

新型 Co(salen)化合物的合成,表征及其硫醚不对称氧化反应

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摘要: 合成并表征了新的 Co(salen)化合物 (**2a~2c** 和 **3a~3c**)。手性 Co^{II}(salen)化合物 **2a~2c** 在硫醚的不对称氧化反应中显示了中等的反应活性,但只获得了较低对映选择性(8%~21% ee),而手性 Co^{III}(salen)化合物 **3a~3c** 在该反应中没有反应活性。通过研究整个配体的构象影响对化合物的低对映选择性进行了讨论。

关键词: salen; 钴化合物; 不对称氧化; 硫醚

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Synthesis, Characterization and Enantioselective Oxidation of PhMeS by New Co(Salen) Complexes

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Abstract: New Co(salen) complexes (**2a~2c** and **3a~3c**) have been synthesized and characterized. Chiral Co^{II}(salen) complexes **2a~2c** showed moderate reactivity with poor enantioselectivity (8%~21% ee) in asymmetric oxidation of PhMeS, but no reaction was observed for chiral Co^{III}(salen) complexes **3a~3c**. Lower asymmetric induction has been discussed by considering the conformation effect of the ligand.

Key words: salen; cobalt complex; asymmetric oxidation; sulfide

0 Introduction

Chiral cobalt complexes have been widely explored because of their excellent performance in asymmetric catalytic reactions. Indeed, Jacobsen's Co(salen) complexes have been recognized as the most efficient catalyst for hydrolytic kinetic resolution (HKR) reaction^[1,2]. Moreover, Co(salen) complexes have also been found to exhibit good to excellent asymmetric induction in asymmetric cyclopropanation reaction^[3] and Diels-Alder (DA) reaction^[4,5]. So far, much effort has been devoted to the study in this area.

To continue our earlier work on asymmetric oxidation of PhMeS using Cu^{II}(salen) complexes^[6] and to explore the detailed mechanistic analysis of the

catalytic system, we report herein the synthesis and characterization of new chiral Co(salen) complexes derived from chiral 1,4-diaminobutanes together with the use of these catalysts for asymmetric oxidation of PhMeS with H₂O₂ as terminal oxidant.

1 Experimental

1.1 General remarks

All solvents were of analytical grade and dried with standard methods and distilled before use. Chiral ligands (**1a~1c**) were prepared according to our previous work^[6]. Co(Salen) complex **3d** was obtained by a reported procedure^[2]. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra (4 000~400 cm⁻¹) were recorded on a Bruker

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Vector 22 FTIR spectrophotometer. ^1H NMR spectra were obtained using a Bruker DRX 500 MHz spectrometer. Electrospray ionization (ESI) mass spectra were recorded employing a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100~1 200 amu. The UV-Vis electronic spectra were performed on a UV-3100 UV-Vis-NIR spectrophotometer. The CD spectra were conducted on a Model J-810 spectropolarimeter. Preparative thin layer chromatography was performed on 0.5 mm \times 20 cm \times 20 cm E. Merck silica gel plate (60F-254).

1.2 Syntheses of Co^{II} (salen) complexes **2a~2c**

General procedure: To a solution of the salen ligand (0.1 mmol) and NEt_3 (0.2 mmol) in methanol (20 mL) was added $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.1 mmol) in methanol (10 mL) under nitrogen atmosphere. The yellow solution turned orange and a precipitate was formed. The reaction mixture was stirred under reflux for 3 h. After filtration the precipitated complex was washed with methanol and dried in vacuum.

(*R, R*)-**2a**: IR (KBr): 1 598 cm^{-1} . ESI-MS m/z (%): 664.3 (100) [**2a**+H] $^+$. Anal. Calcd. for $\text{C}_{38}\text{H}_{56}\text{CoN}_2\text{O}_4$: C, 68.76; H, 8.50; N, 4.22. Found: C, 68.65; H, 8.41; N, 4.26.

(*S, S*)-**2b**: IR (KBr): 1 604 cm^{-1} . ESI-MS m/z (%): 698.3 (100) [**2b**+H] $^+$. Anal. Calcd. for $\text{C}_{41}\text{H}_{54}\text{CoN}_2\text{O}_4$: C, 70.57; H, 7.80; N, 4.01. Found: C, 70.53; H, 7.92; N, 3.94.

(*R, R*)-**2c**: IR (KBr): 1 600 cm^{-1} . ESI-MS m/z (%): 650.4 (100) [**2c**+H] $^+$. Anal. Calcd. for $\text{C}_{37}\text{H}_{54}\text{CoN}_2\text{O}_4$: C, 68.39; H, 8.38; N, 4.31. Found: C, 68.39; H, 8.44; N, 4.28.

1.3 Syntheses of Co^{III} (salen)I complexes **3a~3c**

General procedure: 1 equiv of Co^{II} (salen) complex (**2a~2c**) and 2 equiv of I_2 were dissolved in 20 mL of THF. The mixture was stirred overnight. After removal of solvent and excess I_2 , dark brown solid powders were obtained.

