

Racemic and chiral expanded salen-type complexes derived from biphenol and binaphthol: Salbip and salbin

Joseph M. Grill, Joseph H. Reibenspies, Stephen A. Miller *

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, United States

Received 3 March 2005; revised 18 March 2005; accepted 18 March 2005

Available online 12 May 2005

Abstract

The reaction of 2-fluoronitrobenzene with 2,2'-biphenol or (*R*)-binaphthol, followed by reduction and subsequent reaction of the resulting diamine with two equivalents of a salicylaldehyde, affords expanded salen-type ligands having backbones based on biphenol or binaphthol: salbipH₂, (*R*)-salbinH₂ and (*R*)-salbin(*t*-Bu)₄H₂. Deprotonation of these ligands with sodium methoxide or potassium hydride, followed by metallation with M(OAc)₂ (M = Mn, Co, Ni, or Cu), affords the corresponding metal complexes in good yield (61–85%). The species containing Mn, Co, and Ni all have distorted octahedral geometry, as determined by X-ray crystallography. The ethereal oxygen atoms occupy two coordination sites with metal–oxygen distances ranging from 2.19 to 2.36 Å. The imine nitrogen atoms are *trans* to each other in the solid state, an impossible geometry in traditional salen-type complexes. The species containing Cu are distorted square planar and show much longer metal–ethereal oxygen distances ranging from 2.79 to 3.22 Å. The manganese complexes are competent catalysts for the epoxidation of olefins.

© 2005 Elsevier B.V. All rights reserved.

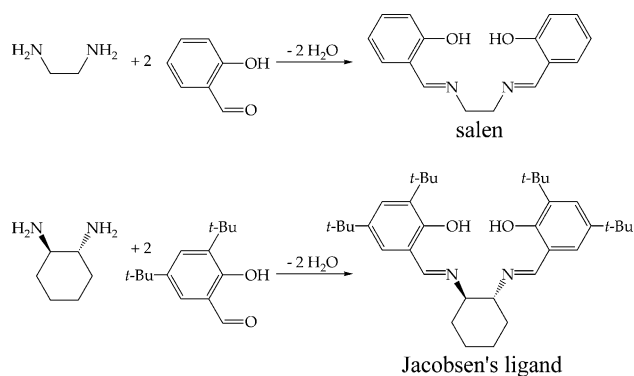
Keywords: Salen; Catalytic epoxidation; *R*-binaphthol; 2,2'-Biphenol; Chiral

1. Introduction

The salen ligand is a versatile, widely used ligand for homogeneous transition metal mediated catalysis [1–11]. The simple salen ligand is synthesized by the condensation of two equivalents of salicylaldehyde with one equivalent of ethylene diamine (Scheme 1) [12]. Transition metal complexes of salen have been known since at least 1931 [12–15], but the most intense investigations have occurred since chiral variants were first applied to asymmetric catalysis in the early 1990s [16,17]. Modified salen complexes have served as catalysts in varied reactions such as asymmetric epoxidation [2], copolymerization of carbon dioxide with epoxides [5,6], and hydrolytic kinetic resolution of racemic epoxides [18,19], depending on the metal employed.

Jacobsen and coworkers [17,20,21] reported the synthesis of a very successful chiral variant of the salen ligand (Scheme 1). The corresponding manganese (III)-based catalyst is useful for the epoxidation of *cis*-disubstituted olefins in the presence of commercial bleach [2]. Overall the asymmetric epoxidation of *cis*-olefins with Jacobsen's catalyst is effective but the optimized conditions rely on a large catalyst loading (6 mol%) and the use of 4-phenylpyridine-*N*-oxide as an additive in order to obtain high enantiomeric excesses (*ee*'s). Gilheany and coworkers [22–25] reported the synthesis of a series of chiral chromium–salen complexes capable of epoxidizing *trans*-disubstituted olefins with poor to good *ee*'s, but the system suffers from limited substrate tolerance and requires high catalyst loading (10 mol%). Furthermore, it requires an expensive additive and an expensive oxidant (PhIO). The *ee*'s obtained by Gilheany range from 10% to 92% depending on the catalyst, the conditions, and the substrate, and the isolated yields

* Corresponding author. Tel.: +979 8452543; fax: +979 8459452.
E-mail address: samiller@mail.chem.tamu.edu (S.A. Miller).



Scheme 1. Synthesis of the original salen ligand and Jacobsen's ligand.

in most cases are 40% or less. The need for new catalysts that are more efficient, less expensive, and more selective is evident.

