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Synthesis and structure of a chromium(III) complex coordinated by 1,1′-Bi-2-naphtholate ligands and its catalytic activity for ethylene polymerization

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Abstract

Reaction of $CrCl_3(THF)_3$ with *rac*-Li_2(binol) (binol = 1,1′-bi-2-naphtholate) gave a new chromium(III) complex, $[Li(THF)]_3[Cr(binol)_3]\cdot 3$(toluene) (**1**). The X-ray crystallographic structure of **1** revealed its propeller-like structure similar to those of the reported rare earth analogues. The complex **1** showed moderate catalytic activities for ethylene polymerization upon activation with modified methylaluminoxane (MMAO) and with diethylaluminum chloride. When **1** was supported on the silica surface, activity increased to two times of homogeneous **1**/MMAO system.

Keywords: Chromium; 1,1′-Bi-2-naphtholate; Ethylene polymerization

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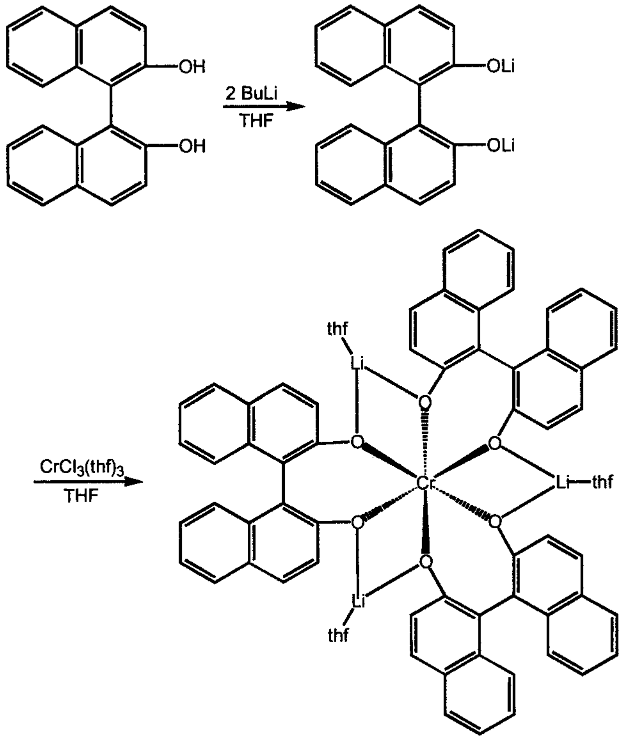
1. Introduction

Chromocene (Cp_2Cr)/silica catalysts discovered by Union Carbide is widely known as the catalyst for the polymerization of ethylene [1–8]. The polymerization mechanism and the active site of this catalyst have been extensively studied, but is still remained unclear. In order to understand this nature of this catalyst, Theopold and co-workers have reported a number of homogeneous catalysts based on chromium coordinated by cyclopentadienyl ligands [9]. The polymerization activity of this catalyst system shows lower (10^4 g mol^{-1} h^{-1} atm^{-1}) than that of silica-supported Cp_2Cr (10^6 g mol^{-1} h^{-1} atm^{-1}). Recently, Cp-free chromium complex catalysts have also been attracting much interest [10–20] and *N*,*N*-, *N*,*N*,*N*-, *N*,*O*-, and *O*,*O*-chelating ligands were reported to be effective for chromium catalysts [13–20]. We selected here a binaphtholate ligand as another *O*,*O*-chelating ligand, which should improve the crystallinity of the chromium complex to ease its isolation and should bring chiral coordination environment to the catalyst metal center. Here we