(*R, R*)-**3a**: IR (KBr): 1 616 cm^{-1} . ESI MS m/z (%): 663 (90) [**3a**-I] $^+$; 1 269 (100) [**3a**-I+**1a**] $^+$. Anal. Calcd. for $\text{C}_{38}\text{H}_{56}\text{CoN}_2\text{O}_4\text{I}$: C, 57.72; H, 7.14; N, 3.54. Found: C, 57.70; H, 7.31; N, 3.28.

(*S, S*)-**3b**: IR (KBr): 1 627 cm^{-1} . ESI MS m/z (%): 697 (60) [**3b**-I] $^+$; 1 269 (100) [**3b**-I+**1b**] $^+$. Anal. Calcd. for $\text{C}_{41}\text{H}_{54}\text{CoN}_2\text{O}_4\text{I}$: C, 59.71; H, 6.60; N, 3.40. Found: C, 59.65; H, 6.82; N, 3.54

(*R, R*)-**3c**: IR (KBr): 1 607 cm^{-1} . ESI MS m/z (%): 593 (80) [**1c**+H] $^+$; 649 (90) [**3c**-I] $^+$; 1 241 (100) [**3c**-I+**1c**] $^+$. Anal. Calcd. for $\text{C}_{37}\text{H}_{54}\text{CoN}_2\text{O}_4\text{I}$: C, 57.22; H, 7.01; N, 3.61. Found: C, 57.39; H, 7.34; N, 3.28.

1.4 General procedure for asymmetric oxidation

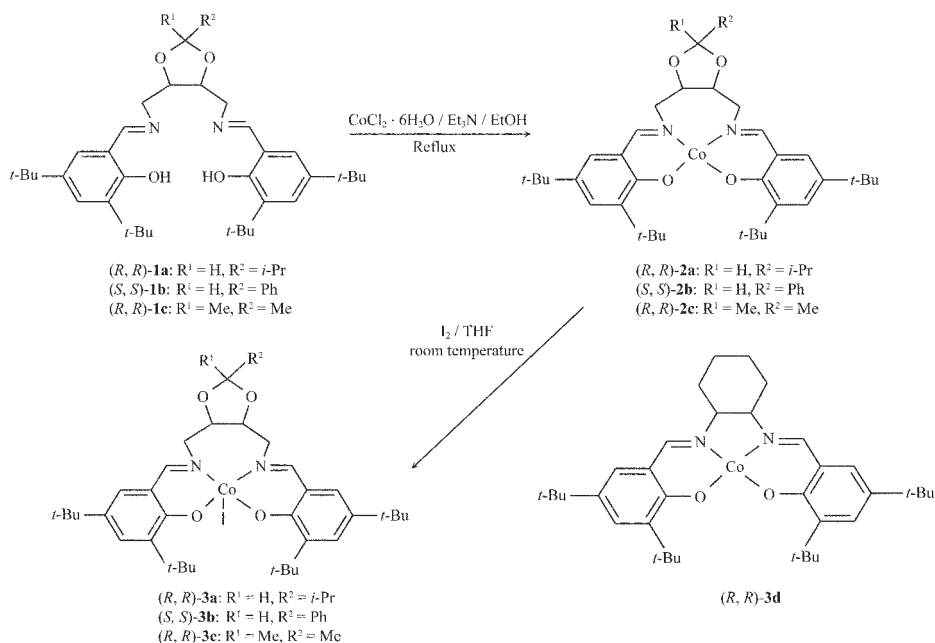
Catalysts (0.02 mmol) were dissolved in CH_2Cl_2 (5 mL) at room temperature. To the solution was added hydrogen peroxide (1.50 mmol) at the same temperature and the mixture was stirred for 20 min, followed by addition of thioanisole (1.00 mmol). The reaction mixture was stirred for 50 h and filtrated through a pad of Celite. No sulfone formation was detected by TLC analysis of the filtrate. The filtrate was concentrated and purified by thin layer chromatography on silica gel (petroleum-ethylacetate=3:1) to give methyl phenyl sulfoxide. The enantiomeric excess of the sulfoxide was determined by HPLC analysis utilizing Daicel Chiralcel OD column (hexane-*i*-PrOH 9:1).

2 Results and discussion

2.1 Preparation and characterization of Co (salen) complexes

The preparation of Co^{II} (salen) complexes (**2a~2c**) was undertaken by a reported procedure^[7]. Oxidation of **2a~2c** with I_2 as oxidant^[8] led to the formation of Co^{III} (salen) complexes (**3a~3c**), accompanied with colour changes from orange to brown (Scheme 1).

The IR spectra showed that the C=N stretching frequency of complexes **2a~2c** was displaced to lower frequency (*c.a.* 1 600 cm^{-1}) against free salen ligand **1a~1c**, indicating a decrease in the C=N bond order due to the coordinate bond of the metal with the azomethine lone pair. Compared with complexes **2a~2c**, moderate red shift for C=N stretching frequency for **3a~3c** was observed due to the reduced strength of Co-N bond caused by a feedback effect of iodine atom. The electronic spectra of the complexes **2a~2c** in CHCl_3 exhibit high intensity charge transfer at 290 nm and while the MLCT lies at 390 nm. The IR and UV-Vis spectra provided fruitful information of bond formation in these compounds, but the compelling evidence supporting the formation of the target Co (salen) complexes came from the ESI-MS and elemental analysis. Obvious parent ion peaks of these Co (salen) complexes were observed from their ESI-MS spectra (see Experimental).



