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Dinuclear Manganese Complexes Containing Chiral 1,4,7-Triazacyclononane-Derived Ligands and Their Catalytic Potential for the Oxidation of Olefins, Alkanes, and Alcohols

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Five new 1,4,7-triazacyclononane-derived compounds, sodium 3-(4,7-dimethyl-1,4,7-triazacyclononan-1-yl)propionate (Na[$L^{Me2R'}$]) as well as the enantiopure derivatives (*S*)-1-(2-methylbutyl)-4,7-dimethyl-1,4,7-triazacyclononane (*S*-$L^{Me2R''}$), *SS-trans*-2,5,8-trimethyl-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane (*SS*-L^{BMe3}), (*S*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (*S*-L^{Me2R}), and (*R*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (*R*-L^{Me2R}), have been synthesized. Reaction of manganese dichloride with the chiral macrocycles *S*-L^{Me2R} and *R*-L^{Me2R} in aqueous ethanol gives, upon oxidation with hydrogen peroxide, the brown dinuclear Mn(III)-Mn(IV) complexes which are enantiomers, $[Mn_2(S\text{-}L^{Me2R})_2(\mu\text{-}O)_2]^{3+}$ (*S*,*S*-**1**) and $[Mn_2(R\text{-}L^{Me2R})_2(\mu\text{-}O)_2]^{3+}$ (*R*,*R*-**1**). The single-crystal X-ray structure analyses of [*S*,*S*-**1**][PF_6]$_3$·0.5$(CH_3)_2CO$ and [*R*,*R*-**1**][PF_6]$_3$·0.5$(CH_3)_2CO$ show both enantiomers to contain Mn(III) and Mn(IV) centers, each of which being coordinated to three nitrogen atoms of a triazacyclononane ligand and each of which being bridged by two oxo and by two chiral hydroxypropyl pendent arms of the macrocycle. The enantiomeric complexes *S*,*S*-**1** and *R*,*R*-**1** were found to catalyze the oxidation of olefins, alkanes, and alcohols with hydrogen peroxide. In the epoxidation of indene the enantiomeric excess values attain 13%. The bond selectivities of the oxidation of linear and branched alkanes suggest the crucial step in this process to be the attack of a sterically hindered high-valent manganese-oxo species on the C–H bond.

Introduction

Manganese complexes containing macrocyclic ligands with three nitrogen-donor atoms have found much interest as model complexes for biologically active systems.[1] In particular, the coordination chemistry of 1,4,7-triazacyclononane and its derivatives has been pioneered by K. Wieghardt in the 1980s: 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L^{Me3}) were found to react with manganese(III) acetate to give the dinuclear manganese(III) complexes $[L_2Mn_2(O)(OOCMe)_2]^{2+}$ and $[(L^{Me3})_2Mn_2(O)(OOCMe)_2]^{2+}$;[2] the latter one reacts in basic media under aerobic conditions to give the manganese(IV) tri-μ-oxo complex $[(L^{Me3})_2Mn_2(O)_3]^{2+}$,[3] while the analogous reaction of the first one leads to the tetranuclear manganese(IV) complex $[L_4Mn_4O_6]^{4+}$.[3,4] A full series of dinuclear Mn(II)-Mn(II), Mn(III)-Mn(III), and Mn(III)-Mn(IV) di-μ-acetato complexes, containing 1,4,7-trimethyl-1,4,7-triazacyclononane $[(L^{Me3})_2Mn_2(OH)(OOCMe)_2]^{+}$, $[(L^{Me3})_2Mn_2(O)(OOCMe)_2]^{2+}$, and $[(L^{Me3})_2Mn_2(O)(OOCMe)_2]^{3+}$ has been described by Wieghardt as model complexes for the active center of photosystem II.[5] Dinuclear Mn(II)-Mn(III) bis-acetato complexes with 1,4,7-triazacyclononane-derived ligand have been reported by Hendrickson and co-workers.[6]

After the discovery of the catalytic activity of these and other Mn(III) and Mn(IV) complexes containing 1,4,7-

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triazacyclononane-derived ligands for low-temperature bleaching,[7] the catalytic oxidation potential of this type of complexes has been demonstrated for the oxidation of phenols[8] and sulfides[9] as well as for the cis-hydroxylation[10] and for the epoxidation[11] of olefins with hydrogen peroxide.

In 1998, G. B. Shul'pin and J. R. Lindsay Smith discovered that the presence of acetic or other carboxylic acid dramatically increases the catalytic oxidation potential of the dinuclear manganese(IV) complex $[(L^{Me3})_2Mn_2(O)_3]^{2+}$ (Wieghardt's complex).[12] Alkanes, including ethane and methane as well as olefins, alcohols, and sulfides, can be efficiently oxidized with hydrogen peroxide[12,13] or with *tert*-butyl hydroperoxide[13c,14] in acetonitrile or in water. The importance of a carboxylate buffer for this catalyst was also demonstrated a few years later for the oxidation of benzylic groups.[15] The role of the carboxylic acid seems to consist in converting $[(L^{Me3})_2Mn_2(O)_3]^{2+}$ into $[(L^{Me3})_2Mn_2(O)_2(OH)]^{+}$, which then reacts with H_2O_2 to form highly active dinuclear Mn(III)-Mn(IV) and even Mn(IV)-Mn(V) species.[13c,e] It has been shown that benzylic C−H bonds can be oxidized in the presence of manganese(III) Schiff-base complex without carboxylic acid as a cocatalyst.[15b,c] The catalytic chemistry of manganese-triazacyclononane-derived systems, including the results of the asymmetric epoxidation catalysis using enantiomerically pure derivatives of 1,4,7-triazacyclononane, has been recently reviewed.[16]

Whereas the methyl substituents in L^{Me3} can be replaced by other alkyl groups without much change in the coordination chemistry,[17] the substitution of only one of the three methyl groups by a hydrogen atom inhibits the formation of the $Mn_2(O)_3$ core.[18] Thus, with the ligand 1,4-dimethyl-1,4,7-triazacyclononane (L^{Me2}) a full series of dinuclear Mn(III)-Mn(III) and Mn(III)-Mn(IV) mono- and di-μ-acetato complexes $[(L^{Me2})_2Mn_2(O)(OOCMe)_2]^{2+}$,[18,19] $[(L^{Me2})_2Mn_2(O)(OOCPh)_2]^{2+}$, $[(L^{Me2})_2Mn_2(O)_2(OOCH)]^{2+}$, and $[(L^{Me2})_2Mn_2(O)_2(OOCMe)]^{2+}$ has been reported.[19]

The cyclization procedures for the synthesis of the 1,4,7-triazacyclononane ring have been established by Richman and Atkins;[20] however, in particular cases the yields are low,[21,22] unless additional precautions are applied.[23] The general strategy for the 1,4,7-triazacyclononane ring synthesis includes the cyclization of fully tosylated triamine *N,N′,N″*-tritosyldiethyleneaminate disodium salt with the ditosyl derivative of 1,2-ethanediol, readily obtained according to published methods.[24] Given that oxidation catalysts based on Wieghardt type complexes are much more active in the presence of carboxylic acids,[12−15] it is interesting to introduce a carboxylato function directly into the 1,4,7-triazacyclononane ring. Mono- (L^{Ac})[25,26] and triacetato-substituted

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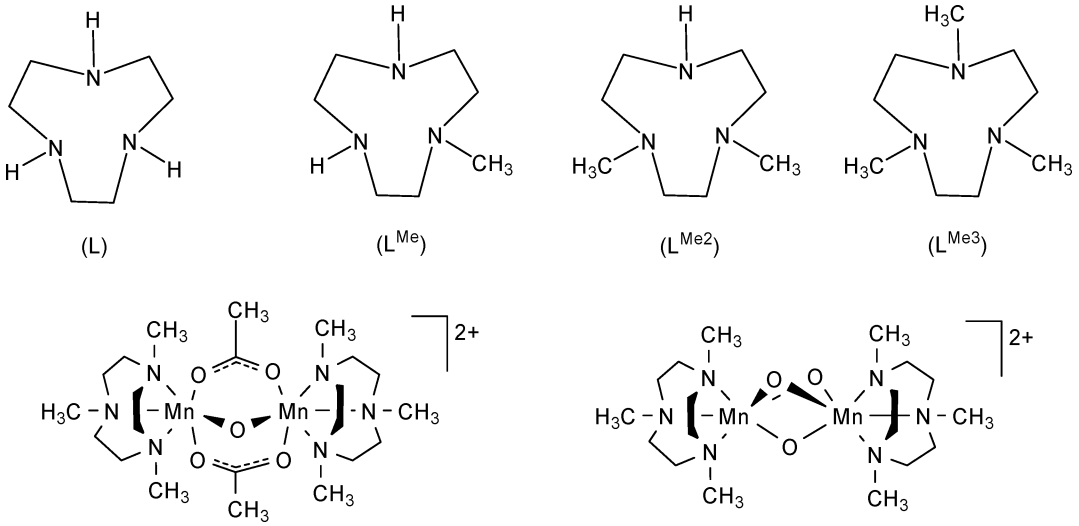
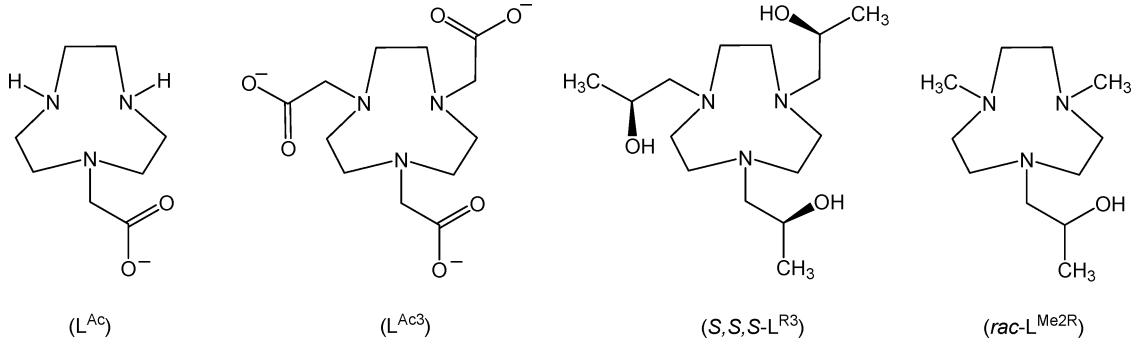
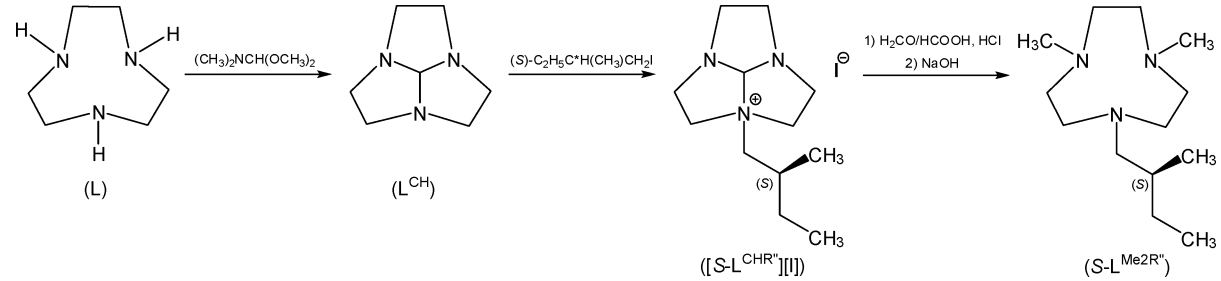
Scheme 1. Triazacyclononane Ligands and Dinuclear Manganese Complexes Containing the Trimethyl Derivative



Scheme 2. Known 1,4,7-Triazacyclononanes Containing Carboxylato- and Hydroxopendent Arms



Scheme 3. Synthesis of the (*S*)-1-(2-Methylbutyl)-4,7-dimethyl-1,4,7-triazacyclononane ([*S*-L$^{Me2R''}$])



(L^{Ac3}) macrocycles[27] (see Scheme 2) as well as two mononuclear (L^{Ac3})Mn(II) and (L^{Ac3})Mn(III) complexes[27] are known; however, their catalytic potential has not been exploited.

