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First example of a silica gel-supported optically active Mn(III)–salen complex as a heterogeneous asymmetric catalyst in the epoxidation of olefins

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Abstract

An optically active Mn(III)–salen complex was supported on silica gel materials: the insoluble systems obtained were employed as catalysts in the asymmetric epoxidation of some aromatic olefins. Enantiomeric excess values up to 58% were obtained.

Among the systems so far developed for the catalytic enantioselective epoxidation of unfunctionalized olefins, chiral Mn(III)–salen complexes have proved to be extremely efficient in the homogeneous phase.[1] On the contrary, few papers devoted to the asymmetric epoxidation of carbon–carbon double bonds in the heterogeneous phase have appeared, mainly concerning the use of organic polymer-bound Mn(III)–salen catalysts.[2] In particular, inorganic insoluble supports have been scarcely investigated, generally relying on non-covalent trapping of the chiral catalyst within the host framework.[3–6]

In our continuing effort towards the development of the heterogeneous asymmetric epoxidation[2b,c] we subsequently became interested in the covalent linking of enantioselective epoxidation catalysts to inorganic materials. Recent results[7] about the construction of chiral salen complexes within an MCM-41 zeolite, by a stepwise approach analogous to that by Sherrington et al.,[2e] prompted us to present our preliminary findings. In particular, we report herein the first successful preparation of two Mn(III)–salen type chiral systems covalently linked to commercial silica gel and their use as heterogeneous catalysts for the enantioselective epoxidation of aromatic cyclic olefins.

The immobilization of the chiral complex onto a silica surface was accomplished following the alternative routes shown in Scheme 1. Commercially available 5 μm LiChrospher Si 100 silica gel was employed as **1** or derivatized with 3-mercaptopropyl groups[8] **2**. In the first case the reaction with the Mn(III)–salen derivative **3** directly afforded the catalyst **4a**, in the second one the γ-mercaptopropylsilanized silica **2** (sulphur content 1.8 mmol/g by elemental analysis) was reacted under radical conditions with **5**[2c] to effect

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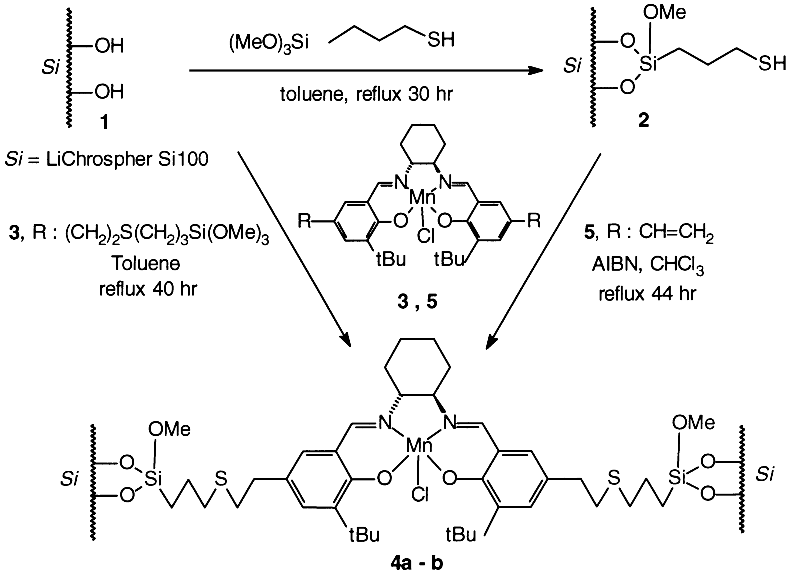
the anchorage leading to **4b**.[9] The derivatization degree of both samples was evaluated by dissolving them in EtOH–20% NaOH and comparing the UV absorbance at 405 nm with that of a standard solution of the model compound **3** under the same conditions. By this method, loadings of 0.28 mmol and 0.07 mmol of chiral catalytic units per gram of derivatized silica gel were determined, respectively, showing that the choice of the anchoring technique allows control to some extent of the concentration of catalytic sites of the inorganic material.



Scheme 1.

Epoxidation of prochiral aromatic olefins was carried out with *m*-chloroperbenzoic acid (*m*-CPBA)/*N*-methylmorpholine-*N*-oxide (NMO)[10] as the oxidant system, in acetonitrile at 0°C, in the presence of the silica-supported catalysts **4a** and **4b**; the results are summarized in Table 1. For all the substrates the reaction was fast; at 0°C good conversions were reached within 10 min. While the enantioselectivity found with the supported catalysts in the epoxidation of dihydronaphthalene and indene was modest (Table 1, entries 1 and 2), a significant 53–58% ee was observed with phenylcyclohexene (Table 1, entry 3).

Although these results fall behind the best ee values reported with polymer[2e] and zeolite-based[7] systems, a comprehensive comparison with most of the heterogeneous catalysts[2–6] is not possible at present, because of the widely scattered reaction conditions and substrates. However, it is interesting to note that the findings obtained with the present silica gel-bound catalyst differ from our previous results with an analogous polystyrene-supported Mn(III)–salen complex.[2c] Indeed, while the *m*-CPBA/NMO oxidation of indene in the presence of the former afforded good stereo- and chemoselectivity values (60% ee and 97% yield), the latter proved far less effective with such substrates (Table 1, entry 2). On the contrary, in the case of dihydronaphthalene and phenylcyclohexene (Table 1, entries 1 and 3), substantial improvements in both yield and enantioselectivity were observed by the use of **4a** and **4b**, in comparison with the catalyst linked to the organic polymer (respectively, 40% yield, 21% ee and 25% yield, 38% ee).[2c] Furthermore it is worth noting that, for all the substrates evaluated, the results with the silica gel-supported Mn(III)–salen **4a** and **4b** mirror each other, demonstrating that the anchoring technique does not significantly affect activity and stereoselectivity of the epoxidation reaction.

In conclusion, the covalent immobilization of a chiral Mn(III)–salen complex onto commercial silica

Table 1
Epoxidation of aromatic olefins with *m*-CPBA/NMO catalyzed by silica-supported Mn(III)–salen **4a** and **4b**[a]

Entry	Substrate	Conversion (%)[c,d]		Yield (%)[b,c,d]		Ee (%)[c,d]	
		4a	**4b**	**4a**	**4b**	**4a**	**4b**
1	1,2-Dihydronaphthalene	75	79	70	69	30	31
2	Indene	70	77	74	67	38	38
3	1-Phenylcyclohexene	64	65	66	51	53	58

[a] Molar ratio olefin/*m*-CPBA/NMO/ supported catalyst = 1/2/5/0.05. Solvent: acetonitrile ; temperature: 0°C .
[b] Corrected for the extent of the olefin conversion.
[c] After 10 min : the values did not change within 120 min.
[d] Conversion, yield and e.e. were determined by HPLC (entries 1 and 2 : CHIRALCEL OB with Hex/IPA 90/10, entry 3 : CHIRALCEL OJ with Hex/IPA 99/1), by integration of peak areas against internal quantitative standards.

gel as starting material was evaluated: the insoluble catalysts, prepared by easy procedures, proved active in the asymmetric epoxidation of olefins affording fair to good chemo- and stereoselectivity values. In spite of the different catalyst loadings for **4a** and **4b** and the presence of an excess of unreacted thiol groups in the case of the latter, no appreciable influence of the anchoring technique was observed. Although yields and ees recorded remain lower in comparison with the best values under homogeneous conditions,[1] the promising results obtained prompt further investigation of this approach for such a class of enantioselective Mn(III)–salen catalytic systems.

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