Scheme 1 Preparation of Co(salen) complexes

2.2 Asymmetric Oxidation of PhMeS with Co^{II}(salen) complexes (**2a**~**2c**)

Initially, we attempted to apply these Co^{II}(salen) complexes (**2a**~**2c**) in a HKR reaction wherein Jacobsen's Co^{II}(salen) compound has been recognized as the most efficient catalyst. However the experimental results has led to a negative conclusion since *in situ* oxidation of **2a**~**2c** with HOAc resulted in fast decomposition of these compounds, which is clearly resulted from low chelating effect of seven-membered rings in **2a**~**2c**. Thus, we then switched our eyesight to other Co^{II}(salen)-mediated reactions.

In fact, Co(salen) compounds have been reported to act as oxidative catalysts in combination with terminal oxidants (O₂ or H₂O₂) in non-enantioselective or enantioselective version^[9,10]. Thus, we attempted to employ these (salen)Co complexes in asymmetric oxidation of PhMeS using H₂O₂ as terminal oxidant. To the best of our knowledge, this is a first example of asymmetric sulfoxidation mediated by Co(salen) compounds.

As indicated by the catalytic results listed in Table 1, the oxidation reaction catalyzed by complexes **2a**~**2c** proceeds smoothly with enantioselectivity in range of 8% to 21%. In addition, the stereochemistry of the predominant product (shown by their retention time in HPLC) is identical although the chiral sense of complexes **2a** and **2b** are opposite. Contrary to our

expectation, Jacobsen's Co^{II}(salen) complex **3d** displayed no reaction activity under the same condition. Co^{III}(Salen) complexes have been proven to catalyze Baeyer-Villiger (B-V) reaction in the presence of H₂O₂^[11], but no reaction was detected in the sulfoxidation reaction catalyzed by Co^{III}(salen) complexes **3a**~**3c**. At present, it is unclear to explicate these unexpected results.

Table 1 Asymmetric oxidation of PhMeS with Co(salen) complexes

Entry	Catalyst	Yield ^a / %	ee ^b / %
1	2a	50	7.5
2	2b	56	21.3
3	2c	62	14.6
4	3a ~ 3c	n. r. ^c	n. d. ^c
5	3d	n. r. ^c	n. d. ^c

^a Isolated yield. ^b The enantiomeric excess of the sulfoxide was determined by HPLC using Daicel Chiralcel OD (hexane:*i*-PrOH=9:1). ^c n. r.=no reaction; n. d.=not determined.

In our previous work, low enantioselectivity observed in Cu^{II}(salen)-mediated asymmetric sulfoxidation was attributable to instability of these compounds and inefficient steric interaction between the substrate and substituents in the salen ligand^[6]. However, a more reasonable sense will be deduced for low ee observed in Co^{II}(salen)-mediated asymmetric reaction if a conformation effect of the salen ligand was taken into account. As well demonstrated by Katsuki^[12], the ap-

proach of substrate is mainly controlled by the ligand conformation, which is primarily dictated by the chiral sense of five-membered chelate ring in traditional Jacobsen's salen catalysts. Accordingly, it is reasonable to assume that one single and stable ligand conformation is essential for achieving high enantioselectivity. In our case, Co^{II} (salen) complexes (**2a~2c**) may take multiple conformation due to the flexibility of seven-membered chelate rings among them, which are also reflected in their CD spectra. The CD spectra of complexes **2a~2c** recorded in CHCl_3 show that these complexes are in the equilibrium mixture of conformation isomers, permitting a number of optional pathways for the substrate's approach. Two representative CD spectra (**2a** and **2b**) are shown in Fig.1.

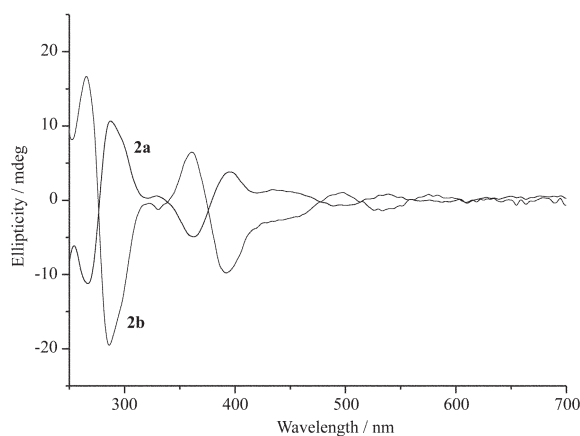


Fig.1 CD spectra of complexes **2a** and **2b**

In conclusion, new Co^{II} and Co^{III} complexes with salen ligand derived from chiral 1, 4-diaminobutanes have been synthesized and characterized. Asymmetric oxidation of PhMeS catalyzed by these Co(salen) complexes has also been investigated. Low ee observed in the reaction was considered to be caused by the multiple conformations of the salen ligand in these compounds.

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