

Synthesis, Structure, and Olefin Polymerization Catalysis of a Novel Vanadium(III) 1,1'-Bi-2-naphtholate Complex

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ABSTRACT: The reaction of VCl_3 with (*S*)-(-)- Na_2 (binol) (binol = 1,1'-bi-2-naphtholate) gave a new vanadium(III) complex, $[Na(OEt_2)]_3[V(binol)_3]$ (Fig. 1). The X-ray crystallographic structure of this complex (Complex 1) in Figure 1 reveals its propeller-like structure, which is similar to those of the reported rare earth analogues. The complex showed moderate catalytic activities for ethylene polymerization upon activation with modified methylaluminoxane (MMAO) and with diethyl-

aluminum chloride (DEAC). The Complex 1/DEAC system also catalyzed the polymerization of propylene to give atactic polypropylene with low activity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1659–1662, 2003

Key words: crystal structures; polyethylene; poly(propylene)

INTRODUCTION

Several vanadium based polymerization catalyst systems are known for their specific selectivity. For example, a heterogeneous Ziegler-type $VCl_4/AlEt_2Cl$ system is a rare example of a syndiospecific catalyst for propylene polymerization.¹ Since Kaminsky reported highly active homogeneous zirconocene catalysts for olefin polymerization, a major part of the homogeneous Ziegler catalysts are based on metallocene type complexes of group IV metals.^{2–4} In contrast, simple vanadocene complexes such as Cp_2VCl and Cp_2VCl_2 combined with methylaluminoxane (MAO) do not show activities for olefin polymerizations but show high activities for the polymerization of conjugated diene.⁵ Recently, homogeneous catalysts of vanadium having various ligand sets, such as tris(acetylacetonato)vanadium,⁶ (aryloxo)(imido)vanadium complexes,⁷ CGC type complexes,⁸ chelating diamido complexes,⁹ and 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridinevanadium.¹⁰ We selected a binaphtholate ligand as an O,O-chelating ligand, which should improve the crystallinity of the vanadium complex to ease its isolation and should also bring a chiral coordinating environment to the catalyst metal center. Here we report the synthesis, structure, and ethylene polymerization activities of a new trivalent vanadium(III) binaphtholate complex.

EXPERIMENTAL

Because of the air and moisture sensitivity of organometallic complexes, all of the manipulations were carried out under pure, dry argon, using standard Schlenk techniques. Solvents such as tetrahydrofuran, n-hexane, and diethyl ether were distilled from Na/K-benzophenone under argon prior to use. Toluene was purified by distillation from sodium-benzophenone. All solvents were stored over sodium. Nuclear magnetic resonance (NMR) spectra were measured on a JEOL JNM-LA400 (400MHz) spectrometer. Chemical shifts of ¹³C-NMR were determined with reference to the carbon resonances of benzene (δ 128.0 ppm) in benzene-*d*. The molecular weights of the polypropylenes were determined by gel permeation chromatography (TOSOH SC-8010) calibrated by using standard poly(methylmethacrylate) P(MMA), and using tetrahydrofuran (THF) as an eluent at 40°C. Gel permeation chromatography (GPC) measurements of polyethylene were performed on a Waters C150 by Nihon-Polyolefin Co. Ltd., Japan. The glass transition temperature (T_g) and the melting temperature (T_m) of polymers were obtained using a Seiko SSC5100-DSC22C apparatus.

Preparation of $[Na(OEt_2)]_3[V(binol)_3]$ (Complex 1)

To a sodium (1.03 g, 44.8 mmol) dispersion in 60 mL of THF was added a solution of (*S*)-(-)-1,1'-bi-2-naphthol (5.12 g, 17.8 mmol) in THF (15 mL) at 0°C. The reaction mixture was warmed up to room temperature and stirred overnight. After filtration to remove the excess sodium, the resulting solution was cooled to 0°C again, and then VCl_3 (0.75 g, 47.7 mmol) was added.

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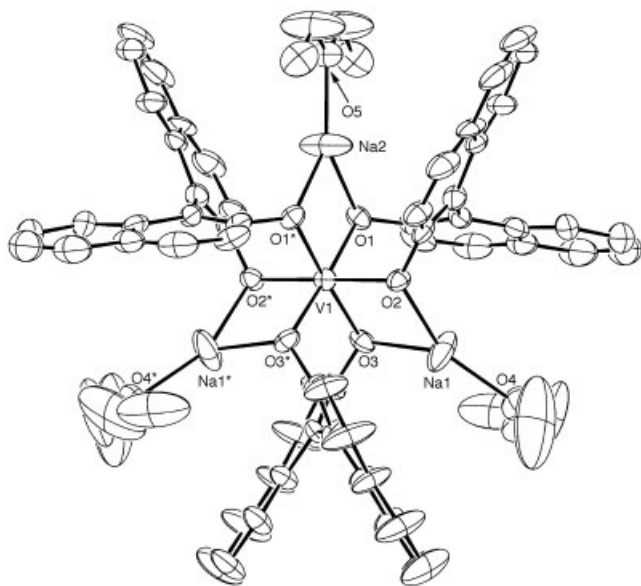


Figure 1 Molecular structure of $[\text{Na}(\text{OEt}_2)_3][\text{V}(\text{binol})_3]$ (Complex 1).

