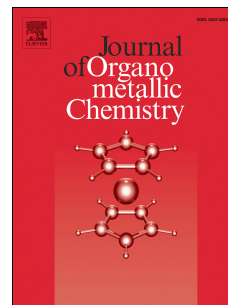


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New Salan and Salen Vanadium Complexes: Syntheses and Application in Sulfoxidation Catalysis

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Abstract

New diamine bis-phenol compounds of salan- (HOPh''CHNH(CH₂)₂NHCHPh''OH, Ph' = 2,4-(CMe₂Ph)₂C₆H₂, **H₂L1**) and salen-type (HOPh''CHN(CHPh)₂NCHPh''OH, Ph'' = 2,4-^tBuC₆H₂, **H₂L2** and HOPh''CHN(1,1'-2-binaphthyl)NCHPh''OH, Ph'' = 2,4-^tBuC₆H₂, **H₂L3**), as well as their oxido vanadium derivatives are described. VO(OⁱPr)₃ was used as starting material for the preparation of [VO(OⁱPr)(L1)], **1**, [VO(OⁱPr)(L2)], **3**, and (μ-O){[VO(OⁱPr)(μ-O)(L3)VO]}₂, **5**. An intramolecular redox process involving the reduction of V(V) to V(IV) converts **3** into [VO(L2)], **4**. The reactions of **1** and **5** with Me₃SiCl give [VOCl(L1)], **2**, and [VOCl(L3)], **6**, respectively. All complexes were tested as catalysts for the sulfoxidation of thioanisole using H₂O₂ as oxidant. In general, the compounds display high activity and selectivity, although salan-type complexes (**1** and **2**) perform better. Comparison of complexes **5** and **6** shows the monomeric species is more active and selective. Well-defined complexes, **5** and **6**, display better catalytic performance than systems using 1:1.5 [VO(acac)₂] and H₂L3.

Introduction

Sulfoxides are an important class of compounds that may be obtained by catalytic oxidation of thioethers using transition metal complexes as catalysts [1]. Among other early transition metals used, vanadium catalyzed sulfoxidation reactions gained prominence, as vanadium is a cheap metal, present in biological systems, and active when H₂O₂ is used as oxidant [2]. Despite the important contributions given to this research field, which include the implementation of bio-inorganic methodologies as well as successful kinetic resolution processes [3], the use of well-defined asymmetric sulfoxidation catalysts still presents several drawbacks [4]. The requirement of laborious and expensive separation procedures and the use of chlorinated solvents, low temperature and controlled addition of oxidants are some of the issues that need further development [4,5]. The implementation of new catalytic systems and a better understanding of their reactivity, through the identification of the species involved and the study of the reactions' mechanisms, using either computational or experimental methods, is thus an essential strategy to attain more efficient sulfoxidation systems.

As part of our research in transition metal catalyzed oxidation reactions [6], we focused on catalytic sulfoxidation of thioethers and described tripodal diamine bis(phenolate) oxidovanadium(V) complexes that are very selective (up to 98%) towards thioanisole sulfoxidation using H₂O₂ as oxidant, without requiring the use of chlorinated solvents [7,8].

Aiming to evaluate the properties of new vanadium complexes in sulfoxidation of thioanisole, we report here the synthesis of new salen- and salan-type vanadium complexes with different ligand frames as binaphthyl and phenyl groups, along with bulky o-phenolate substituents.

Results and Discussion

Synthesis and characterization

The ligand precursors used in this work are depicted in Figure 1. H₂L1 is a salan-type diamine bisphenol that was prepared by a single step Mannich condensation reaction of 2,4-(CMe₂Ph)₂PhOH, formaldehyde and ethylene diamine, adapting a literature procedure [9]. The ¹H and ¹³C-{¹H} NMR spectra of H₂L1 are in agreement with a Cs-symmetric species, displaying only two sets of resonances for the Me and for the Ar-CH groups, one singlet for the ArCH₂N groups and one singlet for the NCH₂CH₂N moiety. H₂L2 and H₂L3 are salen-type diimine bisphenols that were synthesized through reactions of 3,5-di-tert-butyl-2-hydroxybenzaldehyde with the

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