

Synthesis of Three Novel Chiral Binuclear Mn(II)-Schiff-base Complexes and the Application in Asymmetric Epoxidation of *trans*-Stilbene

Yang SUN, Ning TANG*, Xin Wen LIU, Wei Sheng LIU

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000

Abstract: Three novel chiral binuclear Mn(II)-Schiff-base complexes have been synthesized and the application of these complexes in the asymmetric epoxidation of *trans*-stilbene is described, catalytic mechanism is also discussed briefly.

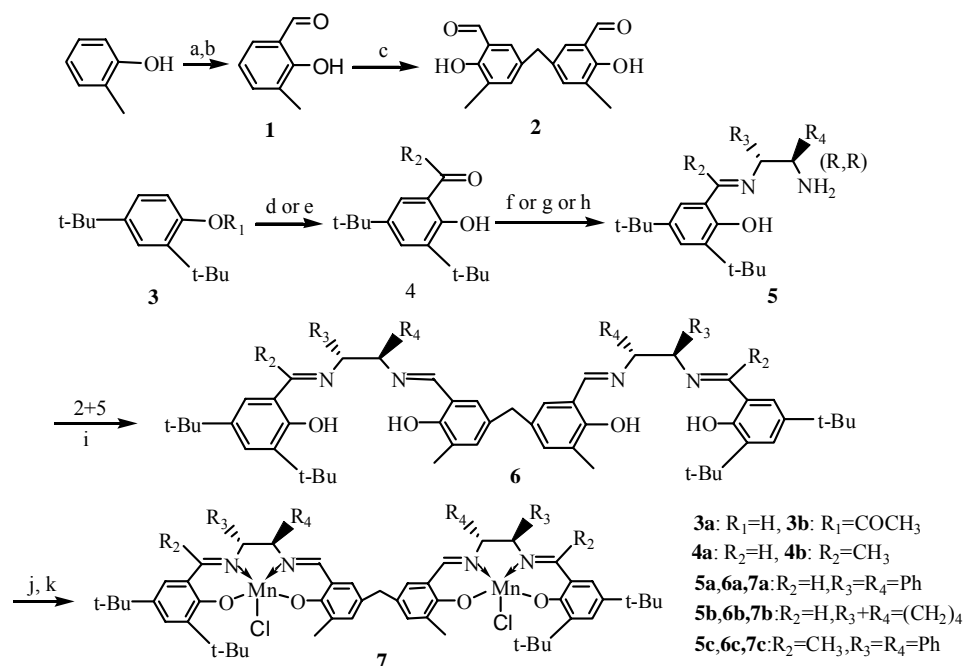
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In the research of asymmetric epoxidation of unfunctionalized alkenes, Jacobsen and Katasuki increased the e.e value of the catalytic product greatly by using different chiral mononuclear Salen complexes^{1,2}. However, reports of the chiral binuclear Schiff-base complexes have been scarce up to now^{3,4}. It was estimated that increasing the number of active reaction sites on the catalysts would result in higher reactivity of catalyst and aiding turnover. Furthermore, increasing the molecular weight of the catalysts would lower their solubility, so the isolation of catalysts and catalyst recovery become more convenient. With these postulated chemical and physical characters of the catalysts in mind, three novel binuclear Mn(II) complex catalysts have been designed and synthesized. There are two innovative points in this letter. First, chiral 1,2-diphenyl- ethylenediamine is introduced into the binuclear catalysts for the first time. Second, to the best of our knowledge, no reports of chiral binuclear Schiff-base complexes containing ketone units as epoxidation catalysts have previously reported. According to the previous reports², although the epoxidation of *cis*-olefins show high selectivity, in contrast, epoxidation of *trans*-olefins still retain poor selectivity². So *trans*-stilbene is selected as substrate. The synthetic procedure is shown in **Scheme 1**. The route is reliable, all reagents is facile.