The reaction mixture was warmed up to room temperature and stirred overnight. After filtration to remove the salts, THF was distilled away under reduced pressure. The residue was extracted with diethyl ether, and recrystallized from an ether/hexane mixed solvent to give light green crystals of Complex 1 (0.543 g, 8.6%).

Crystallographic study of Complex 1

A crystal of Complex 1 suitable for X-ray diffraction was sealed in a glass capillary under an argon atmosphere and mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using $\text{MoK}\alpha$ 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 Complex 1 was solved by direct methods.¹¹ 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 non-hydrogen atoms were refined anisotropically. All hydrogen atoms were not refined.

The pertinent details of data collection and the final cell dimensions for Complex 1 are provided in Table I.

Crystallographic data for the structural analysis of Complex 1 have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 183907. Copies of this information may be obtained free of charge

TABLE I
Crystal Data and Data Collection Parameters

Category	Characteristics
complex	$[\text{Na}(\text{OEt}_2)_3][\text{V}(\text{binol})_3]$ (1)
formula	$\text{C}_{72}\text{H}_{66}\text{Na}_3\text{O}_9\text{V}$
formula weight	1195.22
crystal system	monoclinic
space group	$C2/c$ (#15)
a , Å	21.687(7)
b , Å	15.411(6)
c , Å	19.705(5)
β , °	100.36(2)
V , Å ³	6478(3)
Z	4
radiation	$\text{Mo K}\alpha$
crystal size, mm	$0.2 \times 0.2 \times 0.2$
abs. coeff, cm^{-1}	0.229
scan mode	ω -2 θ
temp, °C	23
scan speed, deg/min	8
scan width, deg	$1.37 + 0.30\tan\theta$
$2\theta_{\text{max}}$, deg	55
unique data [$I > 3\sigma(I)$]	1580
no. of variables	385
R	0.062
R_w	0.063
GOF	1.90

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 <http://www.ccdc.cam.ac.uk>).

Polymerization of ethylene with vanadium complex

An aluminum compound was added to a complex dissolved in dry toluene, and the mixture was stirred

