 0.5 h; ethylene pressure = 1.6 atm; cat. 1, 2, 3 = 1×10^{-5} mol and 4 = 3.6×10^{-6} ; solvent = toluene (300 mL); –, not determined.

The results of the polymerization reactions at 60°C and 40°C are shown on Table I and II, respectively.

It is important to point out that all catalysts presented catalytic activity in ethylene polymerization from low and moderates (complexes 2 and 3) to high (complexes 1 and 4). The highest catalytic activity presented by catalyst 1, was 347 kg PE/(mol_{Zr} h

atm), when Al/Zr ratio was 340 and the temperature 60°C. Complexes similar to 1 such as *o*-C₆H₄(NSiMe₂CH=CH₂)₂ZrCl₂¹⁷ and [1,8C₁₀H₆(NSiMe₃)₂]ZrCl₂⁹ presented catalytic activities much lower (14.2 and 90 kg PE/(mol_{Zr} h atm), respectively). However at 40°C the catalytic activities fell down obtaining for this complex only moderate

TABLE II
Ethylene Polymerizations at 40°C

R	C	Al/M	Rend. (g)	Catalytic activity	T_m (°C)	X_c (%)
1	1	80	0.08	10.0	134.7	51
2	1	170	0.10	12.5	133.1	30
3	1	340	0.18	22.5	134.0	46
4	1	500	0.26	32.5	132.7	25
5	1	670	0.75	93.6	134.2	29
6	1	1340	1.28	160.4	122.8	26
7	2	80	0.08	10.0	118.1	1
8	2	170	0.07	8.8	116.2	0.4
9	2	340	0.17	21.3	117.4	4
10	2	500	0.13	16.3	121.5	3
11	2	670	0.28	35.0	132.5	29
12	2	1340	0.12	15.0	131.5	23
13	3	80	0.18	22.5	130.7	25
14	3	170	0.16	20.0	130.3	20
15	3	340	0.24	30.0	130.8	15
16	3	500	0.09	11.3	130.9	1
17	3	670	0.16	20.0	132.5	23
18	3	1340	0.28	35.0	130.5	9

Al/M, cocatalyst/catalyst; catalytic activity (kg/mol_M h atm); T_m , melting temperature; X_c , crystallinity; polymerization conditions: Time = 0.5 h; Ethylene pressure = 1.6 atm; cat. 1, 2, 3 = 1×10^{-5} mol and 4 = 3.6×10^{-6} ; solvent = toluene (300 mL); –, not determined.

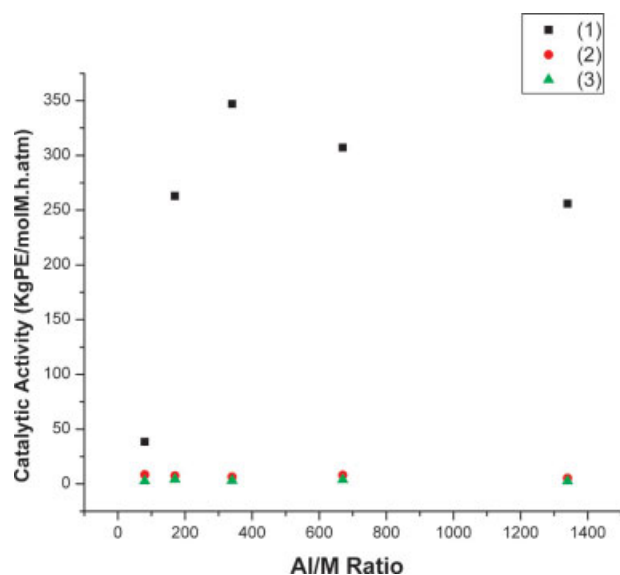


Figure 2 Variation of the catalytic activity of complexes 1, 2, and 3, at 60°C with the Al/M ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

activities [from 10 to 160 kg PE/(mol_{Zr} h atm)]. The molecular weights of the polymers obtained with complex 1 for the reaction at 60°C (in general at lower temperatures M_w tends to increase) were very high (from 863,000 to 1,264,000 g/mol) and the polydispersities quite broad from 3.0 to 6.3, suggesting the possibility of having more than one type of catalytic site. Higher MAO concentrations (Al/Zr = 1340 ratio) did not improve the catalytic activity of this catalyst as it can be seen in Figure 2. The catalytic activity of the complex 1 follows a tendency until a maximum point (Al/Zr = 340) and after that, it decreases. This behavior was already observed with others systems and is believed to be a result of the large coordinative insaturation and electrophilicity of the metal center which drives the cationic complex to coordinate with the solvent or MAO.²¹

