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Olefin polymerization behavior of the cyclopentadienyl cobalt complexes bearing pendant sulfur or oxygen ligands

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Abstract

Four half-sandwich cobalt complexes bearing pendant sulfur or oxygen ligands have been reported and tested as catalysts for olefin polymerization in the presence of MAO. The molecular structure of complexes 1 has been determined by X-ray crystallographic analysis. Complexes 1 and 2 exhibited high activities of up to 10^6 g PE mol⁻¹Co h⁻¹ with moderate molecular weight ($M_w \approx 10^4$ g mol⁻¹) of polyethylene in the ethylene polymerization.

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 η^5 -Cyclopentadienyl derivatives of transition metals are undoubtedly one of the most important classes of organometallic compounds [1]. The half-sandwich complexes containing one cyclopentadienyl ligand with a functionalized side chain have received much attention by numerous research groups [2]. With the functionalized side chain temporarily and reversibly coordinated to the metal center, the cyclopentadienyl ligand becomes a bidendate ligand with a hemilabile binding structure [3]. Thus they are prone to selective reactions and invaluable for catalytic purposes. The constrained geometry catalysts (CGC) with the familiar bridged Cp-amide ligand have showed great catalysis activity in the ethylene polymerization [4]. Functionalized silane as a side chain exemplifies the possibility of immobilizing catalytically active complexes on the surface [5].

In comparison to related N-functionalized cyclopentadienyl complexes, where catalytic applications of such species have been remarkably successful (especially in olefin polymerization) [6], the use of O- and S-functionalized compounds in catalysis seems still underdeveloped. Our previous work indicated that O- and S-functionalized rhodium complexes showed high activities for ethylene polymerization [7]. In this study, we introduce two different functional ligands to cobalt complexes and make further investigations into the effects of the donor ligands and *O*- and *S*-functionalized substituents on cyclopentadienyl as a weak coordination system. Here we report the use of the four cobalt halides with cyclopentadienes bearing sulfur or oxygen functionalized side chains as catalysts for olefin polymerization in the presence of methylaluminoxane as a co-catalyst.

The complexes were prepared as shown in Scheme 1. The starting materials, $[\eta^5-C_5H_4(CH_2)_2SCH_2CH_3]Co$ (CO)₂, $[\eta^5-C_5H_4(CH_2)_2OCH_3]Co(CO)I_2$ (**2**) were prepared by slightly modified literature procedures [8,9]. Complex $[\eta^5-C_5H_4(CH_2)_2SCH_2CH_3]Co(CO)_2$ can be oxidized with elemental iodine in diethyl ether solutions to give the airstable diiodocobalt(III) complexes $[\eta^5-C_5H_4(CH_2)_2SCH_2-$ CH₃]CoI₂ (**1**). Complex **1** is a black-purple crystalline solid. In IR spectrum, the carbonyl absorption is absent. Reaction of $[\eta^{-5}-C_5H_4(CH_2)_2OCH_3]Co(CO)I_2$ (**2**) with equimolar amount of pyridine or triphenyl phosphane in ether leads to the formation of **3** and **4** as black-green, crystalline solids in good yields. All complexes were characterized by EA, IR and ¹H NMR [10].

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The molecular structure of complex **1** was determined by single crystal X-ray diffraction. Suitable crystal was obtained by slow hexane diffusion into a dichloromethane solution at low temperature. As depicted in Fig. 1 [11], it possesses basically a tri-legged half-sandwich CpM structure. In which the sulfur atom was attached via an intermolecular coordination with the cobalt center and form an 18-electron complex. Because of the pendant arm the bond length of Co–C1 (2.055(7) Å) is the shortest and it forms a five membered ring between the cobalt atom, cyclopentadienyl ligand and the pendant arm.

Initially the polymerization of ethylene was studied using the combination of diiodide 1 with MAO as a co-catalyst in toluene (Table 1). For complex 1 the activity rises and falls with the increase of the n(Al)/n(Co) and reaches its pick at 10.4 (10^5 g PE mol⁻¹Co h⁻¹) when the n(Al)/n(Co) stays at 4000:1. But more MAO may deactivate the active center causing the decrease of the activity. Such behavior is well explained by the influence of the aluminum concentration on the termination of polymer chains [12]. The polymer molecular weight decreases when the Al/Co



Fig. 1. ORTEP view of **1** in the crystal. The hydrogen atoms are not shown for clarity. Selected lengths (Å) and angles (°): I(1)-Co(1) 2.5755(13), I(2)-Co(1) 2.6004(13), Co(1)-S(1) 2.246(2), Co(1)-C(1) 2.055(7) and C(1)-Co(1)-S(1) 85.5(2), S(1)-Co(1)-I(1) 92.83(6), S(1)-Co(1)-I(2) 90.43(6), I(1)-Co(1)-I(2) 96.25(4), C(8)-S(1)-Co(1) 109.6(3), C(7)-S(1)-Co(1) 97.4(3).

Table 1			
Polymerization	of ethylene	by 1-4 in	toluene ^a

Entry	Cat	Т	n(Al)/n(Co)	Pressure (atm)	Activity ^b	$M_{\rm w}^{\ \rm c} (10^4)$
		$(^{\circ}C)$				
1	1	20	1000	1	2.4	5.28
2	1	20	2000	1	3.4	4.31
3	1	20	3000	1	7.1	2.48
4	1	20	4000	1	10.4	2.04
5	1	20	5000	1	8.3	2.52
6	1	40	4000	1	3.1	3.52
7	1	60	4000	1	0.6	4.25
8	2	20	4000	1	7.4	3.81
9	3	40	4000	1	5.1	0.34
10	4	60	4000	1	3.0	2.24

^a A 200 ml Schlenk-type glass reactor containing 50 ml toluene was equilibrated with the ethylene monomer.

