



A vanadium(V) complex with a tetradentate [OSSO]-type bis(phenolato) ligand: Synthesis, structure, and ethylene polymerization activity

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ARTICLE INFO

Article history:

Received 19 September 2008

Received in revised form 16 October 2008

Accepted 7 November 2008

Available online 13 November 2008

Keywords:

Vanadium

Chiral complex

Ethylene polymerization

Phenolato ligand

ABSTRACT

Reaction of VOCl_3 with racemic *trans*-1,2-dithiacyclohexanediyl-2,2'-bis(6-*tert*-butyl-4-methylphenol) affords the chiral-at-metal vanadium(V) complex $[\text{V}\{(\text{C}_6\text{H}_2\text{O}-6\text{-}i\text{-tert-Bu-4-Me})_2\text{S}_2\text{C}_6\text{H}_{10}\}\text{OCl}]$ (**1**). The molecular structure of **1** was established by single crystal X-ray diffraction, which shows a *cis-α* configuration of the ligand around the vanadium center. Upon activation with MAO, **1** was found to be a highly active catalyst for the polymerization of ethylene, but was not active in the polymerization of propene and styrene. The influence of temperature and cocatalyst ratio on polymerization activity was studied.

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1. Introduction

The use of vanadium in bioinorganic catalysis [1], asymmetric catalysis [2], and polymerization catalysis [3] has sparked an interest in the study of its coordination chemistry. A recurring object of study is the interaction between vanadium and sulfur [4], since vanadium–sulfur interactions are present in several vanadium-containing enzymes [5] and vanadium complexes bearing chiral ligands are active in the asymmetric oxidation of prochiral sulfides to sulfoxides [2c]. The unique properties of vanadium in Ziegler–Natta-type olefin polymerization catalysis have ensured a continuing interest in their development in spite of generally lower activities that result from a tendency towards reduction to low-valent, inactive species [3,6]. Recently, several research groups have reported new post-metallocene vanadium catalysts featuring aryloxy-based ligands [7], since aryloxides are known to give highly active olefin polymerization catalysts [8] and are of potential interest as chemical models for the active site of vanadium nitrogenase [9]. We have recently introduced a new family of chiral-at-metal group IV metal catalysts precursors supported by linear, tetradentate 1,ω-dithiaalkanediy-bridged bis(phenolato) [OSSO] ligands, which show interesting reactivity towards a variety of olefins [10]. Here, we report the synthesis, structure and olefin polymerization study of a vanadium(V) complex that contains a *trans*-1,2-dithiacyclohexane-bridged bis(phenolato) ligand.

2. Results and discussion

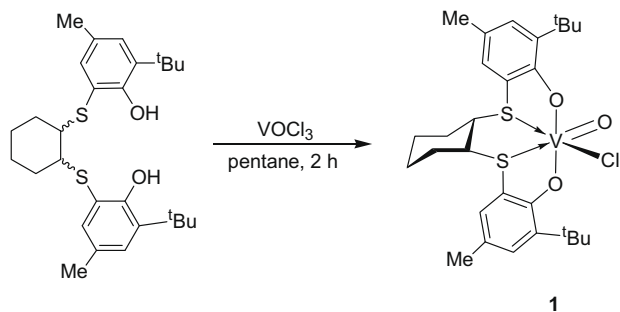
The vanadium complex $[\text{V}\{(\text{C}_6\text{H}_2\text{O}-6\text{-}i\text{-tert-Bu-4-Me})_2\text{S}_2\text{C}_6\text{H}_{10}\}\text{OCl}]$ (**1**) was synthesized by reacting the racemic bis(phenol) 2,2'-{ $\text{HOC}_6\text{H}_2-6\text{-}i\text{-tert-Bu-4-Me}\}$ $\text{S}_2\text{C}_6\text{H}_{10}$ [11] with VOCl_3 (Scheme 1). Complex **1** precipitates from pentane solution and can be isolated as a dark green to dark blue powder in excellent yield, which dissolves to give an intense blue solution (UV–vis: $\lambda_{\text{max}} = 635$ nm, $\epsilon_{\text{max}} = 3575$).

