Immobilization of dicationic Mn(III) salen in the interlayers of montmorillonite clay for enantioselective epoxidation of nonfunctionalized alkenes

R.I. Kureshy*, N.H. Khan, S.H.R. Abdi, I. Ahmad, S. Singh, and R.V. Jasra

Silicates and Catalysis Discipline, Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India

Received 24 June 2003; accepted 24 September 2003

Dicationic chiral Mn(III) salen complex (0.4 mol%) immobilized in the interlayer of montmorillonite clay **4A**, epoxidize bulkier alkenes (epoxide yield 68–99%) with high chiral induction (up to 95% ee) with a catalyst reusability of up to four cycles.

KEY WORDS: immobilization; dicationic; Mn(III) salen; enantioselective; clay; epoxidation.

1. Introduction

Immobilization of homogeneous catalysts has attracted significant interest because it could combine the advantages of both homogeneous and heterogeneous catalysts [1]. In recent years, various approaches for immobilization of chiral Mn(III) salen complexes, viz., anchoring the catalyst on solid inorganic support [2–4] a polymer chain [5–8], encapsulation in a zeolite [9] and physical entrapment in a polydimethylsiloxane membrane [10,11] have been reported. All of these approaches are interesting but demand major modification in the structure of the catalyst or support. In the present study, we report a new approach for immobilization of Mn(III) salen complex comprising synthesis of Mn(III) salen complex in dicationic form and its immobilization in the interlayer space of montmorillonite-type clay by cation exchange process. This complex is easily prepared starting from commercially available 2-*t*-butyl phenol and can be immobilized into clay by simple cation exchange, thus avoiding multistep grafting reported [2–11] for heterogenization. Epoxidation of styrene, with thus immobilized Mn(III) salen catalyst showed significant enhancement in enantiomeric excess (70%) compared to that obtained (45%) under homogeneous conditions.

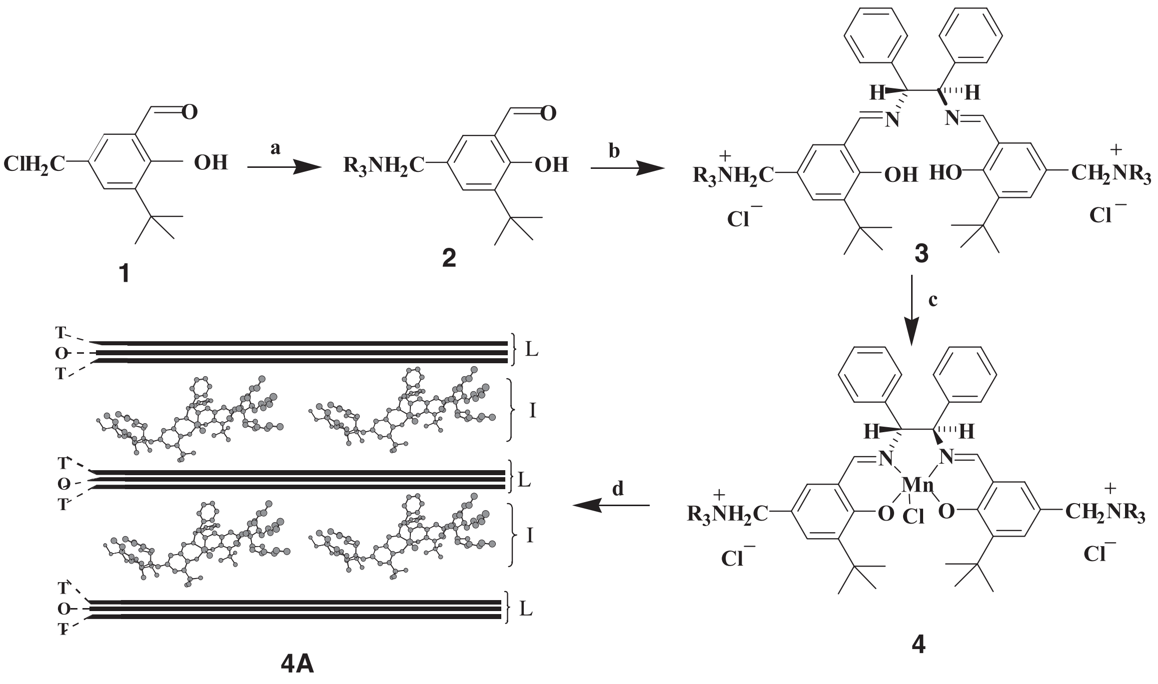
Dicationic complex **4** was synthesized by chloromethylation of 3-*t*-butyl salicylaldehyde to get 5-chloromethyl-3-*t*-butyl-2-hydroxy benzaldehyde **1** as per reported procedure [12], followed by its interaction with tri-isooctylamine to give 2-hydroxy-3-*t*-butyl-5-(tri-isooctyl aminomethyl) benzaldehyde chloride [13] **2**, which on condensation with 1*S*,2*S*-(-)-diphenyldiamine in 2 : 1 molar ratio in ethanol gave ligand [14] **3**, which was reacted with Mn(II)/LiCl to give [15] the Mn(III) salen complex **4**. This complex **4** was exchanged into the interlayer of the clay from its solution in absolute ethanol with constant stirring at room temperature for 48 h to get immobilized complex **4A** [16] (scheme 1).