Since Wieghardt's complex, $[(L^{Me3})_2Mn_2(O)_3]^{2+}$, catalyzes the hydroxylation of hydrocarbons in the presence of carboxylic acids with a high degree of bond- and stereoselectivity,[13,28] it is interesting to introduce an alkyl-functionalized substituent bearing a stereogenic center into the macrocyclic ligand and to study the corresponding manganese complex as asymmetric epoxidation catalysts. The syntheses of the macrocycles *rac*-L^{Me2R} [29] and of *S,S,S*-L^{R3} [30] (see Scheme 3) have been reported; the latter one catalyzes in combination with manganese(II) acetate the enantioselective epoxidation of olefins with ee values up to 55%.[31]

Three 1,4,7-triazacyclononane ligands (L, L^{Me2}, and L^{Me3}) being already known,[23,32] we decided to use L and L^{Me2} for the preparation of macrocyclic ligands containing a carboxylato function or a stereogenic center. As it is known that bulky *N*-alkyl substituents (ethyl, isopropyl, etc.) lead to low yields in the complexation with manganese, the oxidation potential of the corresponding manganese complexes being decreased,[17,18] we chose 1,4-dimethyl-1,4,7-triazacyclononane

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(L^{Me2}) as a starting material to introduce a third functionality into the 1,4,7-triazacyclononane ring. Indeed, replacing only one of the three methyl groups in L^{Me3}, the most active catalyst precursor, could provide new insights into the oxidation mechanism as well as the possibility to tune the electronic and steric properties of the corresponding manganese complexes. Given that the C_2 axis plays an important role in catalytic epoxidation reactions,[46] we introduced *SS-trans*-cyclohexyldiamine into the 1,4,7-triazacyclononane system to get a chiral bicyclic ligand.

Experimental Section

General. Solvents for catalytic experiments were of analytical grade (Acros, Merck or Cambridge Isotope Laboratories) and used without distillation and only stored over a molecular sieve and under a nitrogen atmosphere. Solvents for synthesis were of technical grade and were purified by distillation under nitrogen and dried according to standard laboratory practices.[33] Water was doubly distilled and stored under nitrogen. Laboratory gases were purchased from Carbagas and used directly from the cylinders without further purification.

The macrocyclic ligand precursors 1,4,7-triazacyclononane,[22] 1,4-dimethyl-1,4,7-triazacyclononane,[32] 1,4,7-triazatricyclo[5.2.1.$0^{4,10}$]-decane,[34] and *SS-trans*-2,5,8-tritosyl-2,5,8-triazabicyclo[7.4.$0^{1,9}$]-tridecane[35] were synthesized and purified according to the published methods. All other commercial compounds were of analytical grade and used as received (Acros, Aldrich or Fluka). Hydrogen peroxide was used as a solution in water (30%, not stabilized, Fluka) and stored at 4 °C. The exact concentration was determined using potassium permanganate titration and by UV-spectroscopy (230 nm, $\epsilon = 81\ M^{-1}\ cm^{-1}$). Hydrobromic acid was used as a solution in glacial acetic acid (33%, Riedel de Haën).

Instrumentation and Analyses. All syntheses were carried out by standard Schlenk techniques under nitrogen or argon atmosphere unless stated otherwise. Silica (60 Å, 63−200 mesh) for column chromatography was purchased from Chemie Brunschwig AG. UV−vis spectra were recorded using an UVICON-930 spectrophotometer; the samples were placed in quartz 2 mm or 10 mm high-precision cells with an appropriate solvent used as reference. Microsoft Excel was used for data analysis. Infrared spectra were recorded with a Perkin-Elmer spectrum one spectrometer in transmission mode where the absorptions are given in reciprocal centimeters (cm^{-1}). Intensity data are described with the following abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. Circular dichroism spectra were recorded using a JASCO J-710 instrument with 2 nm bandwidth, 0.5 nm step resolution, and 4 s response time in quartz 10 mm high-precision cells with an appropriate solvent used as reference. Microsoft Excel was used for data analysis. Nuclear magnetic resonance spectra were recorded using a Bruker AMX 400. ^1H and ^{13}C {^1H-decoupled} NMR: internal standard − solvent. ESI mass spectra were measured by the Analytical Service of the University of Neuchâtel (Switzerland) using a LCQ Finnigan spectrometer. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

X-ray Crystallography. Crystal data for [*S*,*S*-**1**][PF_6]$_3$·0.5$(CH_3)_2$CO and [*R*,*R*-**1**][PF_6]$_3$·0.5$(CH_3)_2$CO: The crystals were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo−Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0−200°, increment of 0.8°, 2θ range from 2.0−26°, $D_{max}-D_{min}$ = 12.45−0.81 Å. The structures were solved by direct methods using the program SHELXS-97.[36] The refinement and all further calculations were carried out using SHELXL-97,[37] with 431 and 313 parameters, respectively. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. Semiempirical absorption correction was applied for [*R*,*R*-**1**] using DIFABS (PLATON03,[38] T_{min}=0.346, T_{max}=0.767). In both cases, data sets corresponding to omission of the missing solvent and disordered anions were generated with the SQUEEZE algorithm,[39] and the structures were refined to convergence. In [*R*,*R*-**1**], one disordered hexafluorophosphate anion was modeled and fixed. Crystallographic details are summarized in Table 1. Molecular structure representations were drawn with ORTEP[40] and POV-RAY.[41]

Gas Chromatography. GC-analyses were performed on a Dani 86.10 gas chromatograph equipped with a split-mode capillary injection system and flame ionization detector using a CP-WAX52CB capillary column (25 m × 0.32 mm × 0.25 μm), integrator SP-4400, and helium as carrier gas. Acetonitrile or nitromethane was used as internal standards. The flame ionization detector response factors were obtained after calibration experiments, using a standard substrate mixtures.

High Performance Liquid Chromatography. The HPLC analyzes were done on an Agilent/Hewlett-Packard 1100 modular HPLC system equipped with a UV-detector using nitrobenzene as internal standard. The chiral product separation was performed using a Daicel Chiracel OB-H (25 cm × 4.6 mm, for 1-phenylethanol) and Daicel Chiracel OJ-H (25 cm × 4.6 mm, with precolumn, for indene oxide) columns and analyzed with the Agilent Chemport software. In isocratic conditions the retention times were as follows: (hexane/isopropyl alcohol 50/1, 0.9 mL/min) 11 (nitrobenzene), 16 (*S*-1-phenylethanol), 17 (acetophenone), and 25 min (*R*-1-phenylethanol); (hexane/isopropyl alcohol 50/1, 0.8 mL/min) 7 (indene), 11 (nitrobenzene), 16 (2-indanone), 18 (1*R*,2*S*-indene oxide), 20 (1*S*,2*R*-indene oxide), and 29 min (2-indanol). The calibration experiments were performed using standard substrate mixtures and verified by ^1H NMR and UV-spectroscopy. The mixture of racemic indene oxide and 2-indanone was obtained according to the published procedure[42] and fractionalized on a silica

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Table 1. Crystallographic and Selected Experimental Data for [*S*,*S*-**1**][PF_6]$_3$·0.5$(CH_3)_2CO$ and [*R*,*R*-**1**][PF_6]$_3$·0.5$(CH_3)_2CO$

	[*S*,*S*-**1**][PF_6]$_3$	[*R*,*R*-**1**][PF_6]$_3$
chemical formula	$C_{22}H_{50}F_{18}Mn_2N_6O_4P_3$	$C_{22}H_{50}F_{18}Mn_2N_6O_4P_3$
formula weight	1007.47	1007.47
crystal system	tetragonal	tetragonal
space group	*P*4	*I*4
crystal color and shape	brown block	brown block
crystal size	0.25 × 0.20 × 0.20	0.30 × 0.22 × 0.12
a (Å)	18.680(3)	18.884(1)
b (Å)	18.680(3)	18.884(1)
c (Å)	24.730(5)	12.5586(6)
V (Å^3)	8629(3)	4478.4(4)
Z	8	4
T (K)	173(2)	173(2)
D_c (g·cm^{-3})	1.551	1.494
μ(mm^{-1})	0.809	0.780
scan range (°)	4.36 < 2θ < 52.02	4.32 < 2θ < 51.96
unique reflections	5720	8742
reflections used [$I > 2\sigma(I)$]	2349	3947
R_{int}	0.1078	0.1228
flack parameter	0.00(6)	0.23(6)
final *R* indices [$I > 2\sigma(I)$][a]	0.0669, wR_2 0.1497	0.1185, wR_2 0.2865
R indices (all data)	0.1371, wR_2 0.1698	0.1644, wR_2 0.3169
goodness-of-fit	0.799	0.920
max, min $\Delta\rho$/e (Å^{-3})	0.818, −0.447	0.821, −0.985

[a] Structures were refined on F_o^2: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^- = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

column (eluent CH_2Cl_2, ^{1}H NMR analysis). The 1*R*,2*S*-indene oxide enriched sample was prepared (Jacobsen protocol[43]) using Mn(III)-*R*,*R*-salen complex (Aldrich), pyridine N-oxide as terminal ligand, and chlorobenzene as solvent.

Catalytic Experiments. Oxidation of Alkanes. The oxidation of higher alkanes was carried out in thermostated cylindrical vessels connected to a reflux tube; when the reaction temperature was higher than 40 °C, the vessel was opened to air. In a typical experiment, a portion of hydrogen peroxide was added to the solution of the catalyst and the substrate cyclohexane in acetonitrile. After certain time intervals samples (0.6 mL) were taken. The samples were analyzed twice: before and after addition of triphenylphosphine to reduce the remaining hydrogen peroxide to water and the alkyl hydroperoxide to the corresponding alcohol,[13b,d,g,44] the reaction is complete after 15 min. Each sample was injected in the GC twice, 0.2 μL each time. The comparison of the concentrations of cyclohexanone and cyclohexanol before and after reduction allows us to estimate the real concentrations of cyclohexyl hydroperoxide, cyclohexanone, and cyclohexanol present in the reaction mixture.[13b,d,g,44]

Oxidation of Alkenes. The epoxidation of indene was carried out with vigorous stirring under air in a small glass vessel cooled by an ice bath. The total volume of the reaction solution was 2 mL. In a typical experiment, hydrogen peroxide (30% aqueous solution, 0.20 M) was added to a mixture containing a catalyst, cocatalyst, and a substrate in aqueous acetonitrile (50%) or in acetone. After 2 h the reaction products were extracted with ether (3 × 2 mL) (the acetone solution was concentrated in the stream of nitrogen), dried over anhydrous Na_2SO_4, and filtered through silica using diethyl ether (10 mL) as eluent. To the resulting solution (total volume 15−16 mL) 10 μL of nitrobenzene was added, and the samples were analyzed by HPLC using a Daicel Chiracel OJ-H column.

Oxidation of Alcohols. The oxidation of isopropyl alcohol was carried out in air in thermostated cylindrical Pyrex vessels with vigorous stirring. The total volume of the reaction solution was 10 mL. In a typical experiment, hydrogen peroxide (30% aqueous solution, 0.50 M) was added to a mixture containing the catalyst, cocatalyst, and substrate in water or in acetonitrile. Blank experiments were carried out without catalyst. The samples of the reaction solution were analyzed by GC.