Titanium complexes 2 and 3 presented low activities at 60°C. Complex 2 presented catalytic activities between 5 and 8 kg PE/(mol_{Ti} h atm), except for

high amounts of MAO (Al/Ti = 1340) and complex 3 between 2 and 7 kg PE/(mol_{Ti} h atm), those activities increased to moderated activities [from 9 to 35 for complex 2 and from 11 to 35 kg PE/(mol_{Ti} h atm) for complex 3] at 40°C. In general, titanium complexes are more active at lower temperatures than zirconium complexes.¹⁹ The change of the halogen ligand, Cl by Br, between complexes 3 and 2 did not change significantly the catalytic activity. The melting temperatures were, practically constant, exception of complex 2 between Al/Ti ratios of 80 and 500, where the melting temperatures and also of the crystallinities significant decrease. It is probable that these polymers that show low activity be contaminated by little amounts of cocatalyst and secondary products that could have not been completely eliminated during the purification, producing these low melting points and crystallinities.

Complex 4, at Al/Zr ratio 4000, gave a very high catalytic activity [1686 kg PE/(mol_{Zr} h atm)], much higher than the one of complex 1. However, to reach this activity it was necessary a great amount of cocatalyst which is not recommended due to the high cost of MAO and also because the purification of the polymer is more difficult. It is good to point out that this complex has already been tested in ethylene polymerization at 25°C, Al/Zr = 1000–3000, $P_E = 1$ atm giving low activities [1–9 kg PE/(mol_{Zr} h atm)].²¹ Molecular weights were much lower than those obtained with complex 1, on the other hand, the molecular weight distributions were close to 2, suggesting a single site catalyst. Melting points and crystallinities of all the polymers obtained at both temperatures are typical of high density polyethylene.

As catalysts 1 and 4 gave the best catalytic activities among the one studied they were also tested in ethylene copolymerization with 1-hexene (170 mmol) at 60°C. The results are shown in Table III.

It can be observed that the copolymers presented a significant decrease in melting temperature, indicating 1-hexene incorporation. Complex 1 continuous to maintain high catalytic activities also in copolymerization but complex 4 catalytic activities

TABLE III
Copolymerizations With 1-Hexene: Temperature 60°C

Entry	C	Al/Zr	Rend. (g)	Catalytic Activity	T_m (°C)	X_c (%)
1	1	340	2.20	275.0	112	22
2	1	670	1.82	227.5	110	26
3	4	4000	0.08	31.7	a: 112.6 b: 126.8	5 1
4	4	5000	0.09	38.1	127.5	7

Al/Zr, cocatalyst/catalyst; catalytic activity (kg/mol_{Zr} h atm); T_m , melting temperature; X_c , crystallinity; polymerization conditions: time = 0.5 h; ethylene pressure = 1.6 atm; cat. 1 = 1×10^{-5} mol and 4 = 3.6×10^{-6} ; solvent = toluene (300 mL).

were reduced to moderates [32 and 38 kg PE/(mol_{Zr} h atm)] by the copolymerization even using a high Al/Zr ratio. By ¹³C NMR, it is possible to see that the polymer obtained at entry 1 (Table III) has 2.1 mol % of 1-hexene in its chain. The molecular weight of the copolymer obtained with catalyst **1** at Al/Zr = 340 was lower (773,910 g/mol) comparing with the homopolymerization reaction keeping the same polydispersity, showing that the comonomer acts as a transfer agent reducing molecular weight. At entry 3, catalyst **4** gave a copolymer with two melting temperatures, probably, because of the high Al/Zr ratio used that could promote the formation of another active site.

CONCLUSIONS

All complexes studied presented catalytic activity in ethylene polymerization using mild conditions. The best result was obtain with complex **1** (Zr) that was more active than the complexes **2** and **3** (Ti). For the zirconium complexes **1** and **4**, the best reaction temperature was 60°C, and for the titanium complexes (**2**, **3**) 40°C. Complex **1** can be used in ethylene-1-hexene copolymerization reactions being the best result reached at Al/Zr 340 and 60°C. Complex **1** with the phenylene bridge seems more interesting that complex **4** with the ethylene bridge because it can be polymerized with high activities using lower ratios of Al/Zr than complex **4**. Complex **1** can be a good alternative to obtain linear polyethylenes or copolymers with high molecular weights with mild conditions.

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