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Highly Active Half-Metallocene Chromium(III) Catalysts for Ethylene Polymerization Activated by Trialkylaluminum

Tieqi Xu, Ying Mu,* Wei Gao, Jianguo Ni, Ling Ye, and Yanchun Tao

Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

Received October 5, 2006; E-mail: ymu@mail.jlu.edu.cn

Polyolefins are the largest volume synthetic materials used in the world and have been almost applied in every aspect of our daily lives and productions. The growing demand for high performance polyolefin products in recent years has inspired extensive industrial and academic interest to develop high performance olefin polymerization catalysts.[1] Metallocene type catalysts can produce a variety of high performance polyolefin products, including isotactic polypropylene,[2] syndiotactic polypropylene,[3] atactic polypropylene,[4] high-density polyethylene,[5] linear low-density polyethylene,[6] syndiotactic polystyrene,[7] and cyclo-olefin copolymer.[8] Despite the success of metallocene-based catalysts in catalyzing the above-mentioned olefin polymerization reactions, they also exhibit disadvantageous features. A large amount of methylaluminoxane (MAO) or expensive fluorinated borate such as $Ph_3C^+B(C_6F_5)_4^-$ is generally required as cocatalyst or activator for obtaining acceptable polymerization activity,[9] which raises issues of the high cost of the metallocene type catalyst systems and the high ash content (Al_2O_3) of the product polymers. Consequently, there is a great need to develop new catalyst systems which can provide equivalent catalytic activity with no need for large amounts of expensive cocatalyst.[10,11] Recent development of chromium-based olefin polymerization catalysts has attracted intensive research interest.[12−16] So far, except that some of nonmetallocene type chromium complexes have been known to show reasonable catalytic activity for ethylene polymerization when activated with Et_2AlCl, a few half-metallocene type chromium catalyst systems have also been reported. Complexes $[Cp^*CrL_2R]^+A^-$ (L = py, 1/2dppe, MeCN, THF; R = Me, Et; A = PF_6, BPh_4) were first reported to show catalytic activity for ethylene polymerization.[14] A $Cp^*Cr(acac)Cl/Et_3Al$ (Al/Cr = 300) system was found to show a catalytic activity of 4.2×10^4 g PE mol Cr^{-1} h^{-1} under 50 atm of ethylene at room temperature.[15] Another similar system, $Cp^*Cr(C_6F_5)(\eta^3\text{-Bz})/Et_3Al$ (Bz = benzyl, Al/Cr = 90), produced oligomers with a catalytic activity of 2.1×10^5 g PE mol Cr^{-1} h^{-1} under 1.1 atm of ethylene at room temperature.[16a] We herein report a novel half-metallocene type chromium(III) catalyst system, $Cp^*Cr[2,4\text{-}^tBu_2\text{-}6\text{-}(CH{=}NR)\text{-}C_6H_2O]Cl/AlR'_3$ [R = ^tBu (**1**), Ph (**2**), 2,6-$^iPr_2C_6H_3$ (**3**); R′ = Me, Et, ^iBu], that catalyzes ethylene polymerization to produce high molecular weight polyethylene in high catalytic activity when activated with only a small amount of AlR_3 (Al/Cr ≈ 25).

The green color Cr(III) complexes **1**−**3** were synthesized in 50−60% yields via the reaction of $[Cp^*CrCl_2]_2$ with the lithium salt of the corresponding salicylaldiminato ligand in tetrahydrofuran at −78 °C. Their molecular structures have been determined by single-crystal X-ray diffraction, and the representative structure of complex **1** along with selected bond distances and angles is depicted in Figure 1. All three complexes adopt a pseudo-octahedral coordination environment of a three-legged piano stool. Most of the metal−ligand bond lengths in these complexes, including the Cp*−Cr, Cr−Cl, and Cr−O bond lengths, are close to the ones observed in some salicylaldiminato chromium complexes[12a] and cyclopentadienyl chromium complexes.[4a] The Cr−N bond lengths are obviously affected by the R group on N and are 2.071(4) Å for **1**, 2.049(4) Å for **2**, and 2.097(2) Å for **3**. The order of the dihedral angles between the Cp* ring and the phenoxide ring is 83.7° (**3**) > 34.0° (**2**) > 5.5° (**1**), while the dihedral angles between the Cp* ring and the plane through Cr, O, and N atoms are changed in a similar sequence of 56.5° (**3**) > 48.4° (**2**) > 48.2° (**1**). It is obvious that these dihedral angles are directly related to the sterically opening degree around the chromium atom in these complexes. The latter might play a significant role in allowing the ethylene molecule to coordinate to the chromium atom and to insert into the growing polyethylene chain, as well as in determining the rate of the polymer chain termination.[17] In other words, these dihedral angles might be related to the catalytic activity of these catalysts for ethylene polymerization and the molecular weight of the produced polyethylene.

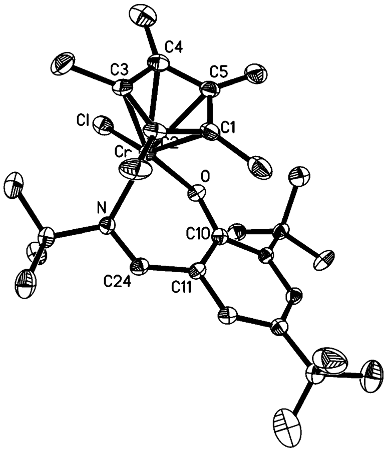

Figure 1. Molecular structure of complex **1**. Selected bond lengths (Å) and angles (deg): Cr−O 1.927(3), Cr−N 2.071(4), Cr−Cl 2.296(4), C_{24}−N 1.291(5), C_{11}−C_{24} 1.438(6), C_{10}−O 1.306(5), O−Cr−N 87.44(14), O−Cr−Cl 92.40(10), N−Cr−Cl 100.60(12).