The oxidation of racemic 1-phenylethanol was carried out with vigorous stirring under air in a small glass vessel cooled by an ice bath. The total volume of the reaction solution was 2 mL. In a typical experiment, hydrogen peroxide (30% aqueous solution, 0.20 M) was added to a mixture containing the catalyst and substrate in aqueous acetonitrile (50%). After 2 h the reaction products were extracted with diethyl ether (3 × 2 mL), dried over anhydrous Na_2SO_4, and filtered through silica using diethyl ether (10 mL) as eluent. To the resulting solution (total volume 15−16 mL) 10 μL of nitrobenzene was added, and the samples were analyzed by HPLC using a Daicel Chiracel OB-H column.

Syntheses. (*S*)-1-(2-Methylbutyl)-4,7-diaza-1-azoniatricyclo-[5.2.1.0^{4,10}]decane Iodide ([*S*-L$^{CHR''}$][I]). In a 50 mL Schlenk tube was dissolved 1.11 g (8.0 mmol) of freshly distilled methine-bridged triamine 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane in 5 mL of absolute THF at 0 °C, and a solution of (*S*)-1-iodo-2-methylbutane (1.10 mL, 8.4 mmol) was added dropwise in 5 mL of THF (10 min). After stirring at 0 °C for 1 h, the mixture was warmed to room temperature and stirred in the dark for 96 h. The resulting white-yellowish crystals precipitated from the solution were filtered under nitrogen atmosphere, washed 4 times with 5 mL of THF, and dried in vacuo (0.05 mbar, 20 °C, 24 h).

[*S*-L$^{CHR''}$][I]: Yield 42−52%. ^{1}H NMR (400 MHz, CD_3OD) δ = 5.65 (s, 1H, N_3CH), 3.82−3.68 (m, 6H, NCH*H*CH*H*N), 3.4−3.2 (m, 7H, NC*H*HC*H*HN, NC*H*HCH$(CH_3)C_2H_5$), 3.00 (m, 1H, NCH*H*CH$(CH_3)C_2H_5$), 2.13 (m, 1H, $NCH_2CH(CH_3)C_2H_5$), 1.61 (m, 1H, $NCH_2CH(CH_3)CHHCH_3$), 1.42 (m, 1H, $NCH_2CH(CH_3)$-CH*H*CH_3), 1.18 (d, 3H, $NCH_2CH(CH_3)CH_2CH_3$, ^3J = 6.8 Hz), and 1.03 ppm (t, 3H, $NCH_2CH(CH_3)CH_2CH_3$, ^3J = 7.4 Hz). ^{13}C NMR {^{1}H decoupled} (100 MHz, CD_3OD) δ = 129.4, 64.3, 58.3, 57.6, 57.3, 53.2, 52.9, 33.1, 29.6, 19.0, and 11.4 ppm. MS (ESI positive mode, CH_3OH): *m*/*z* 210.2 (60%, [R^{2S}L-CH]$^+$), 200.4 (24%, [R^{2S}L + H]$^+$), 228 (8%, [R^{2S}L-COH + H]$^+$, methine-bridge opening), and 340.3 (6%, [R^{2S}L-CH + I + 3H]$^{3+}$); MS/MS {*m*/*z* 210.2 fragment} *m*/*z* 140.1 ([R^{2S}L-CH + H − $CH_2CH(CH_3)CH_2CH_3$]$^+$). IR (KBr pellets) ν (cm^{-1}): 2962 (s), 2881 (s), 1462 (s), 1385 (s), 1288 (s), 1214 (s), 1085 (vs), 713 (s), and 601 (m). UV−vis (CH_3-

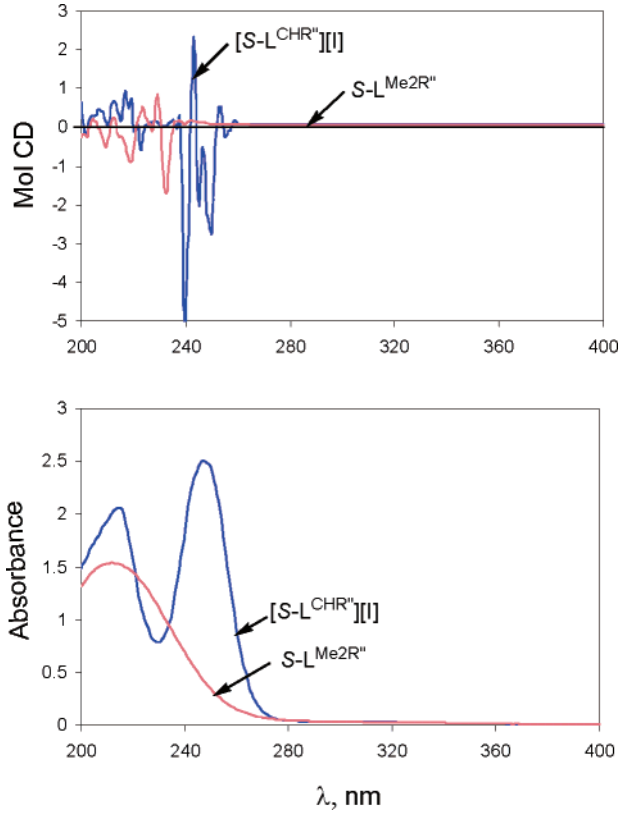


Figure 1. Molar circular dichroism (CD) and UV spectra of [*S*-L$^{CHR''}$][I] precursor and *S*-L$^{Me2R''}$ ligand in acetonitrile ([(*S*-L$^{CHR''}$)$^+$] = [*S*-L$^{Me2R''}$] = 0.20 mM).

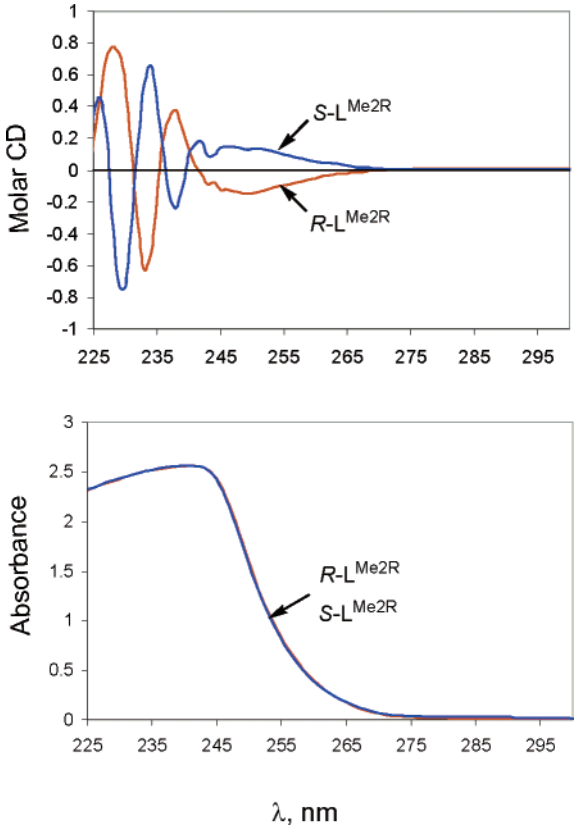


Figure 2. Molar circular dichroism (CD) and UV spectra of (*R*) and (*S*) isomers (curves perfectly superimposed) of 1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane in hexane ([*S*-L^{Me2R}] = [*R*-L^{Me2R}] = 1.45 mM).

CN) λ_{max} (nm): 214 (ϵ = 10200 M^{-1} cm^{-1}), 247 (12500). CD (CH$_3$CN) λ_{max} (nm): 243 ($\Delta\epsilon$ = +2.34 M^{-1} cm^{-1}), 239.5 (−5.1).

(*S*)-1-(2-Methylbutyl)-4,7-dimethyl-1,4,7-triazacyclononane (*S*-L$^{Me2R''}$). In a 100 mL flask was dissolved (*S*)-1-(2-methylbutyl)-4,7-diaza-1-azoniatricyclo [5.2.1.0^{4,10}]decane iodide ([*S*-L$^{CHR''}$][I]) (1.40 g, 4.15 mmol) in a mixture of 37% formaldehyde (20 mL) and formic acid (20 mL), and the mixture was heated to reflux for 24 h. After subsequent cooling, an excess of 37% HCl (30 mL) was added, and the solution was rotary evaporated. The yellow-brownish solids were dissolved in 20 mL of 5 M NaOH (pH > 12) and then extracted with chloroform (3 × 30 mL), dried over anhydrous Na_2SO_4, and rotary evaporated. The crude product was distilled (bulb-to-bulb) under reduced pressure (0.1 mbar, 95 °C) to give a colorless oil which is kept under an argon atmosphere.

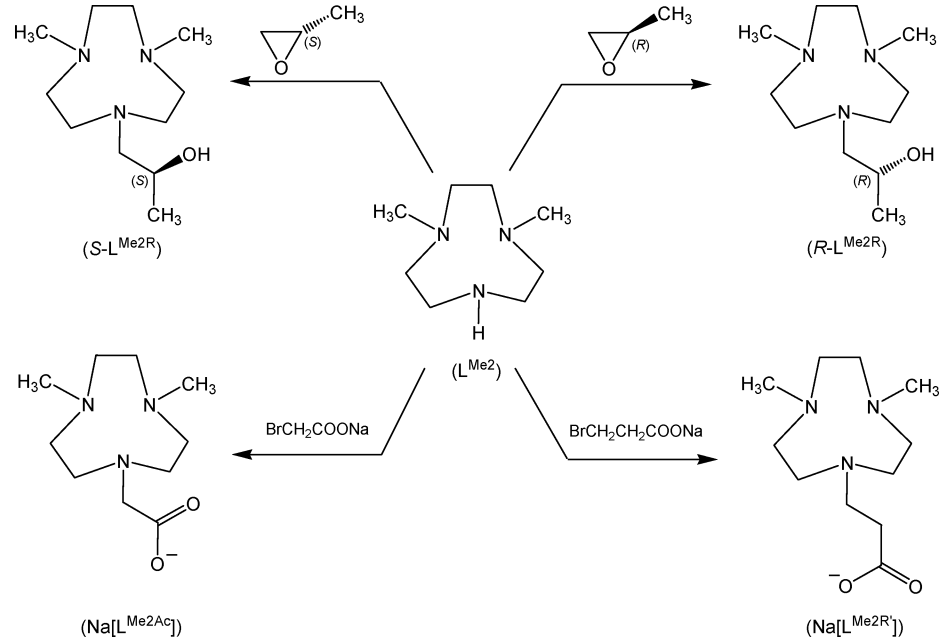
***S*-L$^{Me2R''}$**: Yield 75−81%. ^{1}H NMR (400 MHz, CD$_3$OD) δ = 2.93−2.62 (m, 12H, NC*H*$_2$C*H*$_2$N), 2.37 (s, 6H, NC*H*$_3$), 2.25 (m, 1H, NC*H*HCH(CH$_3$)C$_2$H$_5$), 2.19 (m, 1H, NCH*H*CH(CH$_3$)C$_2$H$_5$), 1.54 (m, 1H, NCH$_2$C*H*(CH$_3$)C$_2$H$_5$), 1.49 (m, 1H, NCH$_2$CH(CH$_3$)-C*H*HCH$_3$), 1.12 (m, 1H, NCH$_2$CH(CH$_3$)CH*H*CH$_3$), 0.93 (d, 3H, NCH$_2$CH(C*H*$_3$)CH$_2$CH$_3$, ^3J = 6.6 Hz), and 0.90 ppm (t, 3H, NCH$_2$-CH(CH$_3$)CH$_2$C*H*$_3$, ^3J = 7.4 Hz). ^{13}C NMR {^{1}H decoupled} (100 MHz, CDCl$_3$) δ = 67.3 (1 × NC*H*$_2$CH(CH$_3$)CH$_2$CH$_3$), 57.6, 57.3, 56.5 (6 × NC*H*$_2$C*H*$_2$N), 46.2 (2 × NC*H*$_3$), 33.7 (1 × NCH$_2$C*H*-(CH$_3$)CH$_2$CH$_3$), 27.7 (1 × NCH$_2$CH(CH$_3$)C*H*$_2$CH$_3$), 18.1 (1 × NCH$_2$CH(C*H*$_3$)CH$_2$CH$_3$), and 11.4 ppm (1 × NCH$_2$CH(CH$_3$)-CH$_2$C*H*$_3$). MS (ESI positive mode, CH$_3$OH): *m*/*z* 228.2 ([R^{2S}L-Me$_2$ + H]$^+$). IR (film) ν (cm^{-1}): 2923 (s), 2782 (s), 1454 (s), 1368 (s), 1298 (m), 1109 (s), 1031 (s), 869 (m), and 752 (m). UV−vis (CH$_3$CN) λ_{max} (nm): 212 (ϵ = 7700 M^{-1} cm^{-1}). CD (CH$_3$CN) λ_{max} (nm): 232.5 ($\Delta\epsilon$ = −1.7 M^{-1} cm^{-1}), 229 (+0.87).

