Journal of Molecular Catalysis A: Chemical 381 (2014) 148–160

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Vanadium(V) complexes with chiral tridentate Schiff base ligands derived from *1S,2R*(+)-2-amino-1,2-diphenylethanol and with acetohydroxamate co-ligand: Synthesis, characterization and catalytic activity in the oxidation of prochiral sulfides and olefins

Grzegorz Romanowski*, Jaromir Kira, Michał Wera

Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, PL-80952 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 14 October 2013
Accepted 16 October 2013
Available online 26 October 2013

Keywords:
Vanadium(V)
Schiff base
Sulfoxidation
Styrene
Cyclohexene

ABSTRACT

A series of vanadium(V) complexes with chiral tridentate Schiff base ligands were prepared. Five-coordinate complexes were obtained by a single condensation of *1S,2R*(+)-2-amino-1,2-diphenylethanol with salicylaldehyde and its derivatives. Furthermore, six-coordinate complexes were synthesized with the same Schiff base ligands and also with monoanionic bidentate acetohydroxamate co-ligand. The complexes were characterized by elemental analysis and by their IR, CD, UV–vis, one- (^{1}H, ^{51}V) and two-dimensional (COSY, gHSQC and NOESY) NMR spectra. The X-ray analyses of the ligand, *1S,2R*(+)-2-[(1-hydroxy-1,2-diphenylethyl)iminomethyl]-4-nitrophenol, **7**, and its complex, (acetohydroxamato-κ^2O,O'){*1S,2R*(+)-2-[(1-oxido-1,2-diphenylethyl)iminomethyl]-4-nitrophenolato-κ^3N,O,O'}oxidovanadium(V), **7b**, have been also performed. The five-coordinate vanadium(V) complexes have ability to catalyze the oxidation of prochiral sulfides [PhSR (R = Me, Bz)] in good yields and enantiomeric excesses. Moreover, catalytic activity of these complexes and also those derived from *1S,2S*(−)-1,2-diphenyl-1,2-diaminoethane were tested in the oxidation of styrene and cyclohexene.

1. Introduction

The coordination chemistry of vanadium is of interest for number of biological and therapeutic reasons. Vanadium complexes have many attractive features that constitute the basis for their utility as insulin-mimetic drugs stimulating glucose uptake [1], potential anti-tumor agents exerting preventive effects against carcinogenesis [2] or promising agents against some of parasitic diseases [3]. The presence of vanadium [4–8] and hydroxamic acids [9] in the active sites of some biological enzymes has also resulted in increased interest in the study of their structural properties.

Optically active N-salicyl-β-amino alcohol Schiff bases are considered as a member of the well-known “privileged ligands” group [10]. These ligands can be readily synthesized from naturally available chiral amino acids [11] and have been widely employed as catalysts in the enantioselective trimethylsilylcyanations [12] and oxidation of organic sulfides [13,14], the asymmetric alkynylation of aldehydes [13], the epoxidation of cyclooctene [15], the oxidation of bromide [16], the stereoselective synthesis of cyclic ethers [16,17] and oxidative kinetic resolution of α-hydroxy esters [18].

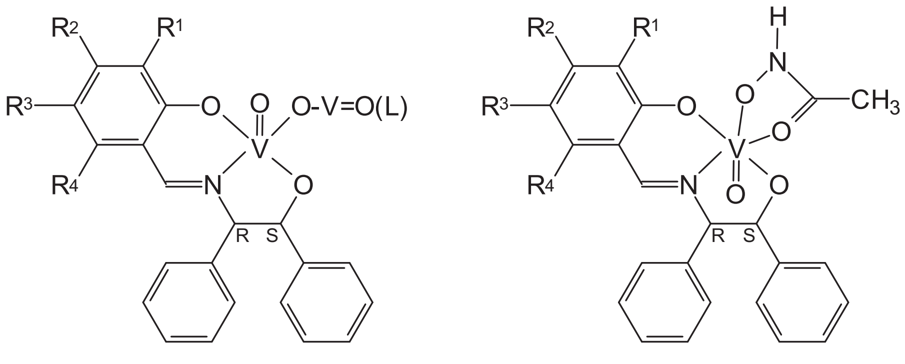
Chiral sulfoxides possess a wide range of biological activities, *e.g.* antimicrobial properties [19], inhibition of biosynthesis of uric acid [20] and gastric acid secretion [21] or regulation of cholesterol catabolism [22]. As efficient chiral auxiliaries they lead to many important asymmetric transformations [23] and are valuable starting materials in asymmetric synthesis as well as important chiral ligands in enantioselective catalysis. Since epoxides are key starting materials for a wide variety of products the epoxidation of alkenes is one of the most widely studied reactions in organic chemistry. Their importance arises mainly from the ring opening of epoxides, which allows straightforward elaboration to useful generation of new carbon–carbon bonds [24]. Some review articles that focus on the vanadium catalysts (also complexes with Schiff base ligands) in epoxidation of many olefinic compounds have been published recently [25].