Montmorillonite-type clay used was upgraded prior to its use. The characterization of **4A** was done by CHN analysis, FT-IR, UV–vis diffuse reflectance spectroscopy, X-ray diffraction, surface area determination and pore-size determination. The loading of the complex corresponded to 0.0165 mmol/g of clay as determined by spectrophotometry and ICP AES. The C-N ratio was in good agreement with the theoretical value [16]. A shoulder near 427 nm similar to that of complex **4** in the diffuse reflectance spectrum and the presence of bands at 3020 cm^{-1}(C_{arom}-H), 2980 and 2922 cm^{-1} (C_{aliph}-H), 1633, 1543 cm^{-1} in **4A** further confirmed the loading of the complex **4** on to the clay. Comparison of the X-ray diffraction data of virgin clay and clay-loaded complex shows the expansion of interlayer spacing (d_{001}) from 9.9 Å to 13.3 Å after exchange with the complex indicating the presence of the complex inside interlayer clay space. This is further confirmed by the increase in pore diameter from 77 Å of the original to 94 Å as determined from N_2-adsorption data for the complex loaded with clay.

Asymmetric epoxidation of 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene, 6-nitro-2,2-dimethylchromene, 6-methoxy-2,2-dimethylchromene and spiro-[cyclohexane-1,2′-[2H] [1]chromene], indene and styrene as substrates (1.29 mmol) was studied in dichloromethane using buffered NaOCl (pH = 11.3) as the oxidant at 0 °C in the presence of pyridine *N*-oxide as a proximal ligand (0.13 mmol) under homogeneous and heterogeneous conditions using catalysts **4** and **4A** (2 mol%). The results are presented in table 1. As shown in the footnote of table 1, the complex **4** is active and enantioselective for the epoxidation of indene,

---

* To whom correspondence should be addressed.



T = Tetrahedral $[SiO_4]^{4-}$ Sheet; O = Octahedral $[Al_2(OH)_6]$ SheetI = Interstitial Space; L = Layered Sheets;

NR_3 = tri-*iso*octylamino

Scheme 1. Reagents and conditions: (a) tri-isooctylamine, benzene, reflux, 6 h, 97% [13]; (b) (1*S*,2*S*)-(-)-1,2-diphenyldiamine, abs. EtOH, reflux, 8 h, 89% [14]; (c) (1) $Mn(CH_3COO)_2.4H_2O$, EtOH, N_2, reflux, 7 h (2) LiCl, rt, 4 h, 92% [15]; (d) EtOH, stirred, 48 h, rt [16]; **4A** Schematic representation of the energy minimized complex **4** in interlayer of clay.

chromenes and styrene under homogeneous conditions (conversion >99%; ee 45–99%). In chiral catalytic epoxidation, reactivity and enantioselectivity of the catalyst is influenced by steric and electronic features of groups at 5,5′ positions of the salicylaldehyde ligand in the catalyst. While steric feature is largely responsible for determining the enantioselective pathway for the substrate molecule, electronic feature effects the reactivity of the oxo intermediate formed during the catalytic cycle [17]. In order to keep electronic features at par with

Table 1
Enantioselective epoxidation of nonfunctionalized alkenes catalyzed by dicationic chiral Mn(III) salen complexes **4A** and **4** under heterogeneous /homogeneous conditions

Entry	Substrate	Conversion[a] (%)	Time (h)	ee (%)[d]	Configuration[e]
1	Styrene (1st time)	69	7	70	*S*
2	Styrene (2nd time)	68	9	70	*S*
3	Styrene (3rd time)	69	12	70	*S*
4	Styrene (4th time)	69	16	70	*S*
5	Styrene[b]	69	12	70	*S*
6	Styrene	99[c]	4[d]	45	*S*
7	Indene	96	10	65	*1S,2R*
8	Chromene	99	6	82	*3S,4S*
9	NO_2-Chromene	99	8	95	*3S,4S*
10	CN-Chromene	>99	8	93	*3S,4S*
11	MeO-Chromene	98	10	84	*3S,4S*
12	Cy-Chromene	>99	8	69	*3S,4S*

[a] Determined on gas chromatography.