General Procedure for (*S*)-1-(2-Hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (*S*-L^{Me2R}) and (*R*)-1-(2-Hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (*R*-L^{Me2R}). In a 20 mL Schlenk tube was dissolved 1.57 g (10.0 mmol) of freshly distilled 1,4-dimethyl-1,4,7-triazacyclononane (L-Me$_2$) in 3 mL of absolute ethanol at −10 °C, and a solution of the corresponding enantiopure (*S*)-propylene oxide (0.82 g, 15 mmol, for *S*-L^{Me2R}) or (*R*)-propylene oxide (0.82 g, 15 mmol, for *R*-L^{Me2R}) in 3 mL of ethanol was added dropwise through a septum (5 min). After stirring at −10 °C for 1 h, the mixture was warmed to room temperature and stirred in the dark for 48 h. The low-boiling components were evaporated before the crude product was distilled (bulb-to-bulb) under reduced pressure (0.1 mbar, 95 °C) to give a colorless oil. The oil is kept under argon.

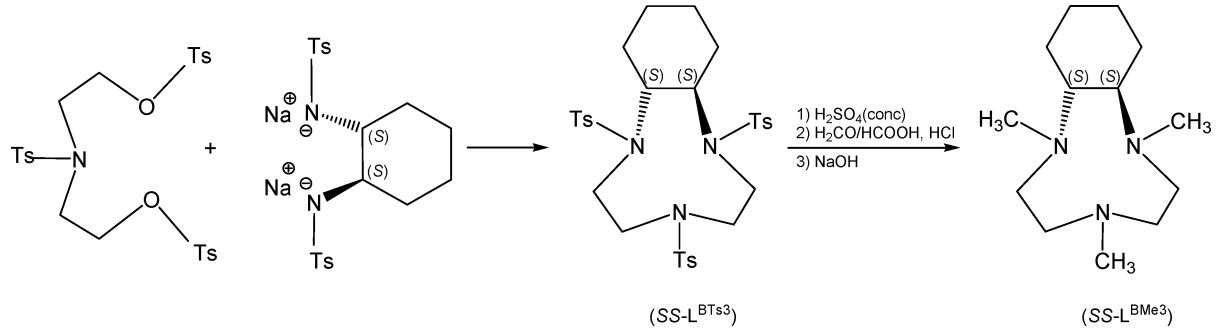
***R*-L^{Me2R}**: Yield 70%. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.76 (m, 1H, NCH$_2$C*H*(OH)CH$_3$), 2.70−2.60 (m, 12H, NC*H*$_2$C*H*$_2$N), 2.60−2.37 (m, 2H, NC*H*$_2$CH(OH)CH$_3$), 2.20 (s, 6H, NC*H*$_3$), and 1.03 (d, 3H, NCH$_2$CH(OH)C*H*$_3$, ^3J = 6.3 Hz). ^{13}C NMR {^{1}H decoupled} (100 MHz, CDCl$_3$) δ = 66.1 (NCH$_2$CH(OH)CH$_3$), 65.9 (NCH$_2$*C*H(OH)CH$_3$), 58.7, 58.1, 57.0 (3 × NC*H*$_2$C*H*$_2$N), 46.3 (NC*H*$_3$), and 19.6 (NCH$_2$CH(OH)*C*H$_3$) ppm. MS (ESI positive mode, CH$_3$OH): *m*/*z* 216 ([R^{1R}L-Me$_2$ + H]$^+$). IR (film) ν (cm^{-1}): 3207 (s), 2928 (s), 2796 (s), 1455 (s), 1367 (s), 1319 (s), 1089 (s), 1035 (s), 986 (s) 878 (m), and 775 (m). UV−vis (hexane) λ_{max} (nm): 212 (ϵ = 1800 M^{-1} cm^{-1}). CD (hexane) λ_{max} (nm): 249 ($\Delta\epsilon$ = −0.15 M^{-1} cm^{-1}), 238 (+0.38), 233 (−0.62), and 228 (+0.78).

The NMR, MS, and UV data are the same as for the enantiomer *R*-L^{Me2R}. In C$_6$D$_6$, the OH proton (not visible in CDCl$_3$) can be observed for both enantiomers: *S*-L^{Me2R}: Yield 70%. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ = 5.54 (br, 1H, NCH$_2$CH(O*H*)CH$_3$), 3.83 (m, 1H, NCH$_2$C*H*(OH)CH$_3$), 2.57 (m, 4H, R*NC*H*$_2$CH$_2$N), 2.49 (m, 8H, NC*H*$_2$C*H*$_2$N), 2.34−2.27 (m, 2H, NC*H*$_2$CH(OH)CH$_3$), 2.20 (s, 6H,

Scheme 4. Syntheses of 1,4-Dimethyl-1,4,7-triazacyclononane (L-Me_2) Derived Ligands



Scheme 5. Synthesis of the C_2-Symmetric Enantiomerically Pure *SS*-L^{BMe3} (*SS-trans*-2,5,8-Trimethyl-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane)

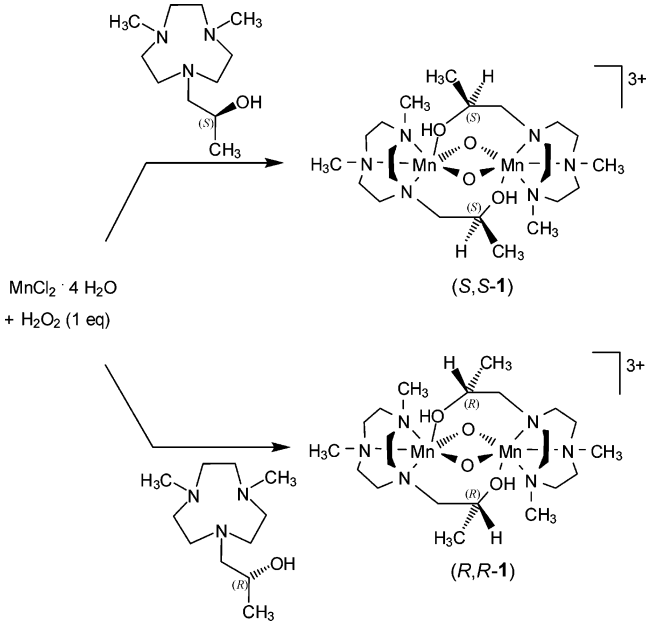


$NC\mathit{H}_3$), and 1.17 (d, 3H, $NCH_2CH(OH)C\mathit{H}_3$, ^3J = 6.2 Hz). CD (hexane) λ_{max} (nm): 249 ($\Delta\epsilon$ = +0.15 M^{-1} cm^{-1}), 238 (−0.24), 234 (+0.65), and 229 (−0.73).

Sodium 3-(4,7-Dimethyl-1,4,7-triazacyclononan-1-yl)propionate (Na[$L^{Me2R'}$]). In a 100 mL Schlenk tube was dissolved 3.14 g (20.0 mmol) of freshly distilled 1,4-dimethyl-1,4,7-triazacyclononane (L-Me_2) in 10 mL of water at room temperature, and an aqueous solution of sodium 3-bromopropionate (20 mmol, 10 mL), prepared by neutralization of 3.06 g (20 mmol) of 3-bromopropionic acid with 0.80 g (20 mmol) of NaOH, was added dropwise (5 min). The temperature was raised to 50 °C, and 1.00 g (25 mmol) of NaOH dissolved in 5 mL of water was added dropwise. The temperature was maintained at 50 °C for 2 h, until the reaction was complete. The light-yellow solution was evaporated (0.05 mbar, 50 °C), and the solid product was extracted with $CHCl_3$ (3 × 50 mL), dried over anhydrous Na_2SO_4, and filtered under a nitrogen atmosphere. The white-yellowish hygroscopic powder was obtained after solvent evaporation and drying in vacuo (0.01 mbar, 50 °C, 48 h).

Na[$L^{Me2R'}$]: Yield 75%. ^{1}H NMR (400 MHz, CD_3OD) δ = 2.80 (t, 2H, $NC\mathit{H}_2CH_2COONa$, ^3J = 7.0 Hz), 2.65−2.63 (m, 12H, $NC\mathit{H}_2C\mathit{H}_2N$), 2.38 (s, 6H, $NC\mathit{H}_3$), and 2.36 (t, 2H, $NCH_2C\mathit{H}_2COONa$, ^3J = 9.9 Hz). ^{13}C NMR {^{1}H decoupled} (100 MHz, CD_3OD) δ = 181.1 ($NCH_2CH_2\mathit{C}OONa$), 56.5, 56.1, 55.5 (3 × $NCH_2\mathit{C}H_2N$), 53.7 (NCH_2CH_2COONa), 46.1 (NCH_3), and 36.6 ($NCH_2\mathit{C}H_2COONa$). MS (ESI negative mode, acetone): *m*/*z* 228.3 ([Pr-L-Me_2]$^-$), (ESI positive mode, acetone): *m*/*z* 230.3 ([Pr-L-Me_2 + 2H]$^+$) and 252.1 ([Pr-L-Me_2 + H + Na]$^+$). IR (KBr pellets)

Scheme 6. Synthesis of the Dinuclear Mn(III)-Mn(IV) Complexes Containing Chiral 1-(2-Hydroxypropyl)-4,7-dimethyltriazacyclononane as Well as Oxo Ligands



ν (cm^{-1}): 3459 (s), 2934 (s), 2852 (s), 2784 (s), 1611 (vs), 1581 (vs), 1464 (s), 1420 (s), 1367 (s), 1320 (m), 1077 (s), 1033 (s), 752 (m), and 623 (m). Anal. Calcd for $C_{11}H_{22}N_3O_2Na \cdot 0.5CHCl_3 \cdot H_2O$: C, 41.98; H, 7.51; N, 12.77. Found: C, 42.25; H, 7.71; N, 13.16.