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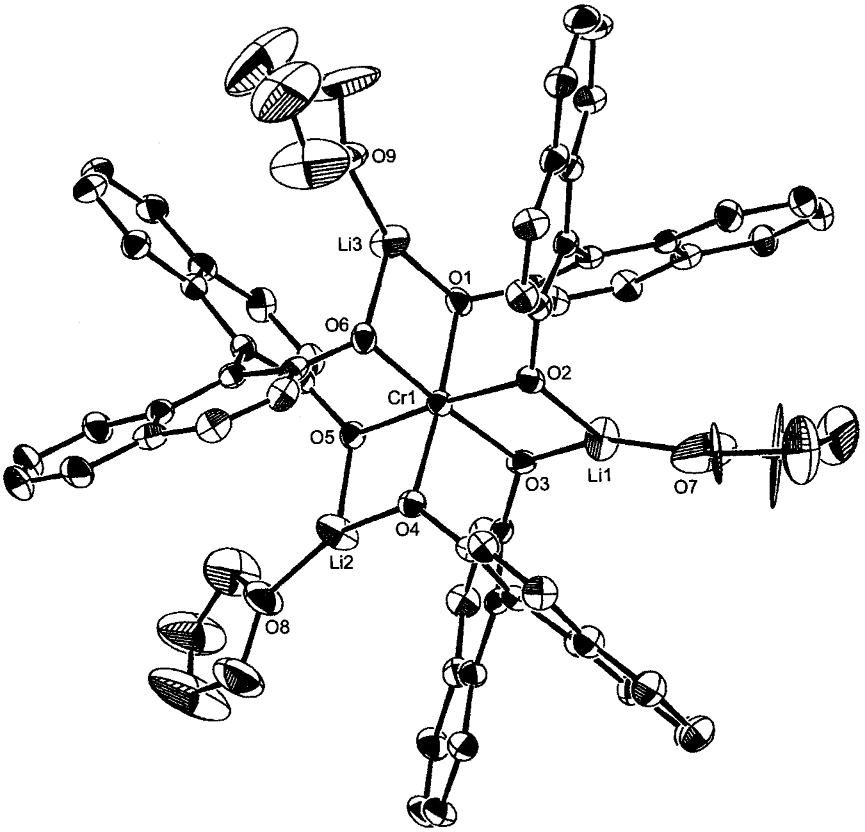

Fig. 1. Molecular Structure of $[Li(THF)]_3[Cr(binol)_3]\cdot3(toluene)$ (**1**). The solvent molecules are omitted for clarify.

report a synthesis, structure, and ethylene polymerization activities of a new trivalent chromium binaphtholate complex.

2. Results and discussion

2.1. Preparation of the complex

rac-1,1′-Bi-2-naphthol (binolH_2) was lithiated with two equivalents of ^{n}BuLi to give *rac*-Li_2(binol) [21], which was successively reacted with one equivalent of $CrCl_3(THF)_3$ in THF Eq. (1). Extraction with toluene and recrystallization from toluene–THF of the product did not give desired CrCl(binol), but gave $[Li(THF)]_3[Cr(binol)_3]\cdot3(toluene)$ (**1**) as green crystals in 6% yield. Our efforts to isolate any other chromium compounds from this reaction were unsuccessful.

The molecular structure of **1** was determined by X-ray crystallography as shown in Fig. 1, and the selected bond distances and angles are listed in Table 1. The chromium atom is coordinated by three binol ligands in *S*,*S*,*S*- or *R*,*R*,*R*-combination. The overall propeller-like framework of **1** is very similar to those of the rare earth derivatives, $[ML_2]_3[Ln(binol)_3]\cdot x(solvent)$ [M = Li, Na, K; L = OEt_2, THF; Ln = rare earth metals (La, Pr, Nd, Eu)], which were found to be excellent enantioselective catalysts for nitroaldol reactions, Michael reactions, and for hydrophosphonilations of imines or aldehydes by Shibasaki et al. [22,23]. A clear difference between the chromium complex **1** and the rare earth derivatives is the coordination num-