Complexes bearing [OSSO]-type ligands adopt helical *cis-α* and *cis-β* conformations, which render the complex chiral at the metal center [12]. Due to the different substituents on the vanadium center, both *cis-α* and *cis-β* configurations for **1** have C_1 -symmetry. Thus, for the *cis-β* configuration there are eight possible stereoisomers, whereas for C_2 -symmetrical *cis-α* coordination mode of the ligand four stereoisomers are possible. From the observation of a single set of product resonances in ^1H and ^{13}C NMR spectra (C_6D_6) follows that the complexation of the racemic ligand to the VOCl fragment proceeds diastereoselectively. The ^1H NMR spectrum shows four singlets for the *tert*-butyl and methyl resonances and four doublets ($^4J_{\text{HH}} = 1.0$ and 1.8 Hz) for the aromatic protons, which confirms the C_1 -symmetry of **1**.

To determine the configuration of **1**, single crystals suitable for X-ray analysis were grown from a 1:1 mixture of THF and pentane at room temperature. Complex **1** crystallizes as a conglomerate rather than a racemic mixture. The Δ,S,S isomer is shown in Fig. 1. The [OSSO] ligand adopts a *cis-α* conformation around the octahedral vanadium(V) center. Analogous group IV [OSSO] ML_2 complexes [13] and structurally characterized vanadium(II–IV)

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Scheme 1.

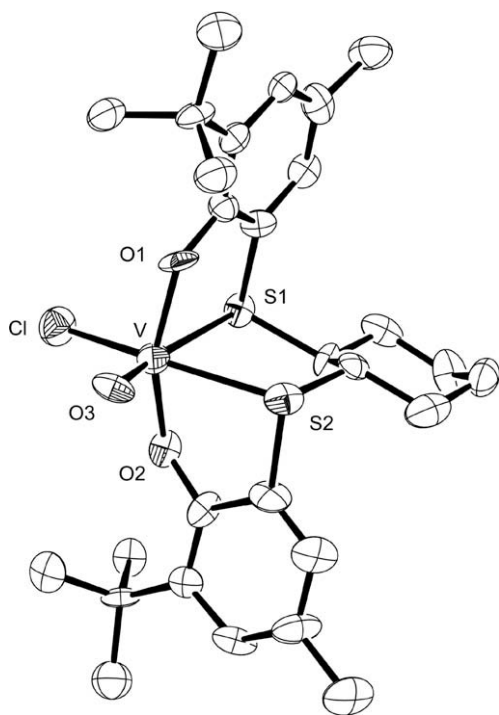


Fig. 1. ORTEP diagram of complex **1**. Hydrogen atoms were omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): V–O1 1.831(7), V–O2 1.855(7), V–O3 1.662(7), V–Cl 2.245(4), V–S1 2.715(3), V–S2 2.530(4), O1–V–O2 156.1(3), S1–V–S2 79.44(10), O3–V–Cl 105.1(3).

complexes bearing tetradentate $[(C_6H_4S)_2(S_2C_2H_4)]$ and $[(C_5H_4N)_2(S_2C_2H_4)]$ ligands published by Rehder and coworkers also adopt *cis-α* conformations [14]. In complex **1** the aryloxy moieties in the apical positions are slightly bent away from their ideal positions ($O1-V-O2 = 156.1(3)^\circ$) and the dithiacyclohexane bridge in the equatorial plane coordinates in an asymmetrical fashion. With 1.662(7) Å the V–O3 bond distance is ca. 0.2 Å shorter than its phenolic counterparts, clearly showing its double bond character.

The V–S bond distance of the sulfur atom *trans* to the chloride ligand (V–S2 = 2.530(4) Å) falls within the range commonly observed for V(I–V)-thioether complexes (2.45–2.60 Å), but is significantly shorter in comparison to $[Ti(OSSO)Cl_2]$ complexes (2.61–2.63 Å) [11]. In contrast, the large *trans*-influence of the vanadyl oxygen causes elongation of the V–S1 bond to 2.715(3) Å. A similar *trans*-influence has also been reported for mono-sulfur-bridged bis(phenolato) complexes $[V\{(C_6H_2O-6-tert-Bu-4-Me)_2S\}O(L)]_2$ (L = OH, OEt) [15].

Upon activation with MAO complex **1** does not polymerize propene and shows only trace activity for the polymerization of sty-

Table 1
Ethylene polymerization with complex **1**.