In continuation of our studies on synthesis, structure, spectroscopic and catalytic properties of vanadium(V) complexes incorporating chiral tridentate Schiff base ligands [26–28], we prepared a series of new five-coordinate oxidovanadium(V) complexes with ONO donor Schiff base ligands, products of monocondensation of *1S,2R*(+)-2-amino-1,2-diphenylethanol with aromatic *o*-hydroxyaldehydes. Moreover, the same Schiff base ligands were used to synthesize six-coordinate complexes with monoanionic bidentate acetohydroxamate co-ligand (Fig. 1). Their

---

* Corresponding author. Tel.: +48 585235102; fax: +48 585235012.
E-mail address: grzegorz.romanowski@ug.edu.pl (G. Romanowski).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.10.011



1a - 10a **1b - 10b**

Fig. 1. Structural formulae of vanadium(V) complexes.

spectroscopic properties by 1D and 2D NMR, UV–vis, CD and IR have been examined. The catalytic potential of five-coordinate complexes in the asymmetric oxidation, *i.e.* enantioselective sulfoxidation of methyl phenyl sulfide (PhSMe) and benzyl phenyl sulfide (PhSBz), utilizing aqueous 30% H_2O_2 as oxidant, has been studied. Moreover, they were also used as catalysts in the oxidation of olefins, *i.e.* styrene and cyclohexene using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant. For comparison, the catalytic activity in styrene and cyclohexene oxidation of very similar dioxidovanadium(V) Schiff base complexes derived from *1S,2S*(−)-1,2-diphenyl-1,2-diaminoethane, synthesized and characterized earlier [26], under the same reaction conditions has been also tested. Crystal and molecular structure of the ligand, *1S,2R*(+)-2-[(1-hydroxy-1,2-diphenylethyl)iminomethyl]-4-nitrophenol, **7**, and its complex, (acetohydroxamato-κ^2*O,O′*){*1S,2R*(+)-2-[(1-oxido-1,2-diphenylethyl)iminomethyl]-4-nitrophenolato-κ^3*N,O,O′*}oxidovanadium(V), **7b**, are also reported.

2. Experimental

2.1. Measurements

All chemicals and reagents were obtained from commercial sources and used without further purification unless stated otherwise. Carbon, hydrogen and nitrogen contents were determined on a Carlo Erba MOD 1106 elemental analyzer. IR spectra of solid samples (KBr pellets) were run on a Bruker IFS 66, and electronic spectra on the Perkin-Elmer LAMBDA 18 spectrophotometer. Circular dichroism spectra were measured with a Jasco J-815 spectropolarimeter. NMR spectra were obtained in CD_3OD solutions with a Varian Mercury-400BB (400 MHz) spectrometer using TMS (^{1}H) and $VOCl_3$ (^{51}V) as reference compounds. A Perkin-Elmer Clarus 500 gas chromatograph with a DB-5 capillary column (30 m × 0.25 mm × 0.25 mm) and FID detector were used to analyze the reaction products. The identity of the products was confirmed using a GC–MS model Shimadzu GCMS-QP2010 SE.

2.2. X-ray investigations

Diffraction measurements were made on a Oxford Diffraction Gemini R Ultra Ruby CCD, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 295(2) K and determination of the crystal class, orientation matrix, and accurate unit cell parameters was performed according to established procedures. Data collection and processing parameters are summarized in Table S1. The structure was solved by direct methods and refined with all data on F^2 with SHELXTL [29]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and treated as riding atoms with fixed thermal parameters.

2.3. Catalytic activity

2.3.1. Sulfoxidation

In typical procedure, to a solution of catalyst (0.010 mmol) in 3 ml of CH_2Cl_2/MeOH solution (7:3, v/v), sulfide (1.00 mmol) was added at room temperature or −20 °C, together with 1,3,5-trimethoxybenzene as internal standard. Aqueous 30% H_2O_2 was added (1.10 mmol) by small portions and the resulting mixture was stirred. After the appropriate reaction time, the solution was quenched with 2 ml of sodium sulphite solution (0.1 M) and extracted with CH_2Cl_2 (3 × 5 ml). The combined organic layers were evaporated to dryness. The solid product dissolved in $CDCl_3$ was analyzed (yield and *ee* value) by ^{1}H NMR spectra in the presence of chiral shift reagent Eu(hfc)$_3$ (where Hhfc is 3-(heptafluoropropylhydroxymethylene)-(+)-camphoric acid) [30].

2.3.2. Oxidation of olefins

In typical procedure, styrene or cyclohexene (1.00 mmol), an oxidant (3.00 mmol), *i.e.* aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) – 5.5 M in decane, and catalyst (0.010 mmol) were taken in 10 ml of CH_3CN and the reaction was carried out for 6 h at 80 °C. The reactions were monitored by GC and the yields were recorded as GC yield based on the starting styrene or cyclohexene. The identity of oxidation products was confirmed by GC–MS. The influence of amounts of catalyst and oxidant were also studied to check their effect on the conversion and selectivity of the reaction products.

2.4. Synthesis of vanadium(V) complexes

The complexes were obtained in the following example procedure. A solution of 5 mmol of *1S,2R*(+)-2-amino-1,2-diphenylethanol in absolute ethanol (10 ml) was added with stirring to 5 mmol of an aromatic *o*-hydroxyaldehyde (salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 4,6-dimethoxysalicylaldehyde, 5-methylsalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2,4-dihydroxybenzaldehyde, 3-*tert*-butylsalicylaldehyde, 2-hydroxy-1-naphthaldehyde) in absolute EtOH (20 ml) and heated under reflux for 1 h. In case of **1b**–**10b**, acetohydroxamic acid (5 mmol) in absolute EtOH (10 ml) was also added with an aldehyde. Then a vanadium(V) oxytriethoxide (5 mmol) in absolute EtOH (10 ml) was added and stirred at room temperature for 2 h. After cooling in a fridge a