Table 1
Selected bond distances (Å) and angles (°) of **1**

Bond distances (Å)			
Cr(1)–O(1)	1.973(6)	Cr(1)–O(2)	1.997(6)
Cr(1)–O(3)	1.991(6)	Cr(1)–O(4)	2.001(6)
Cr(1)–O(5)	1.987(6)	Cr(1)–O(6)	1.978(6)
O(1)–Li(3)	1.87(2)	O(2)–Li(1)	1.88(2)
O(3)–Li(1)	1.87(2)	O(4)–Li(2)	1.89(2)
O(5)–Li(2)	1.87(2)	O(6)–Li(3)	1.91(2)
Bond angles (°)			
O(1)–Cr(1)–O(2)	88.9(2)	O(1)–Cr(1)–O(3)	94.8(3)
O(1)–Cr(1)–O(4)	175.8(3)	O(1)–Cr(1)–O(5)	94.1(2)
O(1)–Cr(1)–O(6)	82.2(3)	O(2)–Cr(1)–O(3)	82.7(3)
O(2)–Cr(1)–O(4)	94.6(3)	O(2)–Cr(1)–O(5)	175.3(3)
O(2)–Cr(1)–O(6)	94.1(3)	O(3)–Cr(1)–O(4)	88.1(2)
O(3)–Cr(1)–O(5)	93.4(3)	O(3)–Cr(1)–O(6)	175.7(3)
O(4)–Cr(1)–O(5)	82.7(3)	O(4)–Cr(1)–O(6)	95.0(3)
O(5)–Cr(1)–O(6)	89.9(2)	O(2)–Li(1)–O(3)	89.5(9)
O(2)–Li(1)–O(7)	121(1)	O(3)–Li(1)–O(7)	149(1)
O(4)–Li(2)–O(5)	89.1(8)	O(4)–Li(2)–O(8)	155(1)
O(5)–Li(2)–O(8)	115.3(9)	O(1)–Li(3)–O(6)	86.9(9)
O(1)–Li(3)–O(9)	162(1)	O(6)–Li(3)–O(9)	108.6(9)

Table 2
Polymerization of ethylene catalyzed by **1** [a]

Run	Cocatalyst	Activity (g mol^{-1} h^{-1} atm^{-1})	M_w [b]	M_w/M_n [b]	T_m (°C)
1	None	0	–	–	–
2	MMAO	1.5×10^4	1.2×10^6	107	132.3
3	TIBAL	0	–	–	–
4	DEAC	1.2×10^4	9.3×10^5	149	133.0

[a] In toluene (30 ml), at r.t., 0.1 MPa ethylene, [Al]/[Cr] = 100.
[b] Determined by GPC.

Table 3
Polymerization of ethylene catalyzed by **1**/MMAO [a]

Run	[Al]/[Cr]	Activity (g mol^{-1} h^{-1} atm^{-1})	M_w [b]	M_w/M_n [b]	T_m (°C)
1	0	0	–	–	–
2	25	1.4×10^2	n.d.	n.d.	n.d.
3	50	7.2×10^3	–	109	133.3
4	100	1.5×10^4	1.2×10^6	107	132.3
5	200	9.4×10^3	9.0×10^5	172	132.2
6	500	9.0×10^3	n.d.	n.d.	n.d.
7	1000	7.1×10^3	7.1×10^5	169	131.7

[a] In toluene (30 ml), at r.t., 0.1 MPa ethylene.
[b] Determined by GPC.

Table 4
Polymerization of ethylene catalyzed by **1**/MMAO [a]

Run	Temperature (°C)	Activity (g mol^{-1} h^{-1} atm^{-1})	M_w [b]	M_w/M_n [b]	T_m (°C)
1	60	1.3×10^3	n.d.	n.d.	132.1
2	20	1.5×10^4	1.2×10^6	107	132.3
3	0	4.1×10^2	8.5×10^5	85	n.d.
4	−78	0	–	–	–

[a] In toluene (30 ml), 0.1 MPa ethylene, [Al]/[Cr] = 100.
[b] Determined by GPC.

ber of lithium, three-coordinated lithium in **1** versus four-coordinated one in rare earth analogues. The sums of angles around the lithium atoms in **1** are nearly 360° (359.5° (Li1), 359.4° (Li2), and 357.5° (Li3)), showing their trigonal planer geometry. Lower Lewis acidity of chromium than those of lanthanoids should bring about less electron-deficient lithium atom to result in the three-coordination of lithium. The averaged Cr–O distance of **1** (1.988 Å) is significantly longer than those of the neutral aryloxochromium(III) complexes such as $CrCl_2(OC_6H_2^tBu_2CH_2NHC_6H_3Me_2)(MeCN)_2$ (1.865(3) Å) [18], $Cr(OC_6H_2^tBuCH{=}NC_6H_3^iPr_2)_2Et$ (1.947(3) Å) [19], and $Cr(OC_6H_2^tBuCH{=}NC_6H_3^iPr_2)_2Cl(MeCN)$ (1.917(3) and 1.949(3) Å) [19]. The formal three negative charges on the chromium center of **1** should weaken the π-donation from oxygen to chromium. The Li–O distances of **1** (average 1.88 Å) are even shorter than those of the lithium binaphtholate, $[\{Li(THF)_2\}_2(binol)]_\infty$ [21].