Entry ^a	Al/V ^c	T (°C)	Yield (g)	Activity ^d	$M_n (\times 10^{-5})^e$	M_w/M_n^e
1	1500	10	0.20	65	5.52	1.8
2	2600	10	0.23	74	–	–
3	800	25	0.82	265	5.46	2.1
4	1500	25	1.03	332	5.65	2.3
5	2600	25	1.21	390	5.15	2.1
6	1500	40	1.30	419	4.61	2.6
7	2000	40	1.38	445	5.69	3.3
8	2600	40	1.20	387	5.84	3.0
9 ^b	2600	40	2.40	774	5.60	2.8
10	2600	60	0.52	168	9.46	2.7

^a Polymerization conditions: 3.1 μmol of complex **1**, 300 mL toluene, $t = 60$ min, $p(\text{ethylene}) = 3$ bar.

^b $p(\text{ethylene}) = 5$ bar.

^c Activated by MAO.

^d $\text{kg mol}^{-1} \text{h}^{-1}$.

^e Determined by HT GPC.

rene, but ethylene is polymerized with good activity to very high molecular weight polyethylene (Table 1). Polymerization activity and polydispersity increase with temperature up to 40 °C, after which a sharp drop in activity is observed, likely due to decomposition of the catalyst. At 40 °C the activity is rather insensitive to the amount of cocatalyst, whereas at 25 °C and below a larger excess of MAO clearly benefits polymerization activity. Since **1** does not react instantaneously with an excess of $AlMe_3$ at room temperature, a higher Al/V ratio may serve to generate the active species quicker at lower temperatures. An increase of ethylene pressure from 3 to 5 bar results in a twofold increase of polymerization activity (entry 9).

3. Experimental

3.1. General considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk-line and glovebox techniques. THF and pentane were distilled from sodium benzophenone ketyl; toluene for polymerization was purified by distillation from Na/K alloy. Deuterated solvents were dried over calcium hydride and degassed prior to use. Oxovanadium trichloride was used as received. Methylaluminoxane (MAO) in toluene (10 wt.%) was purchased from Crompton, GmbH and ethylene (3.0 quality) was purchased from Air Liquide. NMR spectra were recorded on a Bruker DRX 400 spectrometer (1H 400.1 MHz, ^{13}C 125.5 MHz). Chemical shifts were referenced internally using residual solvent resonances and reported relative to tetramethylsilane. Assignments were verified by correlated spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of this department. GPC measurements were performed on a Polymer Laboratories PL 220 system operated at 150 °C equipped with 3 PLGel mixed-bed columns and a RI-detector using narrow polystyrene standards for calibration. 1,2,4-Trichlorobenzene, stabilized with 2 mg mL^{-1} Irganox 1010, was used as eluent at a flow rate of 1 $mL \text{ min}^{-1}$.

3.2. Synthesis of $[(C_6H_2O-6-tert-Bu-4-Me)_2S_2C_6H_{10}VOCl]$ (**1**)

A solution of $VOCl_3$ (368 mg, 2.12 mmol, 80 μL) in 13 mL of pentane was added dropwise to a stirred solution of $C_6H_2OH-6-tert-Bu-4-Me)_2S_2C_6H_{10}$ (1.00 g, 2.12 mmol) in 30 mL of pentane at –60 °C. Green coloration and precipitation of a dark solid occurred immediately. The suspension was stirred for 2 h while slowly warming up to room temperature. The reaction mixture was evacuated, washed twice with 20 mL of pentane and dried *in vacuo* to give **1** in 98% yield as a dark green powder (1.19 g, 2.08 mmol).