A typical procedure for the asymmetric epoxidation of *trans*-stilbene catalyzed by **7a-7c**. 2 mL Na₂HPO₄(0.05 mol/L) was combined with 5 mL 13% NaClO solution, then the pH of the mixture was adjust to 11.3 by 1 mol/L HCl and 1 mol/L NaOH. The temperature of reaction system was maintained at about 0°C. The mixture was stirred vigorously at 0°C and monitored by TLC before a pre-cooled solution of 0.025 mmol catalysts **7a-7c**, 1 mmol *trans*-stilbene and 24 mg pyridine N-oxide in 2 mL CH₂Cl₂ were

* E-mail: tangn@lzu.edu.cn

Scheme 1



(a) C_2H_5Br, Mg in dry ether, RT^5 (b) paraformaldehyde, Et_3N in benzene, $80^\circ C^5$ (c) paraformaldehyde in glacial acetic acid, conc. H_2SO_4 , $90-95^\circ C$, under N_2 (d) for **4a**, HMT, CH_3CO_2H , Δ ; H_3O^+ , Δ (e) for **4b**, Fries rearrangement, $TiCl_4$, $MeNO_2$, RT , $8h^6$ (f) for **5a**, (R,R)-1,2-diphenylethylenediamine, dry ethanol, ice bath, 3h (g) (R,R)-1,2-diaminocyclohexane, for **5b**⁴ (h) for **5c**, (R,R)-1,2-diphenylethylenediamine, Na_2SO_4 , dry ethanol, Δ , 20h⁶ (i) in EtOH, RT , 8h (j) $Mn(OAc)_2 \cdot 4H_2O$, ethanol, 8h (k) $LiCl \cdot H_2O$, another half an hour, washed with distilled water, dried over anhydrous Na_2SO_4 .

Table 1 Asymmetric epoxidation of *trans*-stilbene with **7a-7c**

| Entry | Catalyst | Temperature ($^\circ C$) | Time (h) | Yield (%) ^a | ee (%) ^b |
|-------|-----------|----------------------------|----------|------------------------|---------------------|
| 1 | 7a | 0 | 3.5 | 85.35 | 5.45 |
| 2 | 7b | 0 | 4 | 66.67 | 10.34 |
| 3 | 7c | 0 | 4.5 | 43.28 | 40.22 |

Cocatalyst is PNO, PNO=pyridine N-oxide. Absolute configuration of all the epoxide is 1R,2R which determined by the standard enantiomer. The epoxide is a white fragrant solid. (a) Yield of the isolated epoxide. (b) The ee value of the epoxide is measured by HPLC over a chiral column OD-H, eluent is *n*-hexane: 2-propanol = 100:1 (V:V). Velocity of flow is 1.3 mL/min.

added. After a appropriate time, the organic phase of the mixture was extracted by 20 mL CHCl₃, washed with distilled water and saturated NaCl solution twice, then dried over anhydrous Na₂SO₄, and concentrated. Flash chromatography (eluent petroleum ether-CH₂Cl₂) provided the epoxide. An interesting phenomenon appeared in practice, **7a-7c** were found to precipitate from *n*-hexane conveniently, separation of **7a-7c** from the product after the reaction allowed them to be utilized once more. We found these recycled catalysts maintained their catalytic activities except a lower yield than the entries in **Table 1**. The catalytic results are shown in **Table 1**.