[b] Catalyst loading of 0.4 mol%.

[c] Under homogeneous condition; for all other alkenes conversions were >99% under homogeneous condition.

[d] Time required and % ee for homogeneous system; indene = 4 h, 68%; chromene = 2 h, 83%; NO_2-chromene = 0.5 h, >99%; CN-chromene = 4 h, >99%; MeO-chromene = 2 h, 85%; Cy-chromene = 6 h, >99%.

[e] By ^1H NMR using chiral shift reagent (+)$Eu(hfc)_3$/chiral capillary column GTA-type/chiral HPLC column OJ, OB.

previously reported Mn(III) salen complexes [12], and at the same time introducing a quaternary amino group to make dicationic complex, we spaced the nitrogen atom of triisooctylamino group with methylene group at 5,5′ positions of the complex **4**. The reactivity and selectivity obtained with complex **4** in 0.5–6.0 h are in agreement with the values obtained with previously reported Mn(III) salen complexes [12] and the introduction of cationic form has not caused any reactivity change under homogeneous reaction conditions. However, when complex **4** is replaced with **4A**, there is remarkable increase in enantiomeric excess for epoxidation of styrene. This increase is probably due to the steric effect experienced by the complex when loaded in the interlayer space of the clay. A similar observation has been reported for Mn(III) salen complex immobilized on MCM-41 for the substrate α-methyl styrene, *cis*-β-methyl styrene [2] and 4-chlorostyrene [4] for which unique spatial environment constituted by the solid support was described as the possible reason for this behavior [2]. Additionally, the catalyst **4A** works well for even bulkier and nonplanar olefins (except for spiro[cyclohexane-1,2′-[2H] [1]chromene) unlike MCM-41-supported systems, where such substrates are too large to enter the mesopores of the MCM-41 containing Mn(III) salen and fail to catalyze the epoxidation reaction [2]. This may be due to an increase in the interstitial space of flexible interlayer of clay that render Mn(III) salen in **4A** accessible to bulkier alkenes. The catalytic data for catalyst **4A** show that the reaction time taken for completion of epoxidation for an immobilized complex is higher (6–10 h) as compared to catalyst **4**, probably because of the slow diffusion of the reactants and oxidant into the interlayer of clay in the multiphase reaction system. Except for the reaction time taken for the completion of the epoxidation reaction, both homogeneous and heterogeneous catalysts behaved similarly. On the basis of this observation, we speculated that the transition states in both the cases are similar, however, further investigation is needed to strengthen this statement. Nevertheless, similar explanation for this behavior in enantioselective epoxidation using Mn(III) salen in MCM-41 as catalyst has been reported earlier [3,6]. Further, 0.4 mol% of **4A** (entry 5) was found to be sufficient to complete the epoxidation of styrene in 12 h with retention of enantioselectivity.

After the first use, the catalyst **4A** was recovered from the reaction medium by simple filtration or by centrifugation, washed successively with methanol and CH_2Cl_2 and was reused (three times) for the epoxidation of styrene. The results are presented in table 1, (entries 2–4). The characterization of the recovered catalyst **4A** [18] showed partial degradation of the salen complex and entrapment of reactants within the interlayer of the clay causing obstruction for the reactants in subsequent runs. This is reflected in the progressive increase in time to achieve similar conversion of the substrate; however, there was no loss of enantioselectivity observed. Nevertheless, the catalyst could be used for at least three cycles. Further, to rule out leaching of the complex **4** from the clay interlayers, the filtrate of the reaction mixture after each use was collected and both organic and aqueous layers were checked for their manganese content on ICP, which showed no trace of manganese. This indicates that the dicationic complex **4** was strongly held in the interlayer of negatively charged framework of the clay.

In conclusion, we have developed a new approach to heterogenize dicationic Mn(III) salen complex in montmorillonite-type clay. This heterogenized catalyst could epoxidize a wider range of alkenes with enantioselectivities at par with its homogeneous counterpart and showed enhanced asymmetric induction especially for styrene.

Acknowledgments

Two of us, R.I. Kureshy and S. Singh are thankful to DST and CSIR for financial assistance and to Dr. P.K. Ghosh, the Director of the Institute for providing necessary facilities.