2.2. Polymerization of ethylene

The catalytic activity of these complexes for ethylene polymerization was studied in toluene with or without cocatalysts. The complex **1** was found to be inactive for ethylene polymerization without cocatalyst. When **1** was combined with organoaluminum cocatalysts such as modified methylaluminoxane (MMAO), diethylaluminum chloride (DEAC), and triisobutylaluminum (TIBAL) in toluene, the color of the solution changed from green to orange. The **1**/MMAO and **1**/DEAC systems showed good catalytic activities for ethylene polymerization, while TIBAL system was not effective for activation of **1** under the same condition (Table 2). The activities of the **1**/MMAO and **1**/DEAC systems were moderate and the resulting polyethylenes had very broad molecular weight distributions. This indicates that two or more kinds of active species were generated in these systems. We speculate that some of binaphtholate ligands must be removed from chromium center to generate active species and that the various extents of Cr–O bond cleavage may result in a variety of active species to produce polyethylenes with broad molecular weight distributions. The catalytic activity of the **1**/MMAO system shows strong dependence on the Al/Cr ratio, and the highest activity (1.5×10^4 g mol^{-1} h^{-1} atm^{-1}) was observed at a Al/Cr ratio of 100 (Table 3). With increasing the Al/Cr ratio, the molecular weight of the resulting polyethylene tends to decrease, implying that the molecular weight of the polyethylene decrease with loss of the binol ligands from the chromium center. The polymerization temperature also affects the activity of the **1**/MMAO system and this system was found to be the most active at room temperature (Table 4). All the polyethylenes obtained by **1** exhibited similar melting points typical for the linear polyethylene.

In order to heterogenize the catalyst system, we tried to support the complex **1** on the silica. A solution of **1** in toluene was stirred at 45 °C in the presence of silica (Sylopol952). The green colored **1** was absorbed on the silica, and the supported catalyst was activated with MMAO (Al/Cr = 100). The silica-supported **1**/MMAO system exhibited the activity of 2.6×10^4 g mol^{-1} h^{-1} atm^{-1}, almost twice as high as that of the homogeneous system even at 90 °C.

The catalysts **1**/MMAO and **1** supported on silica surface showed no activity or a little catalytic activity for polymerization of methyl methacrylate, methyl acrylate, styrene, acrylonitrile, isoprene and 1-pentene.

3. Conclusion

We prepared a new chromium binaphtholate complex, $[Li(THF)]_3[Cr(binol)_3]$ (**1**). The complex **1** was revealed to have a propeller-like framework similar to those of the corresponding rare earth derivatives. The complex **1** showed moderate catalytic activities for ethylene polymerization upon activation with MMAO and DEAC to give polyethylenes with extremely broad molecular weight distributions. When **1** was supported on the silica surface, activity increased to two times higher than that of the homogeneous **1**/MMAO system.

4. Experimental

4.1. General considerations

Because of air and moisture sensitivity of organochromium compounds, all the manipulations were carried out under a dry Ar atmosphere, using standard Schlenk techniques. Solvents such as THF and n-C_6H_{14} were distilled over Na–K alloy–benzophenone under Ar. Toluene was purified by distillation over Na–benzophenone under Ar before use. The elemental analysis was carried out on a Perkin–Elmer 2400 series II CHN–O analyzer after sealing the sample in the Sn foil under Ar. The gel permeation chromatography (GPC) measurements for polyethylene were carried out using a WATERS 150C model equipped with Shodex-HT806M. The GPC curve was calibrated with standard polystyrene. 1,2,4-Trichlorobenzene was used as an eluent at 140 °C.

