



Chiral calix-salen cobalt complexes, catalysts for the enantioselective dynamic hydrolytic kinetic resolution of epibromohydrin



Hiba Dandachi^{a,b}, Houssein Nasrallah^a, Farah Ibrahim^{a,b}, Xiang Hong^a, Mohamed Mellah^a, Nada Jaber^b, Emmanuelle Schulz^{a,c,*}

^a Equipe de Catalyse Moléculaire, Université Paris-Sud, ICMMO, UMR 8182, Orsay F-91405, France

^b Laboratoire de Chimie Médicinale et des Produits Naturels, Université Libanaise, Faculté des Sciences (1) et PRASE-EDST, Hadath, Beyrouth, Lebanon

^c CNRS, Orsay F-91405, France

ARTICLE INFO

Article history:

Received 24 July 2014

Accepted 7 September 2014

Available online 17 September 2014

Keywords:

Calix-salen

Cobalt complexes

Dynamic hydrolytic kinetic resolution

Asymmetric catalysis

Catalyst reuse

ABSTRACT

New calix-salen cobalt (III) complexes were synthesized as a mixture and as pure trimer or tetramer complexes. These cyclic complexes were used as catalysts to promote the dynamic hydrolytic kinetic resolution (HKR) of epibromohydrin in order to evaluate the effect of the cyclic structures size on the cooperative bimetallic interactions. Since the obtained catalysts were easily recovered from the reaction mixture by simple filtration, their efficiency was evaluated in recycling procedures. It was found that both cyclic oligomer complexes (trimer and tetramer) and the mixture of calix-salen complexes delivered the expected diol with high enantioselectivity and yield. Tetramer calix-salen cobalt complex proved to be the most active and selective catalyst of the series. In this case, an optimal conformation to allow the formation of bimetallic species activating respectively both the epoxide and water as nucleophile is probably responsible for an efficient dual activation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The high efficiency in terms both of activity and enantioselectivity of salen-derived complexes to achieve the formation of new bonds is well documented [1]. Such complexes have been indeed widely used, associated to numerous metallic precursors for the synthesis of valuable enantioenriched syntons [2] even at a large industrial scale [3].

Precisely in the context of epoxide ring-opening reactions [4], Jacobsen and his group demonstrated that catalysis occurred through cooperative bimetallic activation, with one metal centre acting as Lewis acid for epoxide activation, the other one as counterion for the nucleophile [5]. Numerous efforts have thus been devoted to the specific preparation of such catalysts that could favour this bimetallic interaction for efficient dual activation. For instance, salen-cobalt complexes have been modified as styrene derivatives for their homo- or copolymerization leading to either soluble or insoluble (recoverable) polymeric catalysts with catalytic sites placed in the space closed to each other [6]. Such complexes have been also immobilized in the nanocages of mesoporous

materials (SBA-16) leading to enhanced activity and enantioselectivity due to the confinement [7]. Modified salen-cobalt complexes have further been assembled through non-covalent interactions such as urea-urea hydrogen-bonding to favour bimetallic activation [8].

Other examples are currently based on the formation of cyclic oligomer structures incorporating two or more salen derivatives to promote bimetallic interactions, as privileged paths. Such cyclic salen complexes have been obtained by Jacobsen and his group via polycondensation reactions between disalicylaldehydes (separated by a flexible linker) and chiral diamines [9]. Greatly enhanced results in terms both of activity and enantioselectivity were obtained in the presence of these cyclic salen-cobalt catalysts, for various asymmetric epoxide ring-opening reactions. Trigol-bis(aldehyde) and chiral diamines have also been condensed to deliver chiral cyclic dimers for which the corresponding Co^{III}-complexes proved also to be efficient and recyclable catalysts in hydrolytic kinetic resolutions (HKR) [10]. Olefin metathesis has also been exploited as a useful tool for the synthesis of macrocyclic oligomeric multinuclear salen-cobalt catalysts to access efficient cooperative catalysis [11]. Salen-cobalt complexes have also been installed in an original way on the upper rim of a calix-arene scaffold and they demonstrated cooperative activation [12].

In our ongoing studies, we have developed an heterogeneization procedure of salen complexes modified in the 5,5'-position

* Corresponding author at: Equipe de Catalyse Moléculaire, Université Paris-Sud, ICMMO, UMR 8182, Orsay F-91405, France. Tel.: +33 169157356.

E-mail address: emmanuelle.schulz@u-psud.fr (E. Schulz).

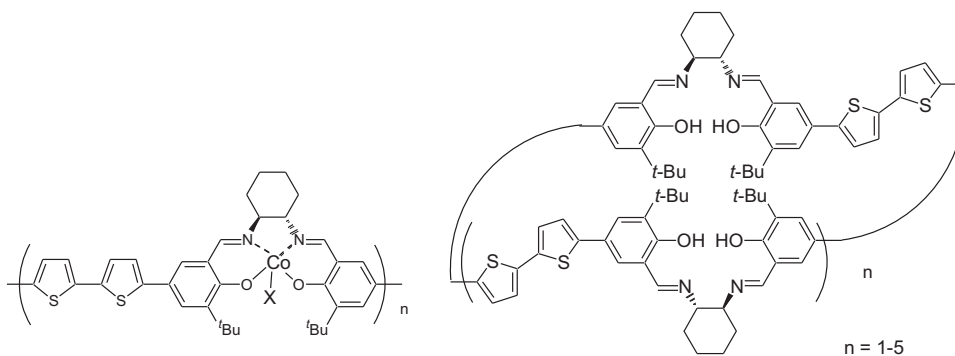


Fig. 1. Electrogenerated salen–cobalt complexes (1) and polycondensed (2) calix-salen chiral structures.

of the salicylaldehyde core by polymerizable thiophene moieties. Electrochemical [13] or chemical oxidation [14] delivered indeed corresponding insoluble oligomers that could be engaged in various asymmetric transformations according to the incorporated metal [15]. These insoluble catalysts proved particularly stable and promoted the hydrolytic kinetic resolution of various terminal epoxides (even in a multi-substrate recovery procedure) in an efficient way, without the need for a reactivation step. The recovery methodology involved either a simple filtration in a batch reactor [15d] or a flow procedure with the catalyst dispersed in a silica support [14]. Nevertheless, bimetallic activation in those immobilized salen systems as a pearl neck lace could remain doubtful, since the enantioselectivity and activity obtained for the hydrolytic kinetic resolution in these conditions did not reach the high levels achieved in the case of the corresponding monomeric precursors.