***SS*-*trans*-2,5,8-Trimethyl-2,5,8-triazabicyclo[7.4.0^{1,9}]-tridecane (*SS*-L^{BMe3})**. In a 100 mL flask was dissolved *SS*-*trans*-2,5,8-tritosyl-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane[33] (2.09 g, 3.23 mmol) in 25 mL of 96% sulfuric acid, and the solution was heated at 130 °C for 72 h. After the mixture was cooled to 0 °C, 15 mL of diethyl ether was added, and the dark viscous precipitate was separated by decantation and dried in vacuo (0.05 mbar, 20 °C, 15 min). An ice-cold 10 M NaOH (50 mL) solution was slowly added to the slurry (pH > 12), and the resulting solution was extracted with $CHCl_3$ (3 × 50 mL), and the combined organic fractions were rotary evaporated affording a yellow oil. This product was dissolved in a mixture of 37% formaldehyde (15 mL) and formic acid (15 mL) and heated to reflux for 24 h. After subsequent cooling an excess of 37% HCl (25 mL) was added, and the solution was rotary evaporated. The yellow-brownish solids were dissolved in 20 mL of 5 M NaOH (pH > 12) and then extracted with chloroform (3 × 30 mL), dried over anhydrous Na_2SO_4, and rotary evaporated. The crude product was distilled (bulb-to-bulb) under reduced pressure (0.1 mbar, 105 °C) to give a colorless oil which is kept under an argon atmosphere.

***SS*-L^{BMe3}**: Yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.7−2.4 (m, 8H, NC*H*$_2$C*H*$_2$N), 2.35 (br, 2H, NC*HC*H*N), 2.26 (s, 3H, NC*H*$_3$), 2.22 (s, 6H, NC*H*$_3$), 1.80 (br, 2H), 1.71 (br, 2H), and 1.13 (br, 4H, cyclohexyl ring) ppm. ^{13}C NMR {^{1}H decoupled} (100 MHz, $CDCl_3$) δ = 64.2, 63.9, 55.0, 46.1, 40.6, 26.1, and 23.2 ppm. MS (ESI positive mode, acetone): *m*/*z* 226.2 ([R^{SS}L-Me$_3$ + H]$^+$). IR (film) ν (cm^{-1}): 2923 (s), 2775 (s), 1455 (s), 1366 (s), 1272 (s), 1172 (s), 1065 (s), 1026 (s), 951 (m), 877 (m), 853 (m), and 545 (m). UV−vis (CH_3CN) λ_{max} (nm): 229 (ϵ = 2200 M^{-1} cm^{-1}). CD (CH_3CN) λ_{max} (nm): 263 ($\Delta\epsilon$ = +0.49 M^{-1} cm^{-1}), 245 (−0.33), 230 (+0.57), 222 (−1.41), and 210 (+0.45).

General Procedure for [(*S*-L^{Me2R})$_2$Mn$_2$(O)$_2$][PF$_6$]$_3$ ([*S*,*S*-1][PF$_6$]$_3$ and [(*R*-L^{Me2R})$_2$Mn$_2$(O)$_2$][PF$_6$]$_3$ ([*R*,*R*-1][PF$_6$]$_3$). In a 50 mL Schlenk tube, an aqueous ethanol (70%, 5 mL) solution containing the chiral *S*-L^{Me2R} or *R*-L^{Me2R} ligand (140 mg, 0.65 mmol), $MnCl_2 \cdot 4H_2O$ (128 mg, 0.65 mmol), and KPF_6 (178 mg, 0.97 mmol) was stirred at room temperature (10 min) and then heated to 50 °C for 20 min. The resulting brown-red solution was cooled to 0 °C, before 1.5 mL of a freshly prepared aqueous solution containing H_2O_2 (65 μL, 0.65 mmol) and NaOH (31 mg, 0.78 mmol) was added. The pH of the brown-green solution was adjusted to 7.5 with 2 M H_2SO_4 and stirred at 20 °C for 2 h. After filtration through Celite and washing with 2 mL of acetonitrile, the filtrate was evaporated in vacuo. The solid residue was washed 3 times with 10 mL of ethanol, dried, and extracted with acetone. Single crystals suitable for X-ray analysis were grown from an acetone solution into which diethyl ether was allowed to slowly diffuse within 48 h.

[(*S*-L^{Me2R})$_2$Mn$_2$(O)$_2$][PF$_6$]$_3$ ([*S*,*S*-1][PF$_6$]$_3$: Yield 25−35%. MS (ESI positive mode, acetone): *m*/*z* 715.0 (55%, [**1** − 2H][PF$_6$]), 548.2 (40%, [**1** − C(CH_3)OH + Na]). IR (KBr pellets) ν (cm^{-1}): 3674 (m), 3436 (m), 2928 (m), 1583 (m), 1467 (s), 1014 (m), 839 (vs), 648 (s), and 558 (s). UV−vis (CH_3CN) λ_{max} (nm): 575 (ϵ = 320 M^{-1} cm^{-1}), 281 (14700), and 225 (12600). CD (CH_3CN) λ_{max} (nm): 474 ($\Delta\epsilon$ = −1.5 M^{-1} cm^{-1}), 432 (+0.4), 360 (−5.2), 310 (+5.0), 256 (+6.4), and 224 (−6.2) nm. Anal. Calcd for $C_{22}H_{50}F_{18}Mn_2N_6O_4P_3 \cdot 0.5$acetone: C, 27.23; H, 5.15; N, 8.11. Found: C, 27.33; H, 5.21; N, 8.53.

[(*R*-L^{Me2R})$_2$Mn$_2$(O)$_2$][PF$_6$]$_3$ ([*R*,*R*-1][PF$_6$]$_3$: Yield 25−35%. MS (ESI positive mode, acetone): *m*/*z* 715.0 (40%, [**1** − 2H][PF$_6$]), 548.2 (60%, [**1** − C(CH_3)OH + Na]). IR (KBr pellets) ν (cm^{-1}): 3674 (m), 3435 (s), 2927 (m), 1631 (m), 1467 (s), 1145 (m), 1070 (s), 1015 (s) 838 (vs), 647 (s), and 558 (s). UV−vis (CH_3CN) λ_{max} (nm): 575 (ϵ = 320 M^{-1} cm^{-1}), 281 (14700), and 225 (12600). CD (CH_3CN) λ_{max} (nm): 474 ($\Delta\epsilon$ = +1.5 M^{-1} cm^{-1}), 432 (−0.4), 360 (+4.7), 310 (−4.0), 256 (−6.4), and 224 (+5.4) nm. Anal. Calcd for $C_{22}H_{50}F_{18}Mn_2N_6O_4P_3 \cdot 0.5$acetone: C, 27.23; H, 5.15; N, 8.11. Found: C, 27.62; H, 5.19; N, 8.57.

Results and Discussion

Ligand Synthesis. For the selective incorporation of one chiral substituent into the 1,4,7-triazacyclononane ring the strategy depicted in Scheme 3 was applied.[17,18] The methine-bridged triamine, 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (L^{CH}), formed by the reaction of L with *N*,*N*′-dimethylaminoformaldehyde dimethyl acetal, can only give one product in the nucleophilic substitution with (*S*)-2-methylbutyl iodide, namely (*S*)-1-(2-methylbutyl)-4,7-diaza-1-azoniatricyclo-[5.2.1.0^{4,10}]decane iodide ([*S*-L$^{CH''}$][I]), which is further converted into the macrocyclic ligand *S*-L$^{Me2R''}$ (Scheme 3).

The MS and NMR data of [*S*-L$^{CHR''}$][I] are presented in the Experimental Section. The nonequivalence of the two (CH_3-*CH*$_2$-C*H) methylene protons in the ^{1}H NMR spectrum of [*S*-L$^{CHR''}$]$^+$ in CD_3OD is caused by the chiral carbon center, with δ = 1.41(m) and 1.61(m) ppm. The circular dichroism (CD) spectrum is bisignate and related to the strong UV absorbance in the 200−270 nm region (Figure 1). The difference in the molar extinction coefficients is maximal at λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 243 (+2.34) and 239.5 (−5.1) nm.

S-L$^{Me2R''}$ has been isolated in the form of the free base (colorless oil) using bulb-to-bulb distillation under reduced pressure. The ESI-MS spectrum presents one peak at *m*/*z* 228.2 ([*S*-L$^{Me2R''}$ + H]$^+$) in the positive mode. The ^{1}H NMR spectrum of the CD_3OD solution reflects the nonequivalence of the two (CH_3-*CH*$_2$-C*H) methylene protons, caused by the chiral carbon center, with δ = 1.12(m) and 1.49(m) ppm. The CD spectrum is bisignate and related to the strong UV absorbance with a maximum centered around 212 nm. For the *S*-L$^{Me2R''}$ ligand the difference in the molar extinction coefficients is maximal at λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 232.5 (−1.7) and 229 (+0.87) nm.

The two chiral ligands (*S*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (*S*-L^{Me2R}) and (*R*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (*R*-L^{Me2R}) are obtained from L^{Me2} using the ring-opening of the corresponding enantiomerically pure epoxides, see Scheme 4. The nucleophilic attack was shown to be 100% regiospecific and proceeds at the less hindered carbon atom of the epoxide, so the absolute configuration at the neighboring carbon center is conserved.[11e,30]

The ^{1}H and ^{13}C NMR spectra of both enantiomers, *S*-L^{Me2R} and *R*-L^{Me2R}, are in accordance with those reported for the racemic *rac*-L^{Me2R}.[30] The CD spectra of the *S*-L^{Me2R} and *R*-L^{Me2R} solutions in hexane indicate the enantiomeric relationship between these two molecules and result in the mirror images of each other (Figure 2). The CD curves are

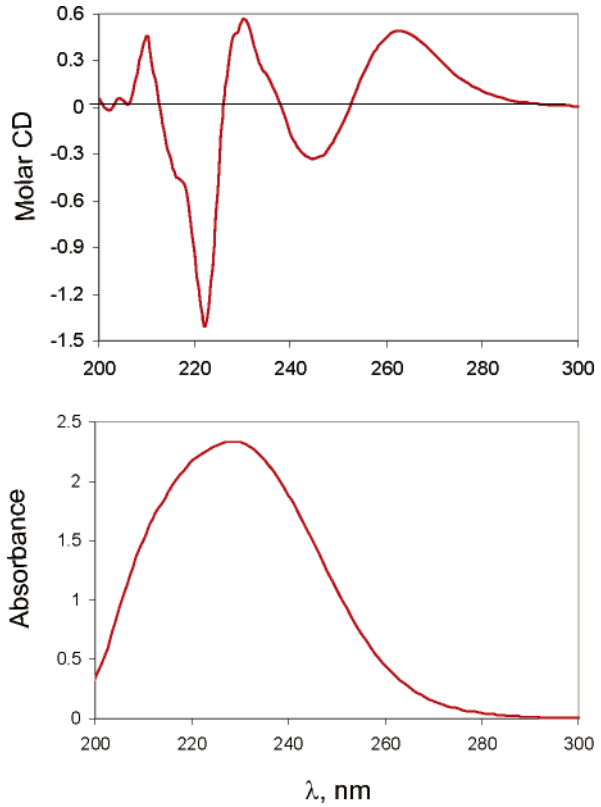


Figure 3. Molar circular dichroism (CD) and UV spectra of *SS-trans*-2,5,8-trimethyl-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane in hexane ([*SS*-L^{BMe3}] = 1.06 mM).

bisignate and related to the strong UV absorbance in the 220−260 nm region. For the *R*-L^{Me2R} enantiomer, the molar CD spectrum shows four maxima centered around λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 249 (−0.15), 238 (+0.38), 233 (−0.62), and 228 (+0.78) nm; for the *S*-L^{Me2R} enantiomer: λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 246 (+0.15), 238 (−0.24), 234 (+0.65), and 229 (−0.73) nm.

The anionic ligands 2-(4,7-dimethyl-1,4,7-triazacyclononan-1-yl)acetate ([L^{Me2Ac}]$^-$)[45] and 3-(4,7-dimethyl-1,4,7-triazacyclononan-1-yl)propionate ([L$^{Me2R'}$]$^-$) containing a pendent carboxylato arm are readily obtained as sodium salts by reaction of the 1,4-dimethyl-1,4,7-triazacyclononane (L^{Me2}) with sodium bromoacetate or 3-bromopropionate, by modification of previously described procedure[11,27] for L^{Ac3} (see Scheme 4). In contrast to L^{Ac3}, both Na[L^{Me2Ac}] and Na[L$^{Me2R'}$] can be successfully isolated from the alkaline aqueous solution (by extraction with chloroform) in the form of the corresponding sodium salts.