 5 10⁵g PE mol⁻¹Co h⁻¹g mol⁻¹.

^c The molecular weight of the polymer was measured by the Ubbelohde calibrated viscosimeter technique through the investigation of the intrinsic viscosity.

molar ratio becomes higher. Higher Al/Co molar ratio increases the chain transfer reaction with MAO as the acceptor; this results in lower polymer molecular weight. The effect of temperature is very obvious, activity actually decrease a lot increasing the temperature. Obviously, the high temperature may deactivate the active center and decrease the solubility of ethylene in toluene. Furthermore, increase in temperature results in the reduction of molecular weight. At higher temperatures, there is an increase in the rate of chain transfer. When the rate of chain propagation is much slower than that of chain transfer, the molecular weight of the polymer drops greatly.

For complexes 2–4, we set the best ratio of n(Al)/n(Co) at 4000 the same condition when complex 1 reaches its highest activity. The activities of ethylene polymerization by complexes 2–4 with the same substituted cyclopentadie-nyl group have slight differences for different ligand carbonyl, pyridine or triphenylphosphorine. The less bulky and weak electron-donated ligand led to an increase in activity.

Comparing complexes 1 and 2, we see that complex 1 containing S-functionalized side-arm exhibits higher activity than complex 2 containing O-functionalized side-arm. The sulfur atom of side-arm coordinated to center cobalt in complex 1 led to an increase in the activity, probably due to its hemilabile binding structure. For all the complexes, the activities of ethylene polymerization are from 10.3 to 3.0×10^5 g PE mol⁻¹Co h⁻¹ [n(Al)/n(Co)=4000:1]. The results show that half-sandwich cobalt complexes have large tolerance for changing electronic and steric effect in their structures.

Although the detailed mechanism of the catalytic olefin polymerization is not clear, we suggest that a cationic methyl cobalt complex is formed in the presence of co-catalyst (MAO) and that a vacant site (active site) for coordination of the olefin must be generated. Further investigations of the olefin polymerization of such complexes and of the polymerization mechanism are ongoing.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006. 01.010.

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- [10] [η⁵-C₅H₄(CH₂)₂SCH₂CH₃]CoI₂ (1): Yield 72%. Anal. Calcd. for C₉H₁₃CoSI₂ (465.99 g/mol): C, 23.20; H, 2.81. Found: C, 23.38; H, 2.48. IR (film): v(CSC) 831 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, ppm): δ 5.22 (t, 2H, Cp), 5.08 (t, 2H, Cp), 3.99 (t, 2H, SCH₂), 2.49 (t, 2H, CH₂), 2.96 (q, 2H, SCH₂), 1.34 (t, 3H, CH₃, ${}^{3}J_{HH} = 7.3$ Hz). ${}^{13}C$ NMR (125 MHz, CDCl₃, ppm): δ 113.7, 85.3, 83.7, 82.8, 81.6, (C₅H₄), 35.7 (CH₂CH₂S), 30.3 (CpCH₂), 25.4 (SCH₂CH₃), 13.6 (CH_3) . [η^{5} -C₅H₄(CH₂)₂OCH₃]Co(py)I₂ (3): Yield 65%. Anal. Found: C 30.1%, H 3.15%, N 2.81% Calc. for C13H16ONCoI2: C 30.3%, H 3.13%, N 2.72%. ¹H NMR (CDCl₃, 500 MHz) δ: 5.29 (t, 2H, Cp), 5.15 (t, 2H, Cp), 3.52 (t, 2H, OCH₂), 3.27 (s, 3H, CH₃), 2.46 (t, 2H, CpCH₂), 10.06, 7.78, 7.30 (m, 5H, py). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 144.4, 137.8, 124.9, (CH^{py}), 98.0, 85.2, 79.9, (C₅H₄), 70.3(CH₂O), 58.4(OCH₃), 28.3(CpCH₂). IR (KBr) v (cm⁻¹): 3428, 3044, 2875, 1604, 1484, 1445, 1228, 1106, 1066, 833, 753, 691. $[n^{5}]$ C5H4(CH2)2OCH3]Co(PPh3)I2 (4): Yield 80%. Anal. Found: C 44.4%, H 3.72% Calc. for C26H26OPCoI2: C 44.7%, H 3.75%. ¹H NMR (CDCl₃, 500 MHz) *b*: 5.40 (t, 2H, Cp), 4.09 (t, 2H, Cp), 3.85 (t, 2H, OCH₂), 3.38 (s, 3H, CH₃), 3.32 (t, 2H, CpCH₂), 7.84–7.47 (m, 15H, Ph). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 137.9, 134.0, 130.4, 127.8, (CH^{PPh3}), 104.7, 91.2, 79.6, (C₅H₄), 71.8 (CH₂O), 58.4 (OCH₃), 29.7 (CpCH₂). IR (KBr) v (cm⁻¹): 3390, 2921, 1621,1480, 1433, 1089, 801, 749.691.
- [11] *Crystal data for I*: C₉H₁₃CoI₂S, $M_r = 465.98$, monoclinic, space group, P2(1)/c, a = 9.989(3), b = 8.8215(2), c=16.162(4) (Å), V = 1263.9(6) (Å³), Z = 4, $D_c = 2.449$ (mg/m³), F(000) = 864, reflections measured (2.14° < θ < 26.00°), R(wR) = 0.0673 (0.1091) for 2481 reflections with I > 2(I). The diffraction data were collected on a Siemens SMART CCD diffractometer. The structures are solved using direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX 97 program package. All atoms except for hydrogen were refined anisotropically. Crystallographic data for the structure of 1 reported in this paper has been deposited in the Cambridge Crystallographic Data Centre Nos. CCDC-293517. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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