In this context we turned our attention towards the preparation of corresponding cyclic structures, called calix-salen, aiming at favouring cooperative multimetallic interactions. We have thus recently described the synthesis of new calix-salen derivatives via polycondensation reactions between various dialdehydes and enantiomerically pure diamines [16] and the use of the corresponding chromium complexes in ring opening of epoxides with trimethylsilylazide, in hetero-Diels Alder reactions, in dimethylzinc addition to aldehydes and in Henry reactions [17]. For these transformations, enantioselectivities could be indeed raised up in comparison to the values obtained from the linear counterparts.

Consequently, we report here the efficiency of calix-salen cobalt complexes in the hydrolytic kinetic resolution (HKR) of terminal epoxides, particularly for the dynamic HKR of epibromohydrin with a specific care on the effect of the cyclic structures size.

2. Results and discussion

For a direct comparison with the electrogenerated heterogeneous salen–cobalt complex (1, Fig. 1), we have firstly prepared the analogous cyclic ligand counterpart, by polycondensation between 5,5'-di(3-*tert*-butyl-2-hydroxy-benzaldehyde)-2,2'-bithiophene) and (*S,S*)-cyclohexane-1,2-diamine (2, Fig. 1) in ethanol [16]. The calix-salen was obtained in nearly quantitative yield and analyzed by Maldi-Tof spectroscopy as a mixture of cyclic oligomers from 2 to 6 repeating units. This mixture was then added to $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ salts and further oxidized in corresponding Co^{III} complexes (2- Co^{III} -OAc) by air oxidation in the presence of acetic acid.

The benchmark transformation used to evaluate the efficiency of both thiophene-derived salen catalysts is the hydrolytic kinetic resolution of epibromohydrin 3. This substrate undergoes indeed fast racemization in the HKR conditions and the resulting diol 4 can consequently be obtained with complete conversion since, in this case, kinetic hydrolytic resolution proceeds in dynamic mode. The

product can then be recovered and analyzed as acetonide derivative 5 for a straightforward determination of the transformation selectivity. Jacobsen and his group reported that 3-bromo-propane-1,2-diol was isolated in 93% yield and 96% ee, with 1.5 equiv. of H_2O in THF, in the presence of 2 mol% of the classical bis-*tert*-butylcyclohexyl-salen Co^{III} -OAc catalyst [18] (Scheme 1).

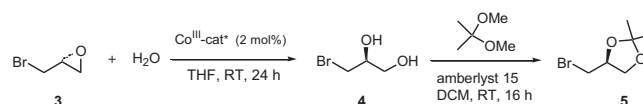
In these conditions, catalyst 1 delivered the targeted product in nearly quantitative isolated yield and with up to 87% ee. This heterogeneous catalyst was easily recovered, could be reused without the need for a reactivation step, and was highly stable, even after 11 consecutive catalytic runs [15d]. Accordingly, the Co^{III} catalyst derived from the thiophene-salen based ligand structure 2 provided acetonide 5 in 96% yield with 80% ee.

Based on these results, our previously synthesized calix-salen derivatives 7, [16] prepared from disalicylaldehydes possessing a central phenyl backbone, were tested for their propensity to promote this transformation, as a mixture of cyclic cobalt-containing catalysts, but also as pure catalysts, after ligand isolation.

Disalicylaldehyde 6 was thus prepared in nearly quantitative yield by Suzuki coupling between 1,4-dibromo-benzene and 3-*tert*-butyl-2-hydroxy-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzaldehyde obtained from 2-*tert*-butylphenol.

Subsequent condensation with (*S,S*)-cyclohexane-1,2-diamine delivered calix-salen 7 as a mixture of oligomers possessing 2, 3, 4 or 5 salen units. Controlling the dilution of this last step of the transformation allowed for the targeted synthesis of either the dimeric or the tetrameric species as major product. The calix-salen derivatives could be hence isolated in their pure form, after chromatographic separation on silicagel [16] (Scheme 2).

Cobalt complexes were prepared from these ligands in two steps, in the presence of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ to yield corresponding calix-salen Co^{II} complexes 8 which were further oxidized with acetic acid under oxygen atmosphere. Due to the very poor solubility of these structures in organic solvents, a precise structural characterization was not straightforward. Specifically, the reaction performed between cobalt salts and the dimeric calix-salen ligand that should deliver 9- Co_2 -OAc led to a mixture soluble in dichloromethane. Comparative UV measurements were thus performed that produced UV-vis spectra showing almost no difference between the ligand and the targeted complex with two absorption maxima at about 258 and 305–310 nm for both species (see UV spectra in ESI). This was confirmed by mass analyses indicating that no cobalt was coordinated into the salen moieties. Both samples



Scheme 1. Hydrolytic kinetic dynamic resolution of epibromohydrin 3.

Download English Version:

<https://daneshyari.com/en/article/65345>

Download Persian Version:

<https://daneshyari.com/article/65345>

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