Given that the C_2-element of symmetry plays an important role in epoxidation catalysis,[46] we introduced this element also in the asymmetric analogue of 1,4,7-triazacyclononane. Thus, we synthesized *SS-trans*-2,5,8-trimethyl-2,5,8-triazabicyclo[7.4.0^{1,9}]tridecane (*SS*-L^{BMe3}, Scheme 5); however, as in the case of its known *RR*-enantiomer,[35a,b] the yields are quite low.

The chiroptical properties of the *SS*-L^{BMe3} solution in hexane result in the CD spectrum shown in Figure 3. The CD curve is bisignate and related to the strong UV absorbance in the 200−300 nm region. For the *SS*-L^{BMe3} molar CD spectrum gives five maxima centered around λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 263 (+0.49), 245 (−0.33), 230 (+0.57), 222 (−1.41), and 210 (+0.45) nm.

The isolation of manganese complexes containing *SS*-L^{BMe3} in our hands was not successful; however, a low-yield synthesis for its (*R*,*R*) enantiomer has been reported.[35b] For the *S*-L$^{Me2R''}$ ligand no crystalline material could be obtained using manganese(II) chloride and manganese(III) acetate as a starting material. Fortunately, we succeeded in the isolation and the characterization of dinuclear manganese complexes containing *R*-L^{Me2R} and *S*-L^{Me2R} ligands.

Complex Synthesis and Structure. Two dinuclear Mn(III)-Mn(IV) complexes [(*S*-L^{Me2R})$_2$Mn$_2$(O)$_2$]$^{3+}$ (*S*,*S*-**1**) and [(*R*-L^{Me2R})$_2$Mn$_2$(O)$_2$]$^{3+}$ (*R*,*R*-**1**) are synthesized by reacting $MnCl_2 \cdot H_2O$ with the chiral ligand in moist ethanol, followed by the addition of an alkaline solution of hydrogen peroxide (Scheme 6). Two manganese centers in *S*,*S*-**1** and *R*,*R*-**1** are bridged by two oxo ligands as well as by two chiral pendent arms from the triazacyclononane rings. Both complexes *S*,*S*-**1** and *R*,*R*-**1** can be isolated as the hexafluorophosphate salts, which are well soluble in acetone and acetonitrile, but sparingly soluble in ethanol, isopropyl alcohol, and water.

The ESI-MS spectra of *S*,*S*-**1** and *R*,*R*-**1** show the parent peak at *m*/*z* 715.1 ([**1** − 2H][PF_6]) in the positive mode. The absorptions at 648 cm^{-1}, observed in the infrared spectra, can be ascribed to the breathing mode of the Mn_2O_2 core,[47] which are shifted to the lower frequencies as compared to those observed for [(L^{Me2})$_2$Mn$_2$(O)$_2$(OOCH)]$^{2+}$ (690, 668 cm^{-1}) and [(L^{Me2})$_2$Mn$_2$(O)$_2$(OOCMe)]$^{2+}$ (686, 661 cm^{-1}) containing a μ-carboxylato bridge.[19] The presence of hydroxo groups in the bridging pendent arms of *S*,*S*-**1** and *R*,*R*-**1** is established by a O−H stretching frequency at 3674 cm^{-1}. In the UV/vis spectra, the acetonitrile solutions of *S*,*S*-**1** and *R*,*R*-**1** show three absorption maxima λ (ϵ, M^{-1} cm^{-1}) 575 (320), 281 (14700), 225 (12600) nm. The CD spectra of the *S*,*S*-**1** and *R*,*R*-**1** solutions in acetonitrile indicate the enantiomeric relationship between these two complexes and result in the mirror images of each other (Figure 4). The CD curves are bisignate and for *S*,*S*-**1** shows the maxima centered around λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 474 (−1.5), 432 (+0.4), 360 (−5.2), 310 (+5.0), 256 (+6.4) and 224 (−6.2) nm; for *R*,*R*-**1**: λ ($\Delta\epsilon$, M^{-1} cm^{-1}) 474 (+1.5), 432 (−0.4), 360 (+4.7), 310 (−4.0), 256 (−6.4), and 224 (+5.4) nm.

Brown-green X-ray quality crystals of [*S*,*S*-**1**][PF_6]$_3 \cdot$0.5$(CH_3)_2CO$ and [*R*,*R*-**1**][PF_6]$_3 \cdot$0.5$(CH_3)_2CO$ were obtained by slow diffusion of ether into an acetone solution containing *S*,*S*-**1** and *R*,*R*-**1** respectively. The molecular structures of *S*,*S*-**1** and *R*,*R*-**1** are shown in Figures 5 and 6. *S*,*S*-**1** and *R*,*R*-**1** are the first examples of a dinuclear manganese complex bridged by two chiral pendent arms.

The molecular structures of the Mn(III)-Mn(IV) dioxo complexes [(*S*-L^{Me2R})$_2$Mn$_2$(O)$_2$]$^{3+}$ (*S*,*S*-**1**) and [(*R*-L^{Me2R})$_2$Mn$_2$(O)$_2$]$^{3+}$ (*R*,*R*-**1**) show a metal−metal distance of 2.695(3) and 2.699(2) Å, respectively. This distance is slightly longer then those in the isoelectronic Mn(III)-Mn(IV) cations

(47) Pal, S.; Olmstead, M. M.; Armstrong, W. H. *Inorg. Chem.* **1995**, *34*, 4708−4715.

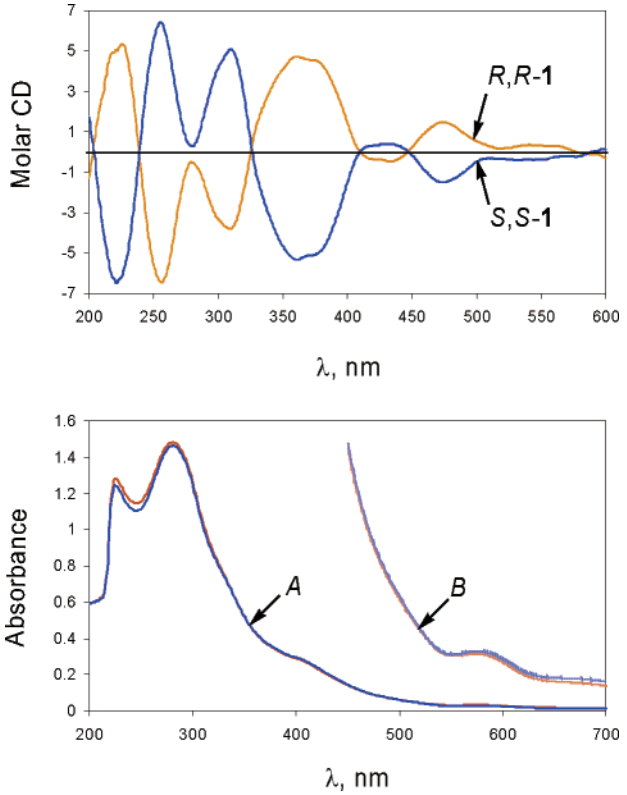


Figure 4. Molar circular dichroism (CD) and UV−vis spectra of [*S*,*S*-**1**]-$[PF_6]_3$ and [*R*,*R*-**1**]$[PF_6]_3$ in acetonitrile; in the UV−vis spectra for *A*: $[S,S\text{-}\mathbf{1}]^{3+} = [R,R\text{-}\mathbf{1}]^{3+} = 1.0 \times 10^{-4}$ M; for *B*: $[S,S\text{-}\mathbf{1}]^{3+} = [R,R\text{-}\mathbf{1}]^{3+} = 1.0 \times 10^{-3}$ M.

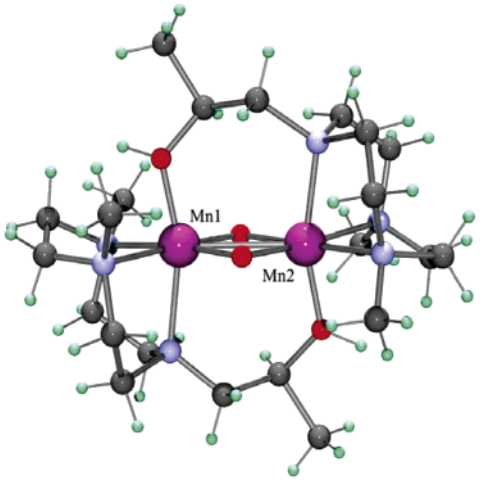


Figure 5. Structural representation of cation *S*,*S*-**1** showing coordination mode of the two manganese centers in [*S*,*S*-**1**]$[PF_6]_3$. Hexafluorophosphate anions and acetone molecule are omitted for clarity.

$[(L^{Me2})_2Mn_2(O)_2(OOCH)]^{2+}$ (2.620(1) Å),[19] $[(L^{Me2})_2Mn_2(O)_2(OOCMe)]^{2+}$ (2.628(4) Å),[19] and $[L_2Mn_2(O)_2(OOCMe)]^{2+}$ (2.588(2) Å)[48] but compares well to those in the dinuclear Mn(III)-Mn(IV) cation $[(L^t)_2Mn_2(O)_2]^{3+}$ (2.679(1) Å, L^t = 2,2′,2″-triaminoethylamine) containing two bridging ethylenediamine and two oxo fragments between clearly distinguishable Mn(III) and Mn(IV) centers.[49] In our case the differentiation of Mn(III) and Mn(IV) centers is problematical, because the environment of the two manganese atoms is practically identical, but on the basis of the distinctly different Mn−O(oxo) bond lengths (see Table 2), the oxidation state IV may be tentatively assigned to Mn1 and the oxidation state III to Mn2.