Some experimental results of ethylene polymerization with complexes **1**−**3** as catalysts are summarized in Table 1. Upon activation with a small amount of $AlMe_3$, complexes **1**−**3** show reasonable to good catalytic activity for ethylene polymerization under 5 bar, producing polyethylene with high molecular weight ($1.00−1.45 \times 10^6$ g/mol). The melt transition temperatures (T_m) of the obtained polyethylenes are in the range of 134−140 °C, and the crystallinity of these polymers is in the range of 56.7−77.1%. ^{13}C NMR analysis on the polymer samples indicates that the polyethylenes produced by these catalysts are linear and have no branch. The catalytic activity of these complexes for ethylene polymerization under similar conditions (see runs 1, 8, and 11 in Table 1) is in the order of **1** > **2** > **3**, which indicates that the catalytic activity of these catalysts is remarkably affected by the nature of the R group on the nitrogen atom of the salicylaldiminato

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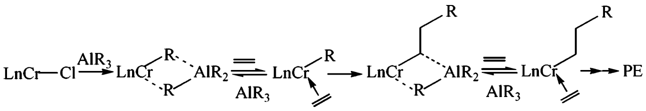
Table 1. Results of Ethylene Polymerization Using Procatalysts **1**−**3**[a]

run	procatalyst (μmol)	activator (μmol/equiv)	yield (g)	activity[b]	M_n[c] ($\times 10^{-4}$)	T_m[d] (°C)	X_c[e] (%)
1	**1** (5)	$AlMe_3$ (125/25)	10.11	4044	101	136.8	60.3
2	**1** (5)	$AlMe_3$ (250/50)	9.44	3776	106	136.7	64.3
3	**1** (5)	$AlMe_3$ (500/100)	5.12	2048	110	136.2	56.7
4	**1** (5)	$AlEt_3$ (125/25)	4.26	1704	120	139.9	57.6
5	**1** (5)	$AlEt_3$ (500/100)	2.52	1008	100	139.3	57.3
6	**1** (10)	Al^iBu_3 (125/25)	1.57	314	109	138.0	62.7
7	**1** (10)	Al^iBu_3 (500/100)	0.83	166	101	137.9	64.9
8	**2** (10)	$AlMe_3$ (125/25)	10.54	2108	126	134.5	70.0
9	**2** (10)	$AlMe_3$ (250/50)	9.52	1904	120	134.9	74.2
10	**2** (10)	$AlMe_3$ (500/100)	4.25	850	110	134.0	65.1
11	**3** (10)	$AlMe_3$ (125/25)	1.62	324	145	138.4	77.1
12	**3** (10)	$AlMe_3$ (250/50)	1.35	270	137	137.8	56.8
13	**3** (10)	$AlMe_3$ (500/100)	0.78	156	135	136.7	64.4

[a] Polymerization conditions: solvent 60 mL of toluene, temperature 20 °C, ethylene pressure 5 bar, time 30 min. [b] Units of kg PE (mol Cr)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}. [e] Crystallinity $X_c = \Delta H_f/\Delta H_f^0$; $\Delta H_f^0 = 273$ J/g for polyethylene.

Scheme 1. Proposed Catalytic Mechanism for the Polymerization Reaction (L = Ligands, R = Me, Et, ^{i}Bu)



ligand. The catalytic activity of **1** with R = ^{t}Bu is much higher than that of **3** with R being the bulky 2,6-$^iPr_2C_6H_3$ group. These results are in agreement with the sequence of the dihedral angles between the Cp* ring and the phenoxide ring mentioned above. It is obvious that the catalytic activity of these complexes is closely related to the sterically opening degree in front of the chromium atom in these complexes. For all complexes, the highest catalytic activity was observed at the Al/Cr radio of 25, and the catalytic activity decreases as the Al/Cr ratio further increases. Similar results have been observed previously for the $Cp^*Cr(C_6F_5)(\eta^3\text{-Bz})/Et_3Al$ system and have been explained based on the formation of a bridged heterobimetallic chromium−aluminum complex.[16a] The effect of trialkylaluminum concentration on the catalytic activity suggests an equilibrium between the bridged heterobimetallic chromium−aluminum complex and the ethylene coordinated mononuclear chromium complex as shown in Scheme 1. Such a mechanism is further supported by the following experimental result: the catalytic activity of **1**/AlR_3 (R = Me, Et, ^{i}Bu) systems is quite different with different R group and decreases in the order of **1**/$AlMe_3$ > **1**/$AlEt_3$ > **1**/Al^iBu_3, which can be attributed to the fact that the bulkier alkyl on the aluminum atom can slow down the ethylene coordination rate and therefore lower the catalytic activity of the catalyst. One other thing that should be mentioned is that the catalytic activity of the present system is much greater than that previously reported for other half-metallocene type chromium complexes activated by trialkylaluminum[15,16a] and has reached the level of cationic metallocene catalysts of titanium and zirconium[18] or constrained geometry chromium catalysts.[19]

In summary, we have successfully developed a new type of half-metallocene chromium(III) catalyst system for ethylene polymerization that catalyzes ethylene polymerization to produce high molecular weight polyethylene in high catalytic activity when activated with only a small amount of AlR_3 (Al/Cr ≈ 25). These new catalysts represent a remarkable addition to the limited list of half-metallocene type chromium ethylene polymerization catalysts. At present, further investigations exploring more high performance catalysts of this type and possibilities applying these types of catalysts to produce copolymers of ethylene with α-olefins are underway.

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Supporting Information Available: Experimental procedures, crystallographic data in CIF format, and selected bond lengths and angles of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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