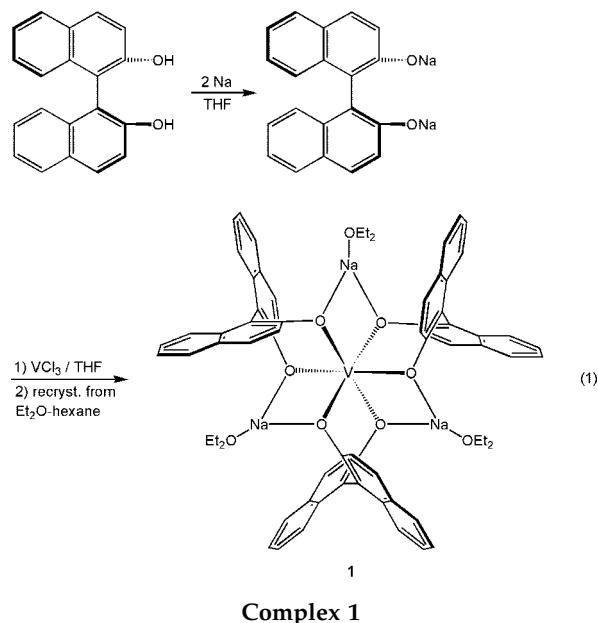


TABLE II
Selected Bond Distances (Å) and Angles (°)
of Complex 1

Bond Distances (Å)	
V(1)—O(1) 2.011 (6)	V(1)—O(2) 2.016 (6)
V(1)—O(3) 2.000 (6)	Na(1)—O(2) 2.209 (7)
Na(1)—O(3) 2.173 (8)	Na(1)—O(4) 2.15 (1)
Na(2)—O(1) 2.183 (8)	Na(2)—O(5) 2.13 (1)
Bond Angles (°)	
O(1)—V(1)—O(1)* 87.5 (4)	O(1)—V(1)—O(2) 89.6 (2)
O(1)—V(1)—O(2)* 90.8 (2)	O(1)—V(1)—O(3) 92.4 (2)
O(1)—V(1)—O(3)* 176.1 (3)	O(1)*—V(1)—O(2) 90.8 (2)
O(1)*—V(1)—O(2)* 89.6 (2)	O(1)*—V(1)—O(3) 176.1 (3)
O(1)*—V(1)—O(3)* 92.4 (2)	O(2)—V(1)—O(2)* 179.5 (4)
O(2)—V(1)—O(3) 85.3 (3)	O(2)—V(1)—O(3)* 94.3 (3)
O(2)*—V(1)—O(3) 94.3 (3)	O(2)*—V(1)—O(3)* 85.3 (3)
O(3)—V(1)—O(3)* 87.9 (3)	O(2)—Na(1)—O(3) 76.8 (3)
O(2)—Na(1)—O(4) 153.1 (6)	O(3)—Na(1)—O(4) 128.7 (8)
O(1)—Na(2)—O(1) 79.1 (3)	O(1)—Na(2)—O(5) 140.5 (2)
O(1)*—Na(2)—O(5) 140.5 (2)	

for 5 min. Ethylene was condensed into the line. Polymerization was carried out at a temperature range from -78°C to room temperature for 10–60 min. The polymerization mixture was quenched with large amount of methanol containing a small amount of 0.1N hydrochloric acid. The precipitate was centrifuged and dried *in vacuo*. GPC and differential scanning calorimetry (DSC) measurements were performed.

Polymerization of propylene with vanadium complex

An aluminum compound was added to a complex dissolved in dry toluene, and the mixture was stirred for 5 min. Propylene was condensed into the line. Polymerization was carried out at 0°C or 20°C for 4 h. The polymerization mixture was quenched with large

amount of methanol containing a small amount of 0.1N hydrochloric acid. The precipitate was centrifuged and dried *in vacuo*. NMR and GPC measurements were performed.

RESULTS AND DISCUSSION

Synthesis and structure of $[\text{Na}(\text{OEt}_2)_3[\text{V}(\text{binol})_3]$ (Complex 1)

The reaction of VCl_3 with three equivalents of sodium 1,1'-bi-2-naphtholate $[\text{Na}_2(\text{binol})]$ prepared from (*S*)-(-)-1,1'-bi-2-naphthol (binolH_2) and sodium gave a vanadium binaphtholate complex, $[\text{Na}(\text{OEt}_2)_3[\text{V}(\text{binol})_3]$ (Complex 1), as light green crystals in 8.6% yield. Even the similar 1:1 reaction of VCl_3 with $\text{Na}_2(\text{binol})$ did not produce the corresponding monochloride complex, $\text{VCl}(\text{binol})$, but yielded Complex 1 in low yield.

Figure 1 shows the molecular structure of Complex 1 determined by X-ray crystallography. The selected bond distances and angles are summarized in Table II. The vanadium atom is coordinated by three (*S*)-binaphtholate ligands in a Λ geometry, in which sodium atoms bridge two binol ligands. A crystallographical C_2 axis passes through the V1, Na2, and O5 atoms. The main framework of Complex 1 is similar to those of the rare earth,^{12,13} aluminum,^{12,13} and chromium analogues.¹⁴ The sodium atoms in Complex 1 have a three-coordinated structure, like the lithium atoms in the chromium analogue $[\text{Li}(\text{thf})_3[\text{Cr}(\text{binol})_3]]$,¹⁴ in contrast to the three-coordinated ones in the rare earth and aluminum complexes. This can be attributed to the lower Lewis acidity of vanadium and chromium than of rare earth metals and aluminum. The geometries of the sodium atoms in Complex 1 are planar because the sums of angles around the sodium atoms are nearly 360° [358.6° (Na1) and 360.1° (Na2)]. The averaged V—O distance of Complex 1 is 2.009 Å, which is significantly longer than those of the neutral

TABLE III
Ethylene Polymerization with $[\text{Na}(\text{OEt}_2)_3[\text{V}(\text{binol})_3]$ /Cocatalyst Systems

Cocat.	[Al]:[V] (mol/mol)	Temp. ($^{\circ}\text{C}$)	Time (min)	Activity (^a)	M_n^b (/ 10^4)	M_w/M_n^b	T_m^c ($^{\circ}\text{C}$)
MAO	100	r.t.	15	trace			
	300	r.t.	15	4.7			119
MMAO	100	r.t.	60	6.2	0.5	77	
	300	r.t.	30	6.7	0.3	400	
AlEt_2Cl	10	-78	10	trace			
	10	0	10	4.4	1.8	37	139
	10	r.t.	10	8.5	1.4	21	135
	10	50	10	5.3	0.7	34	132
AlEt_3	10	r.t.	15	no polym.			
	50	r.t.	15	no polym.			