As the proton at the oxygen atom of the two pendent arms in *S*,*S*-**1** and in *R*,*R*-**1** cannot unambiguously be established by the X-ray analyses nor detected by NMR spectroscopy due to the paramagnetic character of the complexes, we cannot completely rule out **1** to be a Mn(IV)-Mn(V) complex with two deprotonated alcoholato ligands rather than a Mn(III)-Mn(IV) complex with two intact alcohol ligands. However, the presence of the intact OH function in **1** is clearly visible in the IR spectrum (ν_{OH} = 3674 cm^{-1}), and the Mn−Mn distance of 2.7 Å in *S*,*S*-**1** and in *R*,*R*-**1** is in good agreement with those of other Mn(III)-Mn(IV) com-

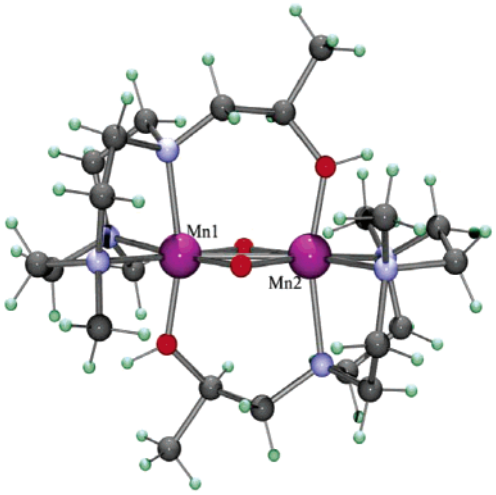


Figure 6. Structural representation of cation *R*,*R*-**1** showing coordination mode of the two manganese centers in [*R*,*R*-**1**]$[PF_6]_3$. Hexafluorophosphate anions and acetone molecule are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [*S*,*S*-**1**]$[PF_6]_3$·0.5·$(CH_3)_2CO$ and [*R*,*R*-**1**]$[PF_6]_3$·0.5·$(CH_3)_2CO$

	[*S*,*S*-**1**]$[PF_6]_3$	[*R*,*R*-**1**]$[PF_6]_3$
Interatomic Distances		
Mn1−Mn2	2.695(3)	2.699(2)
Mn1−O1 (hydroxo)	1.799(6)	1.813(7)
Mn2−O2 (hydroxo)	1.806(7)	1.794(7)
Mn1−O3 (oxo)	1.804(7)	1.784(8)
Mn1−O4 (oxo)	1.778(7)	1.763(9)
Mn2−O3 (oxo)	1.813(7)	1.846(11)
Mn2−O4 (oxo)	1.832(8)	1.836(9)
Mn1−N (R^{1R} arm)	2.176(10)	2.116(10)
Mn1−N (Me)	2.128(10)	2.142(16)
Mn1−N (Me)	2.100(9)	2.103(12)
Mn2−N (R^{1R} arm)	2.090(9)	2.145(9)
Mn2−N (Me)	2.155(10)	2.073(11)
Mn2−N (Me)	2.169(9)	2.138(12)
Angles		
Mn1−O3−Mn2 (oxo)	96.3(3)	96.0(3)
Mn1−O4−Mn2 (oxo)	96.5(3)	97.1(3)
O1−Mn1−Mn2	101.7(3)	99.7(4)
O2−Mn2−Mn1	101.5(3)	100.6(4)

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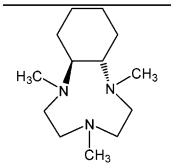
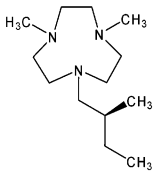
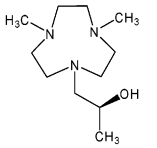
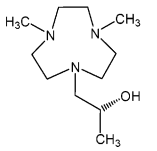
(49) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 967−969.

Table 3. Epoxidation of Indene in MeCN and H_2O/MeCN 50% v/v Mixtures, Catalyzed by the Isolated Compounds [*S*,*S*-**1**][PF_6]$_3$ and [*R*,*R*-**1**][PF_6]$_3$ in the Absence/Presence of Ascorbic or Oxalate Buffer as Cocatalyst[a]

							in water/acetonitrile (50/50 v/v)								
	in acetone without cocatalyst			in acetonitrile without cocatalyst			without cocatalyst			with oxalate			with ascorbate		
complex	ee %	conv %	TON	ee %	conv %	TON	ee %	conv %	TON	ee %	conv %	TON	ee %	conv %	TON
S,*S*-**1**	7 (1*S*,2*R*)	6.4	64	7 (1*R*,2*S*)	2.1	21	13 (1*R*,2*S*)	2.9	29	4.2 (1*R*,2*S*)	10.4	104	11 (1*R*,2*S*)	6.2	62
R,*R*-**1**	7 (1*R*,2*S*)	6.4	64	7 (1*S*,2*R*)	2.1	21	13 (1*S*,2*R*)	2.9	29	4.4 (1*S*,2*R*)	10.5	105	11 (1*S*,2*R*)	6.2	62

[a] 0.3 mM ascorbic (0.15 mM ascH + 0.15 mM ascNa) or 0.3 mM oxalate (0.15 mM $oxaH_2$ + 0.15 mM $oxaNa_2$) buffer as cocatalyst; $[catalyst]_o = 10^{-4}$ M, $[H_2O_2]_o = 0.20$ M, $[indene]_o = 0.10$ M, 2 °C; 2 h. The absolute configuration of indene oxide, which is preferentially formed, is shown in brackets.

Table 4. Epoxidation of Indene in H_2O/MeCN 50% v/v, Catalyzed by in Situ Prepared Manganese Complexes in the Absence/Presence of Ascorbic or Oxalate Buffer as Cocatalyst[a]

		without co-catalyst			with oxalate			with ascorbate		
ligand	name	ee %	conv. %	TON 2h	ee %	conv. %	TON 2h	ee %	conv. %	TON 2h
	*SS*-L^{BMe3}	13 (1*S*,2*R*)	0.68	6.8	1.4 (1*S*,2*R*)	1.26	12.6	10 (1*S*,2*R*)	0.54	5.4
	*S*-$L^{Me2R''}$	5.9 (1*S*,2*R*)	1.46	14.6	4.1 (1*S*,2*R*)	6.0	60	17 (1*S*,2*R*)	0.55	5.5
	*S*-L^{Me2R}	17 (1*R*,2*S*)	4.2	42	3.5 (1*R*,2*S*)	15.9	159	3.3 (1*R*,2*S*)	0.51	5.1
	*R*-L^{Me2R}	17 (1*S*,2*R*)	4.2	42	3.5 (1*S*,2*R*)	16.3	163	3.3 (1*S*,2*R*)	0.49	4.9

[a] 0.3 mM ascorbic (0.15 mM ascH + 0.15 mM ascNa) or 0.3 mM oxalate (0.15 mM $oxaH_2$ + 0.15 mM $oxaNa_2$) buffer; $[MnSO_4]_o = 10^{-4}$ M, $[ligand]_o = 1.5 \times 10^{-4}$ M, $[H_2O_2]_o = 0.20$ M, $[indene]_o = 0.10$ M, 2 °C, 2 h. The absolute configuration of indene oxide, which is preferentially formed, is shown in brackets.

plexes (vide supra) but not with those of rare and unstable Mn(IV)-Mn(V) complexes, for which a manganese−manganese distance has been calculated to be around .9 Å.[50]

Catalytic Potential. We used the isolated salts [*S*,*S*-**1**]-[PF_6]$_3$ and [*R*,*R*-**1**][PF_6]$_3$ as well as the in situ prepared complexes for catalytic oxidation reactions and, in particular, for asymmetric epoxidation reactions. The combinations of $MnSO_4 \cdot H_2O$ with L^{Me2}, *SS*-L^{BMe3}, *S*-L^{Me2R}, *S*-$L^{Me2R''}$, L^{Me2Ac}, and $L^{Me2R'}$ were prepared in situ in water; the stock solution thus formed was then added to the reaction mixture with or without cocatalyst. The effect of carboxylates on the catalytic activity of the dinuclear manganese complexes has been intensively studied.[12−15,19] The beneficial influence of ascorbic acid (ascH) as cocatalyst has been observed in the oxidation of 2-pentanol to give 2-pentanone, catalyzed by a mixture of $Mn(OOCCH_3)_2 \cdot 4H_2O$ and L^{Me3} in moist acetonitrile.[51] The accelerating effect of oxalates added in 3:1 ratio relative manganese catalyst containing L^{Me3} was originally reported by De Vos.[52]

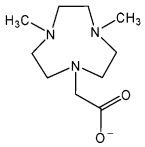
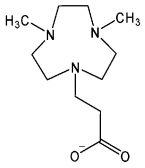
Indene has been chosen as a model substrate for enantioselective epoxidation reactions, it can be epoxidized to give the racemic mixture of (1*R*,2*S*) and (1*S*,2*R*) enantiomers of indene oxide using *m*-chloroperbenzoic acid[42] (2-indanone has been also detected) or to give (1*R*,2*S*)-indene oxide enriched mixture using the Jacobsen protocol with a *R*,*R*-(salen)-Mn-based complex.[43] Both methods were used to prepare the calibration samples for the HPLC separation on

(50) Petrie, S.; Stranger, R. *Inorg. Chem.* **2004**, *43*, 5237−5244.

(51) Berkessel, A.; Sklorz, C. A. *Tetrahedron Lett.* **1999**, *40*, 7965−7968.

(52) De Vos, D. E.; Sels, B. F.; Reynaers, M.; Rao, Y. V. S.; Jacobs, P. A. *Tetrahedron Lett.* **1998**, *39*, 3221−3224.

Table 5. Epoxidation of Indene in H_2O/MeCN 50% v/v, Catalyzed by in Situ Prepared Manganese Complexes with Nonchiral Ligands[a]

ligand	name	catalyst μmol	(1*R*,2*S*)-indene oxide, μmol	(1*S*,2*R*)-indene oxide, μmol	2-indanone μmol	conv. %	TON
	L^{Me2Ac}	0.2	30.26	30.22	4.67	32.6	326
	$L^{Me2R'}$	0.2	41.91	41.92	6.27	45.0	450

[a] $[MnSO_4]_o = 10^{-4}$ M, $[ligand]_o = 1.5 \times 10^{-4}$ M, $[H_2O_2]_o = 0.20$ M, $[indene]_o = 0.10$ M, 2 °C, 2 h.

Table 6. Oxidation of Isopropyl Alcohol in Water and Acetonitrile, Catalyzed by the Complexes *S*,*S*-**1** and *R*,*R*-**1** in the Absence/Presence of Ascorbic or Oxalic Acid as Cocatalyst[a]

	TON in water			TON in acetonitrile		
catalyst	without cocatalyst	with oxalate	with ascorbic acid	without cocatalyst	with oxalate	with ascorbic acid
S,*S*-**1**	12	280	60	15	50	5
R,*R*-**1**	12	280	60	15	50	5

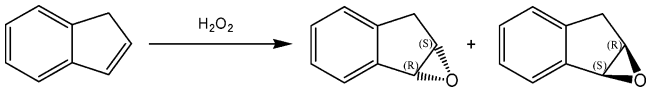
[a] 0.01 M ascorbic acid or 0.02 M oxalic (0.01 M $oxaH_2$ + 0.01 M $oxaNa_2$) buffer in water, 0.02 M oxalic acid in acetonitrile, 20 °C, 1.0×10^{-4} M catalyst, 0.20 M isopropyl alchohol, 0.50 M H_2O_2, 1 h.

Table 7. Oxidation of Racemic 1-Phenylethanol in H_2O/MeCN 50% v/v, Catalyzed by *S*,*S*-**1** and *R*,*R*-**1** in the Absence/Presence of Ascorbic or Oxalate Buffer as Cocatalyst[a]

	without cocatalyst			with oxalate			with ascorbate		
complex	ee %	conv %	TON 2 h	ee %	conv %	TON 2 h	ee %	conv %	TON 2 h
S,*S*-**1**	0.2 (*S*-)	2.4	12	0.1 (*S*-)	29	145	0.2 (*S*-)	26	130
R,*R*-**1**	0.0	2.4	12	0.3 (*S*-)	29	145	0.1 (*R*-)	26	130

[a] 0.3 mM ascorbic (0.15 mM ascH + 0.15 mM ascNa) or 0.3 mM oxalate (0.15 mM $oxaH_2$ + 0.15 mM $oxaNa_2$) buffer as cocatalyst; $[catalyst]_o = 10^{-4}$ M, $[H_2O_2]_o = 0.20$ M, $[1\text{-phenylethanol}]_o = 0.05$ M, 2 °C. The absolute configuration of 1-phenylethanol, which is preferentially oxidized, is shown in brackets.

the Daicel Chiracel OJ-H type column using nitrobenzene as internal standard. The results of the epoxidation studies are shown in Tables 3−5.



In moist acetonitrile the catalytic activity and enantioselectivity of the isolated complexes [*S*,*S*-**1**][PF_6]$_3$ and [*R*,*R*-**1**][PF_6]$_3$ are comparable to those observed for the parent in situ prepared manganese complexes with *S*-L^{Me2R} and *R*-L^{Me2R} ligands. However, upon addition of ascorbic acid/sodium ascorbate, *S*,*S*-**1** and *R*,*R*-**1** are about 10 times more active and 3 times more selective with respect to the corresponding in situ prepared systems (Table 4).

