



Novel bis-Salen Mn(III) chiral complexes of rigid structure axially coordinated with bis-diphenolate and bis-diamine for epoxidation of unfunctionalized olefins

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ABSTRACT

A series of bis-Salen Mn(III) chiral complexes of rigid structure axially coordinated with bis-diphenolate and bis-diamine ligands were synthesized and their catalytic performances in asymmetric epoxidation of indene and α -methylstyrene were investigated in detail. Compared with Jacobsen's catalyst and the corresponding monomer salen Mn(III) catalyst, bis-Salen Mn complex showed higher activity and enantioselectivity under the same reaction conditions. A point worth emphasizing was that the bis-diphenolate axially coordinated bis-Salen Mn catalysts afforded remarkable increases of ee values in the absence of axial base NMO for the asymmetric epoxidation of olefins, especially for the epoxidation of indene (ee: from 55% to 100%), however, the axial base is indispensable for the bis-diamine axially coordinated bis-Salen Mn(III) catalysts, these performance might attribute to the rigid difference of the structure. Furthermore, the catalyst could be conveniently recovered and reused at least five times without significant losses of both activity and enantioselectivity. Specially, it could also be efficiently used in large-scale reactions with superior catalytic disposition being maintained at the same level, which possessed the potentiality for application in industry.

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Introduction

Asymmetric epoxidation of unfunctional olefins catalyzed by chiral salen Mn(III) complex has proved to be one of the most useful reactions in organic synthesis.^{1,2} Great success has been achieved for the asymmetric epoxidation using monomeric Jacobsen chiral salen Mn(III) complex as catalysts.^{3–7} However, a major problem associated with the monomeric catalyst system is the separation and recycling of the chiral catalyst. To address this issue, significant effort has been made to 'heterogenize' the Jacobsen chiral salen Mn(III) complex, such as grafting Chiral Mn(salen)Cl complex monomeric catalyst systems onto organic polymers;⁸ inorganic supports clays,⁹ MCM-41,¹⁰ SBA-15,¹¹ activated silica,¹² zeolites;¹³ organic polymer-inorganic hybrid materials.^{14–17} Unfortunately, although such modified catalysts show the advantages of easy separation and reuse, significant gaps exist in the scope of these methodologies. First, the leaching of salen Mn(III) complexes during reaction is often troublesome. Second, most of modified catalysts are less efficient than their corresponding unmodified catalysts, partly, because of the inaccessibility of the reagents to the active centers in the heterogeneous reaction.¹⁸ Thus, the

development of a novel class of catalyst with high activity, enantioselectivity, and easily separation from the reaction mixture is highly desirable. As we know, appropriately increased molecular weight of the catalysts could lower their solubility in certain solvents, thus opening an opportunity for product isolation and catalyst recovery.¹⁹ Additionally, increasing the catalytically active metal centers of the catalysts could enhance the catalytic activities and recover the catalyst easily.^{20,18} Recently, a series of homogeneous recyclable oligomeric or dimeric chiral salen Mn(III) complexes with chemical bond connection have been synthesized.^{21–25} These kind of catalysts obtained comparable or higher conversion and ee values to the Jacobsen's catalyst in asymmetric epoxidation of unfunctionalized olefins in the presence of axial bases, and part of the di-salen Mn(III) or oligo-salen Mn(III) were recyclable. However, in most of the dimeric or oligomeric chiral salen Mn(III) complexes, only one or several carbon atoms connected the two chiral salen Mn(III) complex.

Also, axial bases have a pronounced effect on the reactivity and selectivity of the enantioselective epoxidation reaction. However, the axial base is gradually degraded during the epoxidation procedure.²⁶ The exceptional phenomenon has been reported by our group recently. It was reported that remarkably increased conversions and ee values were obtained without the axial base NMO in the asymmetric epoxidation of unfunctionalized olefins catalyzed