Conditions: ethylene = 1 atm, solvent = 15 mL of toluene.

^a [$\text{kg PE mol}^{-1} \text{ V atm}^{-1} \text{ h}^{-1}$]

^b Determined by GPC.

^c Determined by DSC.

TABLE IV
Propylene Polymerization with $[\text{Na}(\text{OEt}_2)_3[\text{V}(\text{binol})_3]]$ /
Cocatalyst Systems

Cocat.	[Al]:[V] (mol/mol)	Temp. (°C)	Activity (^a)	M_n^b (/10 ⁴)	M_w/M_n^b
MAO	100	20	no polym.		
	100	0	4.7		
MMAO	100	20	no polym.		
	100	0	no polym.		
AlEt ₂ Cl	10	0	trace		
	10	20	26	11.0	1.54
	3	20	no polym.		
	5	20	no polym.		
	10 ^c	20	63	2.3	10.0
	50 ^c	20	no polym.		
	100	20	no polym.		

Conditions; cat = 0.03 mmol, propylene = 1 atm, solvent = 15 mL toluene, time = 4 h.

^a [PP mol⁻¹ V atm⁻¹ · h⁻¹].

^b Determined by GPC.

^c Cat = 0.09 mmol and solvent = 30 mL toluene.

aryloxovanadium(III) complexes such as $[\text{V}(2\text{-tert-buthylphenolate})_3(\text{thf})_2]$ [average 1.870(6) Å] and $[\text{V}(\text{OMes})_3(\text{thf})_2]$ [1.862(5) Å] [15], and the V—O distance is similar to that in $\{[\text{Li}(\text{OEt}_2)]_3\text{V}(\text{biphenolate})_3\}$ (2.003(8) Å).¹⁵

Polymerization of ethylene and propylene

The catalytic activity of Complex 1 for ethylene polymerization was studied in toluene (Table III). Complex 1 showed no catalytic activity for ethylene polymerization without a cocatalyst. Although Complex 1 was almost insoluble in toluene, it was dissolved in toluene upon the addition of organoaluminum cocatalysts such as modified methylaluminoxane (MMAO), diethylaluminum chloride (DEAC), and triethylaluminum (TEA) to form orange homogeneous solutions. In combination with MMAO or DEAC, Complex 1 catalyzed the polymerization of ethylene with moderate activities (≈ 8.5 kg PE mol⁻¹ V atm⁻¹ h⁻¹). It is notable that a relatively low Al : V ratio of 10 : 1 is enough for the activation of Complex 1 in the Complex 1/DEAC system. In contrast, the corresponding Complex 1/TEA system was inactive under similar conditions. The Complex 1/MMAO system produced polyethylenes with low molecular weights and very broad molecular weight distributions, while the polymers obtained by the Complex 1/DEAC system had higher molecular weights and narrower distributions. The melting points ranged from 132°C to 139°C, which are in accord with the values for typical linear polyethylene.

The chiral and optically active Complex 1 showed catalytic activity for the polymerization of propylene, as summarized in Table IV. In contrast to the ethylene polymerization by Complex 1, MAO and MMAO

were not very effective cocatalysts in propylene polymerization by Complex 1. DEAC was found to be more effective than MAO and MMAO. The activity of Complex 1/DEAC was lower than that of typical vanadium catalysts. This catalyst system showed the highest activity of 63 g PP mol⁻¹ V atm⁻¹ h⁻¹ at the Et₂AlCl : Complex 1 molar ratio of 10 : 1. Although we expected that this chiral catalyst system would produce isotactic polypropylene, the obtained polypropylenes were atactic as indicated by ¹³C-NMR spectra. Because Complex 1 has a six-coordinated structure and no labile ligands such as chloride, we speculate that one or more binol ligand should dissociate from the metal to generate active species. This would result in the formation of a sterically less crowded active site, on which the steric effect of the chiral ligand would not be significant enough to distinguish the prochiral surface of the monomer.

CONCLUSIONS

We prepared a novel vanadium binaphtholate complex, $[\text{Na}(\text{OEt}_2)_3[\text{V}(\text{binol})_3]$ (Complex 1). Complex 1 was revealed to have a propeller-like framework similar to those of the corresponding rare earth derivatives. It showed moderate catalytic activities for ethylene polymerization upon activation with MMAO and DEAC to give polyethylenes with broad molecular weight distributions. The Complex 1/DEAC system also polymerized propylene, although the activity was low and it gave atactic polymer.

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