*4.2. Preparation of $[Li(THF)]_3[Cr(binol)_3]\cdot3(toluene)$ (**1**)*

To a solution of *rac*-1,1′-bi-2-naphthol (Aldrich) (5.39 g, 18.8 mmol) in 100 ml of THF was added ^{n}BuLi (Kanto Chemical) (37.7 mmol, two equivalents) in C_6H_{14} (23.7 ml) at 0 °C via syringe. The reaction mixture was stirred overnight at room temperature (r.t.) to become a white slurry. The slurry containing lithium binaphtholate (123.7 ml, 18.82 mmol, three equivalents) was added to the solution of $CrC1_3(THF)_3$ (Aldrich) (2.35 g, 6.27 mmol) in THF (150 ml) via syringe at 0 °C. The mixture was allowed to warm to r.t. and stirred there overnight. Tetrahydrofuran was removed under reduced pressure and the residue was extracted with $C_6H_5CH_3$. After $C_6H_5CH_3$ was removed, the crude products were recrystallized from THF–$C_6H_5CH_3$ to give green plate crystals of **1** in 6.1% yield (0.54 g, 0.38 mmol). Anal. Calc. for $C_{93}H_{84}CrLi_3O_9$: C, 78.75; H, 5.97. Found: C, 77.39; H, 6.99%.

*4.3. Crystallographic study of **1***

The crystal of **1** suitable for X-ray diffraction sealed in a glass capillary under an Ar atmosphere was mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo–K_α radiation. Three standard reflections were chosen and monitored every 150 reflections. Measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. Empirical absorption correction was carried out based on an azimuthal scan.

The structure of **1** was solved by the direct methods [24]. In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were given in the same temperature factor as that of the carbon atoms to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package. All the non-hydrogen atoms except for carbon atoms of three $C_6H_5CH_3$ were refined anisotropically. The carbon atoms of the $C_6H_5CH_3$ were refined isotropically. All hydrogen atoms were not refined.

The pertinent detail of data collection and the final cell dimensions for **1** are given in Table 5.

Table 5
Crystal data and data collection parameters

Complex	$[Li(THF)]_3[Cr(binol)_3]\cdot 3(toluene)$ (**1**)
Empirical formula	$C_{93}H_{84}CrLi_3O_9$
Formula weight	1418.50
Temperature (°C)	23
Crystal system	Triclinic
Space group	$P\bar{1}$ (#2)
a (Å)	15.332(6)
b (Å)	19.48(2)
c (Å)	15.249(5)
α (°)	97.13(6)
β (°)	119.66(2)
γ (°)	93.36(7)
V (Å^3)	3889(4)
Z	2
Radiation	Mo–K_α
Crystal size (mm)	$0.6 \times 0.3 \times 0.1$
Abs. coefficient (cm^{-1})	2.06
Scan mode	$\omega - 2\theta$
Scan speed (° min^{-1})	16
Scan width (°)	$1.00 + 0.30\tan\theta$
$2\theta_{max}$ (°)	55
Unique data [$I > 3\sigma(I)$]	6023
Number of variables	850
R	0.094
R_w	0.095
Goodness-of-fit	1.99

4.4. Polymerization of C_2H_4 with Cr complexes

A mixture of Cr complex (0.01–0.075 mmol) and distilled $C_6H_5CH_3$ (30 ml) was added to MMAO (Tosoh Akzo Co., 1.0–7.5 mmol) or DEAC, TIBAL (Ethyl Corporations, 1.0–7.5 mmol). The mixture solution was degassed and the polymerization started by introducing C_2H_4 at 1 atm. The polymerization mixture was quenched with large amount of MeOH containing a small amount of HCl. The precipitate was centrifuged, filtered, and dried in vacuo. The white solid was collected.

4.5. Polymerization of C_2H_4 with Cr complexes supported on silica surface

The supporting silica (Sylopol952 grade, specific surface area 300 m^2 g^{-1}, pore volume 1.6 cm^3 g^{-1}, mean particle diameter 80 Å) was purchased from Grace Davison and calcinated at 600 °C for 24 h under N_2 flow. The complex **1** (0.2 wt.%) was supported on the silica in $C_6H_5CH_3$ at 45 °C for 2 h. Then MMAO (Al/Cr = 100) was added and the mixture was stirred at 45 °C for 2 h. After the removal of the solvent, the supported catalyst was suspended in isobutane and C_2H_4 was introduced to the suspension to the start polymerization. The mixture was kept at 90 °C under C_2H_4 pressure of 14 atm for 1 h. The white solid was collected.

5. Supplementary material

Crystallographic data for the structural analysis of **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 169508. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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