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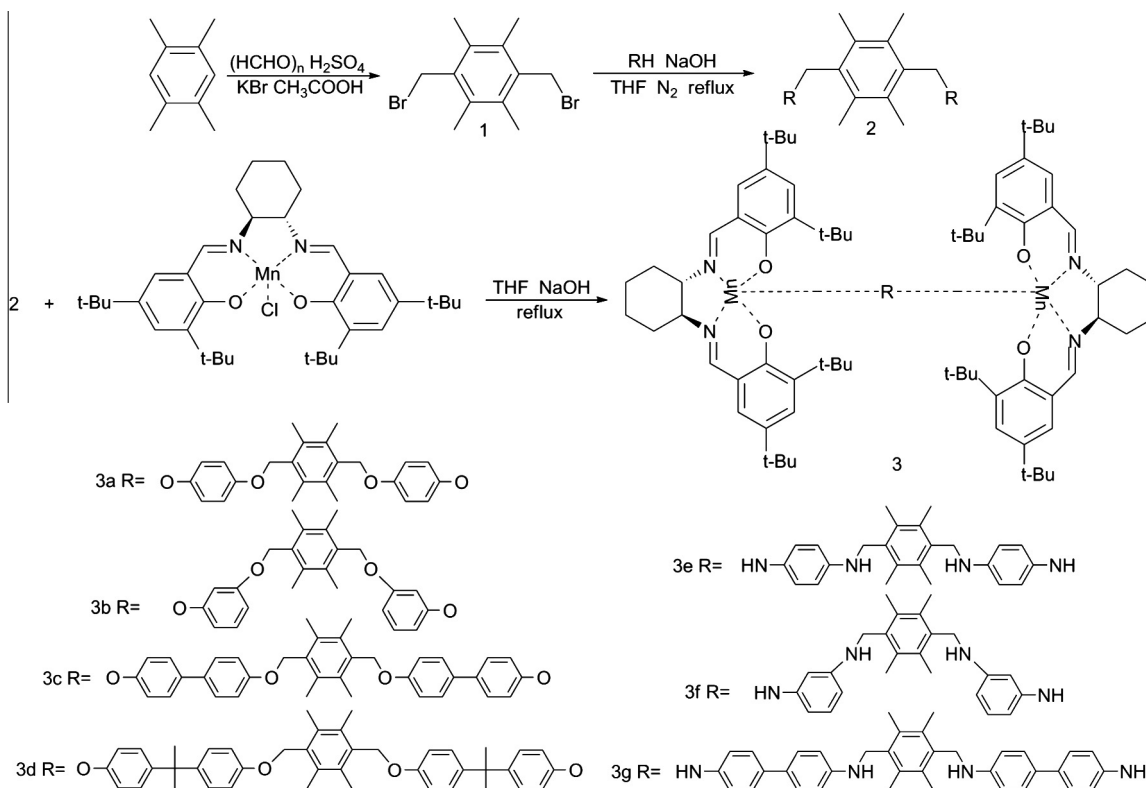
by phenoxy-modified ZPS-PVPA immobilized chiral salen Mn(III) complex.¹⁴ At the same period, List reported that adding such a ligand (NMO) to the reaction mixture resulted in a dramatically reduced enantioselectivity and reactivity in the alkene epoxidation catalyzed by salen Mn(III) phosphate complexes.²⁷ Zhang et al. has reported that axial coordination of the catalyst could improve the enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins.²⁸ Based on these, we herein designed and synthesized a series of rigid structure bis-Salen Mn chiral complexes which were axially coordinated with bis-diphenolate and bis-diamine substituted 1,4-bis(bromomethyl)-2,3,5,6-tetra-methylbenzene derivatives in this Letter (Scheme 1). The prepared catalysts displayed superior catalytic activities and enantioselectivities to the Jacobsen's catalyst in the asymmetric epoxidation of α -methylstyrene and indene with *m*-CPBA as oxidant. Specially, remarkably increased conversions and ee values were obtained without NMO in the asymmetric epoxidation of olefins catalyzed by the bis-diphenolate axially coordinated bis-Salen Mn catalysts, however, the bis-diamine axially coordinated bis-Salen Mn catalysts do not have this phenomenon.

Results and discussion

The catalytic activities and enantioselectivities of catalysts **3a–3g** were explored for the asymmetric epoxidation of indene and α -methylstyrene using *m*-CPBA as an oxidant system. Jacobsen's catalyst and monomer chiral salen Mn(III) catalysts **4a–4b** as outlined in Scheme 2 were also examined for comparison purposes, and the results are summarized in Table 1. All reactions proceeded smoothly, and the bis-Salen Mn chiral catalysts (**3a–3g**) showed higher ee values compared with Jacobsen's catalyst and the monomer chiral salen Mn(III) catalysts. As described in Table 1, the bis-Salen Mn chiral catalyst **3c** showed higher yield and ee values than the monomeric catalyst **4b** in the asymmetric epoxidation of

indene (entry 3 vs 7, ee%, 100 vs 82; conv%, and 97 vs 85) and α -methylstyrene (entry 16 vs 20, ee%, 97 vs. 66; conv%, 100 vs 91). The results of catalysts **3a–3g** were also better than the reported ethyldiamine-bridged bi-Mn(salen) complexes which only got 33% yield and have no enantiomeric excess values.²⁹ This is due to the special structure of the bis-Salen Mn catalysts (Fig. 1) that increased the local concentration of the active sites and the cooperative interaction between the two metal centers present in the catalysts that are not working in isolation.^{24,19} Moreover, bis-diphenolate and bis-diamine ligands in bis-Salen Mn complexes could facilitate the electron transfer between the Mn(salen) complexes.³⁰ Meanwhile, the monomeric catalyst **4b** also showed higher ee values than the Jacobsen's catalyst for indene (ee%, 82–65) and α -methylstyrene (ee%, 66–52). According to this, it was indicated that the rigid caused by the steric effect of the four methyl in special structure of tetramethylbenzene with aromatic bis-diphenolate or bis-diamine linkers was devoted to the increase of ee values by a decrease of the free rotation of two Mn(salen) complexes.

It has been observed previously in homogeneous systems that addition of donor ligands such as pyridine *N*-oxide or *N*-methylimidazole induces a conformational change on the skeleton of the salen Mn(III) complex, resulting in enhancement of reaction rate and an improvement in enantioselectivity. It was interesting to find out here that a remarkable increase of conversion and ee values were obtained for the epoxidations catalyzed by diphenolate axially coordinated salen Mn catalysts in the absence of the axial base, such as the ee values for the epoxides of indene typically increased from 55% to 100% and for α -methylstyrene increased from 90% to 97% without the addition of NMO (Table 1 entries 7 vs 8 and 20 vs 21). However, the axial base was vital in the epoxidations catalyzed by the bis-diamine axially coordinated salen Mn catalysts, such as for indene the ee values decreased from 92% to 87% and for α -methylstyrene decreased from 97% to 69% without the



Scheme 1. Synthesis route of the bis-Salen Mn(III) chiral catalysts.

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