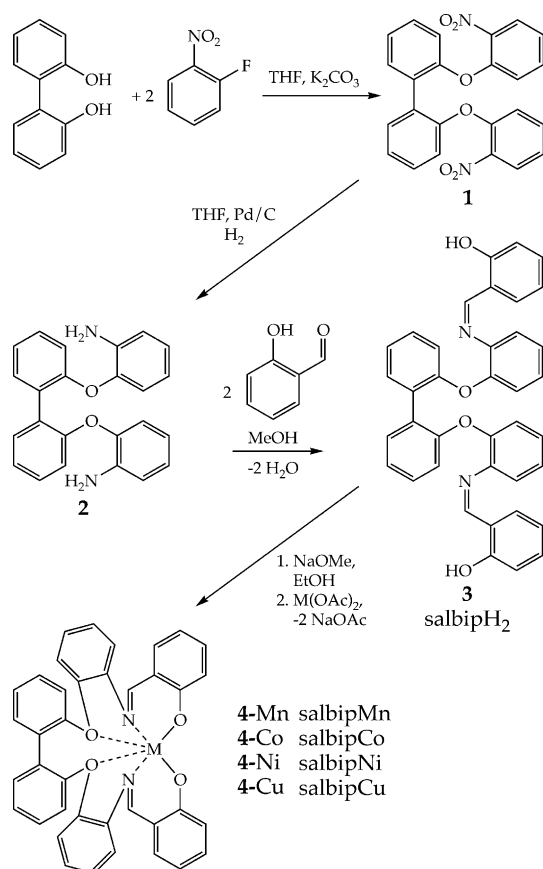
We have general goals of designing and synthesizing new chiral ligands in an efficient and economical manner on large scale. In this work, we exploit an underutilized nucleophilic aromatic substitution reaction for the synthesis of a novel class of racemic and chiral expanded salen-type ligands derived from 2,2'-biphenol and *R*-binaphthol. These new ligands are readily coordinated to manganese, cobalt, nickel, and copper. The X-ray crystal structures of six of these complexes are reported and interpreted. The catalytic abilities of these species are briefly investigated and compared to those of existing systems.

2. Results and discussion

2.1. Complex synthesis and X-ray crystallography

2-fluoronitrobenzene reacts readily with a variety of mildly nucleophilic species, such as alcohols or amines, to generate a new carbon-nucleophile bond and hydrofluoric acid [26]. In order to synthesize new salen-type ligands, we took advantage of this facile nucleophilic aromatic substitution reaction (Scheme 2). 2,2'-biphenol reacts readily with 2-fluoronitrobenzene in refluxing THF to give the doubly arylated product **1**. Reduction of **1** with hydrogen using a palladium on carbon catalyst gives the previously unknown diamine **2** in excellent overall yield (97%).

Reaction of **2** with two equivalents of salicylaldehyde gives the corresponding dialdimine, **3** (Scheme 2). This ligand is an "expanded salen ligand" because it has the usual chelating atoms of salen (two imines, two aryl-oxides) plus two additional neutral donor atoms (ethers). However, since it is derived from salicylaldehyde and biphenol, the moniker salbipH₂ is applied. Facile deprotonation of **3** (salbipH₂) is accomplished with sodium methoxide in ethanol; subsequent exposure

Scheme 2. Synthesis of an expanded salen-type ligand (**3**, salbipH₂) and its coordination to metals.

to transition metal acetates affords salbipM coordination complexes (Scheme 2).

The X-ray structures of **4-Mn**, **4-Co**, **4-Ni** and **4-Cu** were obtained (Fig. 1). Crystallographic data are given in Table 1 and selected bond lengths and angles are given in Table 2. The complexes containing Mn, Co, and Ni have distorted octahedral geometries with *trans* nitrogen atoms. The observation of *trans* nitrogen chelation is quite unusual because in conventional salen complexes, *trans* coordination of the nitrogen atoms is geometrically impossible. The N–M–N angle increases with increasing atomic number (Mn, 159.9°; Co, 167.2°; Ni, 167.6°) as a consequence of the decreasing ionic radius of the metal. In **4-Mn**, **4-Co**, and **4-Ni**, the ethereal oxygen atoms are coordinated to the metal in the solid state. The increase in the N–M–N angle is accompanied by a decrease in average metal–ethereal oxygen distances, which are 2.36, 2.23 and 2.19 Å, respectively. The copper complex **4-Cu** has distorted square planar geometry and its ethereal oxygen atoms are apparently less strongly bound to the metal compared to the Mn, Co, and Ni species. The average metal–ethereal oxygen distance is quite large (2.79 Å) and a N–M–N angle of only 164.6° is observed.

Download English Version:

<https://daneshyari.com/en/article/1324168>

Download Persian Version:

<https://daneshyari.com/article/1324168>

[Daneshyari.com](https://daneshyari.com)