References

[1] B.M. Choudhary, N.S. Chowdari, K. Jyothi and M.L. Kantam, J. Am. Chem. Soc. 124 (2002) 5341.

[2] S. Xiang, Y. Zhang and Q. Xin C. Li, Chem Commun. (2002) 2696.

[3] F. Bigi, L. Moroni, R. Maggi, G. Sartori and Chem Commun. (2002) 716.

[4] C.E. Song and S. Lee, Chem. Rev. 102 (2002) 3495.

[5] F. Minutolo, D. Pini, A. Petri and P. Salvadori, Tetrahedron Asymmetry 7 (1996) 2293.

[6] L. Canali, E. Cowan, H.D. Deleuze, C.L. Gibson and D.C. Sherrington, J. Chem. Soc., Perkin Trans. I (2000) 2055.

[7] T.S. Reger and K.D. Janda, J. Am. Chem. Soc. 122 (2000) 6929.

[8] B.B. Lohray, B.B. De, S. Sivaram and P.K. Dhal, Tetrahedron Asymmetry 6 (1995) 2105.

[9] S.B. Ogunwumi and T. Bein, Chem. Commun. (1997) 901.

[10] F.J. Vankelecom, D. Tas, R.F. Parton, V.V. de. Vyver and P.A. Jacobs, Angew. Chem. Int. Ed. Engl. 35 (1996) 1346.

[11] R.F. Parton, I.F.J. Vankelecom, D. Tas, K.B.M. Janssen, P.P. Knops-Gerrits and P.A. Jacobs, J. Mol. Cat. A: Chemical 113 (1996) 283.

[12] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, P.K. Iyer and R.V. Jasra, J. Catal. 209 (2002) 99.

[13] Viscous oil, ^{1}H NMR (200 MHz, $CDCl_3$) δ 12.00–11.00 (bs, 1H, exchangeable), 9.85 (s, 1H), 7.51 (d, $J = 2$ Hz, 1H), 7.33 (d, $J = 2$ Hz, 1H), 3.49 (s, 2H), 2.57 (m, 3H), 1.42 (s, 27H), 1.25–0.78 (m, 30 H); IR (KBr) cm^{-1} 3378, 2959, 1722; Anal. Calcd. for $C_{36}H_{66}ClNO_2$: C, 74.55; H, 11.39; N, 2.42 Found: C, 74.45, H, 11.30, N, 2.38.

[14] Yield (94%); m.p. 105 °C; (200 MHz, $CDCl_3$) δ 14.0–13.7 (bs, 2H, exchangeable), 8.27 (s, 2H), 1.26 (bs, 2H), 7.19 (s, 10H), 6.8 (bs, 2H), 4.3 (s, 4H), 3.3 (bs, 2H), 2.5 (bs, 6H), 1.38–1.26 (bs, 60 H), 0.8 (s, 54 H); IR (KBr); 3378, 2959, 2873, 2454, 1648, 1442, 1268, 1231, 1160, 978, 893, 774, 710; Anal. Calcd. for $C_{86}H_{144}Cl_2N_4O_2$: C, 77.30; H, 10.79; N, 4.20 Found: C, 77.27, H, 10.71, N, 4.18.

[15] Complex **4**: Yield (90%); m.p. 218 °C Anal. Calcd. for $C_{86}H_{142}MnCl_3N_4O_2$: C, 72.50; H, 9.98; N, 3.93. Found: C, 72.44; H, 9.92; N, 3.89; IR (KBr) cm^{-1} 3446, 3062, 2955, 2869, 1607, 1532, 1344, 1312, 1169, 851; UV–vis. λ_{max} nm (EtOH) 262 (14 500), 315 (14 600), 412 (4810); $[\alpha]_D^{27} = -105.41$ (c = 0.28, MeOH); configuration (*S*); μ_{eff}. (BM) 4.8; Λ_M (MeOH), 109 mho cm^{-1} mol^{-1}.

[16] Complex **4A**: Calcd. C/N, 18.4, Found C/N, 19.6; IR (KBr), cm^{-1} 3030, 2980, 2922, 1828, 1633, 1543, 1423, 1393, 1343; Solid reflectance λ_{max} nm 262, 427^{sh}, XRD (d_{001}) = 13 Å; BET surface area 87 m^2/g^{-1}; pore diameter 94 Å.

[17] C.H. Senanayak and E.N. Jacobsen, Process Chem. Pharm. Ind. 347 (1999).

[18] FTIR, XRD and CHN analysis of the recovered catalyst showed partial degradation of the catalyst **4A** and entrapment of reactant in the pores of clay matrix.