Results and Discussion

The catalytic results indicate the utilization of these binuclear Mn(II) complex catalysts **7a-7c** result in high to moderate yields and poor to moderate ee values (shown in **Table 1**). A rational interpretation is that *trans*-olefins approach Mn-oxo bond (Mn=O) along Mn-N bond axis². The yield of epoxide is determined by the conjoint extent between the olefin and Mn-oxo bond. **7a** and **7b** afford a naked Mn-oxo bond, so the olefin can combine with the Mn-oxo bond more conveniently and firmly, then high yields achieved. Catalyst **7c** cannot afford an accessible Mn-oxo bond for olefin's approaching, the methyl group in the C=N bond makes olefin's approach to Mn-oxo bond along Mn-N bond axis more difficult, then the yield is comparatively depressed. The ee value of the product is mainly determined by the chiral environment where the olefin jointed to the Mn-oxo bond. Although the directions of olefin approach to Mn-oxo bond of **7a-7c** are same, olefin can combine with Mn-oxo bond of **7c** in a more exclusive form because of hindrance of the methyl group in the C=N bond, so the ee value is distinctly improved. Another noteworthy property of these binuclear catalysts is easy recovery. In summary, the binuclear complexes **7a-7c** are high reactive and repeatable catalysts, although the ee values are not so high, **7c** is benefit for improving the selectivity of the epoxidation of *trans*-stilbene. Further research is in progress.

References and Notes

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7. Analytic data of some new compounds:
2: MS(FAB) *m/z* : 284.5 (M⁺); ¹H NMR (CDCl₃, δ ppm), 11.19 (s, 2H), 9.64 (s, 2H), 7.21 (s, 4H), 3.90 (s, 2H), 2.26 (s, 6H); mp 146-148 °C. **6a**: MS(FAB) *m/z* : 1105.5 (M+1)⁺; ¹H NMR (CDCl₃, δ ppm), 12.75 (s, 2H), 12.67 (s, 2H), 8.38 (s, 2H), 8.35 (s, 2H), 7.32-6.75 (m, 28H), 4.72 (s, 4H), 3.62 (s, 2H), 2.22 (s, 6H), 1.33 (s, 18H), 1.23 (s, 18H); IR (KBr, cm⁻¹) 1626.7 ν(H-C=N). **6b**: MS(FAB) *m/z* : 909.6 (M+1)⁺; ¹H NMR (CDCl₃, δ ppm), 13.34 (s, 2H), 13.30 (s, 2H), 8.23 (s, 4H), 7.31-6.79 (m, 8H), 3.76 (s, 4H), 3.33 (s, 2H), 2.14 (s, 6H), 1.42-1.68 (m, 16H), 1.39 (s, 18H), 1.24 (s, 18H); IR (KBr, cm⁻¹) 1620.3 ν(H-C=N). **6c**: MS(FAB) *m/z* : 1133.4 (M+1)⁺; ¹H NMR (CDCl₃, δ ppm), 13.39 (s, 2H), 13.30 (s, 2H), 8.52 (s, 2H), 7.36-6.89 (m, 28H), 5.07 (s, 2H), 4.84 (s, 2H), 3.79 (s, 2H), 2.22 (s, 6H), 2.19 (s, 6H),

1.45 (s, 18H), 1.27 (s, 18H); IR (KBr, cm^{-1}) 1626.8 $\nu(\text{C}=\text{N})$. **7a**: Anal. Calcd. For $\text{C}_{75}\text{H}_{80}\text{Cl}_2\text{Mn}_2\text{N}_4\text{O}_4 \cdot 5\text{H}_2\text{O}$: (%) C 65.64, H 6.61, N 4.08 Found C 65.82, H 6.18, N 3.84. IR (KBr, cm^{-1}) 1605.6 $\nu(\text{H}-\text{C}=\text{N})$. **7b**: Anal. Calcd. For $\text{C}_{59}\text{H}_{76}\text{Cl}_2\text{Mn}_2\text{N}_4\text{O}_4$: (%) C 65.16, H 6.99, N 5.15 Found C 65.12, H 6.86, N 4.94. IR (KBr, cm^{-1}) 1611.6 $\nu(\text{H}-\text{C}=\text{N})$. **7c**: Anal. Calcd. For $\text{C}_{77}\text{H}_{84}\text{Cl}_2\text{Mn}_2\text{N}_4\text{O}_4$ (%) C 70.59, H 6.42, N 4.28 Found C 70.16, H 6.49, N 4.50; IR (KBr, cm^{-1}) 1611.9 $\nu(\text{C}=\text{N})$.

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