Blue-black crystals suitable for X-ray analysis were obtained from slow evaporation of a 1:1 THF/pentane solution at room temperature. ^1H NMR (C_6D_6 , 25 °C): δ 0.15 (m, 2H, CH C_6H_{10}), 0.92 (m, 2H, CH C_6H_{10}), 1.18 (m, 2H, CH C_6H_{10}), 1.52 (m, 1H, CH C_6H_{10}), 1.62 (s, 9H, C(CH₃)₃), 1.64 (s, 9H, C(CH₃)₃), 1.67 (m, 1H, CH C_6H_{10} , overlapping), 2.02 (s, 3H, CH₃), 2.08 (s, 3H, CH₃), 2.12 (m, 1H, CHS), 2.37 (m, 1H, CHS), 6.76 (d, $^4J_{\text{HH}} = 1.0$ Hz, CH C_6H_2), 6.92 (d, $^4J_{\text{HH}} = 1.0$ Hz, CH C_6H_2), 7.11 (d, $^4J_{\text{HH}} = 1.8$ Hz, CH C_6H_2), 7.22 (d, $^4J_{\text{HH}} = 1.8$ Hz, CH C_6H_2). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 20.73 (CH₃), 21.03 (CH₃), 24.98 (CH₂ C_6H_{10}), 25.04 (CH₂ C_6H_{10}), 29.67 (C(CH₃)₃), 30.11 (C(CH₃)₃), 31.34 (CH₂ C_6H_{10}), 32.96 (CH₂ C_6H_{10}), 35.59 (C(CH₃)₃), 35.73 (C(CH₃)₃), 52.73 (CHS), 54.64 (CHS), 111.58 (arom.), 120.31 (arom.), 129.44 (arom.), 129.90 (arom.), 131.62 (arom.), 131.71 (arom.), 134.12 (arom.), 134.78 (arom.), 136.44 (arom.), 139.07 (arom.), 171.93 (arom.), 172.56 (arom.). UV-vis: $\lambda_{\text{max}} = 635$ nm ($\epsilon_{\text{max}} = 3575$, $c = 1.16 \times 10^{-4}$ M, Et₂O). Anal. Calc. for $\text{C}_{28}\text{H}_{38}\text{ClO}_3\text{S}_2\text{V}$: C, 58.68; H, 6.68. Found: C, 58.78; H, 7.24%.

3.3. General polymerization procedure

Polymerizations were carried out in a 600 mL semi-automated double jacket metal reactor. The reactor was filled with 280 mL toluene and flushed with ethylene until the solvent was saturated, after which one part of the MAO was added to reactor via a pressure buret. The polymerization was started by addition of 20 mL catalyst solution, which was pre-activated with the other part of the MAO. Ethylene consumption was monitored by means of a mass flow meter and ethylene pressure was kept constant at 3 bar. The reaction was stopped by venting the reactor and the polymer was precipitated in 500 mL methanol acidified with 10 mL of 15 wt.% HCl. The polymer was filtered off and dried at 60 °C under vacuum to constant weight.

3.4. Crystallographic data for **1**

Complex **1** cocrystallizes with one molecule of pentane and one molecule of THF. Crystallographic data of $[\Delta,S,S\text{-}(\text{C}_6\text{H}_2\text{O}-6\text{-tert-Bu-4-Me})_2\text{S}_2\text{C}_6\text{H}_{10}\text{VOCl}] \times \text{C}_4\text{H}_8\text{O} \times \text{C}_5\text{H}_{12}$ were obtained with a Bruker AXS SMART CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation (0.71073 Å) using ω scans. The data reductions as well as absorption corrections were carried out using the SMART program [16a]. The structures were solved by direct methods and Fourier difference methods using the programs SHELXS-86 [16b] and SHELXL-96 [16c]. Anisotropic thermal parameters were refined for all of the non-hydrogen atoms; the cocrystallized solvent molecules were refined with isotropic thermal parameters. Crystallographic data and refinement parameters of $[\Delta,S,S\text{-}1 \times 0.5\text{C}_4\text{H}_8\text{O} \times 0.5\text{C}_5\text{H}_{12}]$: black blocks, $0.50 \times 0.17 \times 0.10$ mm, $\text{C}_{32.5}\text{H}_{48}\text{ClO}_{3.5}\text{S}_2\text{V}$, $M_r = 645.22$, space group $P2_12_12_1$, orthorhombic, $a = 12.101(5)$ Å, $b = 16.490(7)$ Å, $c = 17.777(7)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 3547(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.208$, $\mu(\text{Mo } K\alpha) = 0.503$ mm⁻¹, $T = 130(2)$ K, θ range = 2.04° – 24.09° , 23331 reflections collected, 5578 unique reflections ($R_{\text{int}} = 0.1791$), index ranges $-11 \leq h \leq 13$, $-18 \leq k \leq 17$, $-20 \leq l \leq 20$, 5578 data, 17 restraints, 357 parameters, GOF (F^2) = 0.939, $R_1 = 0.1485$ and $wR_2 = 0.2248$ for all data, $R_1 = 0.0917$ and $wR_2 = 0.2076$ for $I > 2\sigma(I)$, Flack parameter = 0.06(8), largest residual densities 0.879 and -0.436 e Å⁻³.

4. Supplementary material

CCDC 702251 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from the

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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