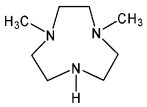
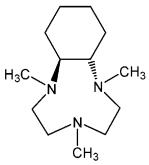
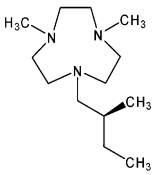
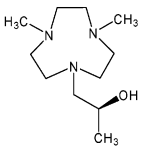
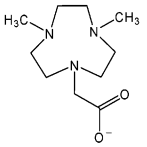
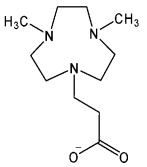
In dry acetonitrile the catalytic activity and enantioselectivity of *S*,*S*-**1** and *R*,*R*-**1** are low, and, upon addition of oxalic acid ($oxaH_2$, 500 equiv with respect to the catalyst), only 2-indanone is observed with a TON of 12 under the same conditions. This means that in acetonitrile solution the nature of the oxidizing species formed from *S*,*S*-**1** and *R*,*R*-**1** is substantially different from those derived from Wieghardt's type $[(L^{Me3})_2Mn_2(O)_3]^{2+}$ precursor, where oxalic acid dramatically increases the catalytic performance.[12−15] Another interesting feature is that by using acetone as solvent the enantioselectivity is inversed. Indeed, the (1*S*,2*R*)-enantiomer of indene oxide is the major epoxidation product with *S*,*S*-**1** in acetone, while (1*R*,2*S*)-enantiomer is predominantly formed when acetonitrile or water is used as solvent (Table 3). Such an inversion has been reported for certain enzymes[53] and catalytic systems.[54]

With the in situ prepared catalysts from manganese(II) sulfate and *SS*-L^{BMe3}, *S*-L^{Me2R}, *R*-L^{Me2R}, or *S*-$L^{Me2R''}$ and hydrogen peroxide as oxidant, we observed by ^{1}H NMR and UV spectroscopy only the formation of the two expected epoxides. Only upon standing at room temperature for 3 days, the formation of 2-indanone, 2-indanol, and 1,2-indanediols was also observed. The catalytic activity is low in the case of *SS*-L^{BMe3} and *S*-$L^{Me2R''}$ without cocatalyst, the corresponding catalytic turnover numbers are 6.8 (ee = 13%) and 14.6 (ee = 5.9%) after 2 h of the reaction with predominant formation of (1*S*,2*R*)-indene oxide. In the case of *R*-L^{Me2R} and *S*-L^{Me2R} ligands the TONs attain 42 (ee = 17%), the (1*S*,2*R*)-enantiomer being the major epoxidation product with *R*-L^{Me2R}, while with the *S*-L^{Me2R} ligand (1*R*,2*S*)-indene oxide

(53) (a) Tawaki, S.; Klibanov, A. M. *J. Am. Chem. Soc.* **1992**, *114*, 1882−1884. (b) Kawasaki, M.; Nakamura, K.; Kawabata, S. *J. Mol. Catal. B: Enzym.* **1999**, *6*, 447−451. (c) Ueji, S.-I.; Tanaka, H.; Hanaoka, T.; Ueda, A.; Watanabe, K.; Kaihatsu, K.; Ebara, Y. *Chem. Lett*. **2001**, *10*, 1066−1067.

(54) (a) Selke, R.; Facklam, C.; Foken, H.; Heller, D. *Tetrahedron: Asymmetry* **1993**, *4*, 369−382. (b) Hess, R.; Vargas, A.; Mallat, T.; Burgi, T.; Baiker, A. *J. Catal.* **2004**, *222*, 117−128. (c) Colston, N. J.; Wells, R. P. K.; Wells, P. B.; Hutchings, G. J. *Catal. Lett.* **2005**, *103*, 117−120. (d) Jenkins, R. L.; Dummer, N.; Li, X.; Bawaked, S. M.; McMorn, P.; Wells, R. P. K.; Burrows, A.; Kiely, C. J.; Hutchings, G. J. *Catal. Lett*. **2006**, *110*, 135−138.

Table 8. Oxidation of Isopropyl Alcohol in Water, Catalyzed by in Situ Prepared Manganese Complexes in the Absence/Presence of Ascorbic Acid or Oxalate Buffer as Cocatalyst[a]

ligand	name	TON in water		
		without co-catalyst	with oxalate	with ascorbic acid
	1,4-dimethyl-1,4,7-triazacyclononane (**L^{Me2}**)	17	77	103
	*SS-trans*-2,5,8-trimethyl-2,5,8-triazabicyclo-[7.4.0^{1,9}] tridecane (**SS-L^{BMe3}**)	0	51	198
	(*S*)-1-(2-methylbutyl)-4,7-dimethyl-1,4,7-triazacyclononane (**S-$L^{Me2R''}$**)	10	1140	78
	(*S*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane (**S-L^{Me2R}**)	14	100	70
	2-(4,7-dimethyl-1,4,7-triazacyclononan-1-yl)acetate (**$[L^{Me2Ac}]^-$**)	72	28	73
	3-(4,7-dimethyl-1,4,7-triazacyclononan-1-yl)propionate (**$[L^{Me2R'}]^-$**)	310	8	71

[a] 0.01 M ascorbic acid or 0.02 M oxalate (0.01 M $oxaH_2$ + 0.01 M $oxaNa_2$) buffer; $[MnSO_4]_o = 10^{-4}$ M, $[ligand]_o = 1.5 \times 10^{-4}$ M, $[H_2O_2]_o = 0.50$ M, $[i\text{-PrOH}]_o = 0.20$ M, 20 °C, 1 h.

is preferentially formed. In the presence of oxalate (3 equiv with respect to Mn^{2+}) the catalytic activity increases (TONs attain 160), but the enantioselectivity decreases to ee = 1−4% (Table 4). This fact demonstrates that in the presence of oxalates a different catalytically active species is formed. With ascorbic acid/sodium ascorbate used as a cocatalyst the catalytic activity is low and gives about 5 turnovers after 2 h of the reaction (Table 4).

The manganese complexes with L^{Me2Ac} and $L^{Me2R'}$ ligands containing pendent carboxylato arms show a significantly higher catalytic activity in the epoxidation of indene; the addition of cocatalyst is not required. Using these in situ prepared combinations under the conditions applied for the enantioselective catalysis, the TONs values attain 326 and 450, the conversions being 32.6% and 45% for L^{Me2Ac} and $L^{Me2R'}$, respectively (the product distribution shows 93% of indene oxide and 7% of 2-indanone, Table 5).

The best catalytic performance (450 turnover numbers after 2 h) of the system $MnSO_4/L^{Me2R'}$ is considerably higher than

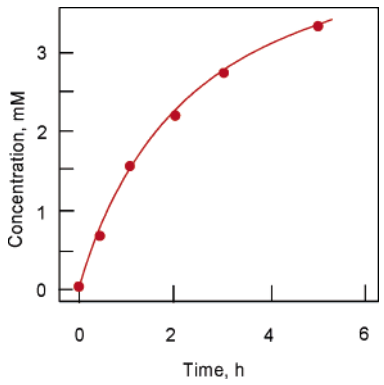


Figure 7. Accumulation of cyclohexyl hydroperoxide in the oxidation of cyclohexane (0.46 M) with H_2O_2 (0.6 M) in MeCN at 25 °C catalyzed by *R*,*R*-**1** (0.05 mM) and oxalic acid (0.05 M) measured with the triphenylphosphine method.[13b,d,g,44]

that of the system $MnSO_4/L^{Ac3}$ (Table 3), for which a TON of 66 was observed after 10 h under optimized conditions.[11d] To the best of our knowledge, the system $MnSO_4/L^{Me2R'}$ gives

Table 9. Selectivity Parameters in Oxidation of Alkanes in Acetonitrile[a]

		C(1) :C(2) :C(3) :C(4)				trans/cis	
entry	system	*n*-hexane	*n*-heptane	*n*-octane	1° :2° :3° isooctane	*cis*-DMCH	*trans*-DMCH
1	*R*,*R*-**1**−oxalic acid in MeCN (25 °C)	1:71:78	1:91:99:68	1:94:99:51	1:5.3:17	0.31	13
2	*R*,*R*-**1**−acetic acid in MeCN (25 °C)	1:42:43			1:3.4:20	0.72	45
3	*R*,*R*-**1**−oxalic acid in MeCN (50 °C)[b]			1:76:32:23			
4	L^{Me3}−Mn^{2+}−$oxaNa_2$ in MeCN (2 °C)	1:164:161	1:100:111:83	1:100:117:90	1:5.3:51	0.18	8.1
5	L^{Me3}−Mn^{2+}−$oxaNa_2$ in acetone (2 °C)	1:71:64	1:80:66:56	1:52:50:42	1:1.9:35	0.13	
6	$L^{Me2R''}$−Mn^{2+}−$oxaNa_2$ in MeCN (2 °C)	1:53:45	1:49:40:31	1:54:57:39	1:2.9:26	0.43	4.4
7	$L^{Me2R''}$−Mn^{2+}−$oxaNa_2$ in acetone (2 °C)					0.9	3.9
8	h*n*−H_2O_2 (20 °C)	1:10:7	1:7:6:7		1:2:6	0.9	1.0
9	$FeSO_4$−H_2O_2 (20 °C)		1:5:5:4.5		1:3:6	1.3	1.2
10	*n*-Bu_4NVO_3−pcaH−H_2O_2 (40 °C)[c]	1.0:6.9:7.0	1.0:5.7:7.2:5.0	1:7.4:8.3:6.1	1.0:1.2:17	0.75	0.8
11	H_2O_2 in CF_3COOH[d]	1.0:364:363			1:52:0		
12	$[(L^{Me3})_2Mn_2O_3]^{2+}$− MeCOOH−$H_2O_2$ (20 °C)[e]		1:46:35:35		1.0:7.9:40	0.34	4.1

[a] All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols. Parameter C(1):C(2):C(3):C(4) is relative normalized reactivities of hydrogen atoms at carbons 1, 2, 3, and 4 of the chain of unbranched alkanes. Parameter 1°:2°:3° is relative normalized reactivities of hydrogen atoms at primary, secondary, and tertiary carbons of branched alkanes. Parameter trans/cis is the ratio of trans-and cis-isomers of *tert*-alcohols formed in the oxidation of *cis*- or *trans*-disubstituted cyclohexanes. *cis*-DMCH and *trans*-DMCH are *cis*-1,2-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane, respectively. [b] *tert*-Butyl hydroperoxide was used instead of hydrogen peroxide. [c] For this system, see ref 56. [d] See ref 57. [e] For this system, see refs 12 and 13.

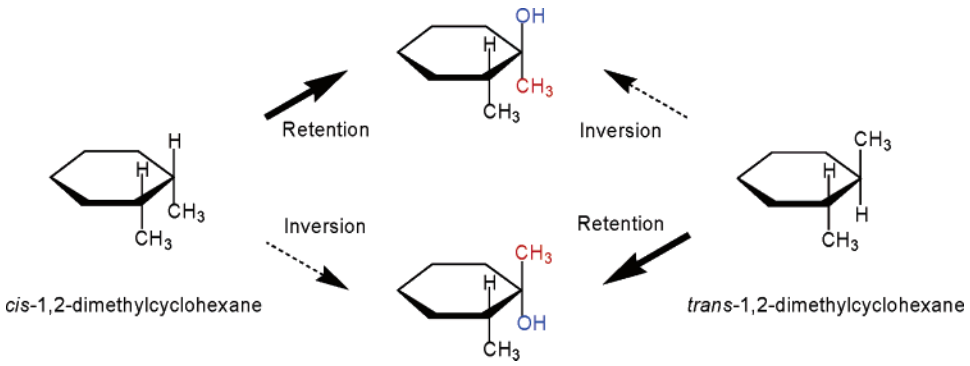
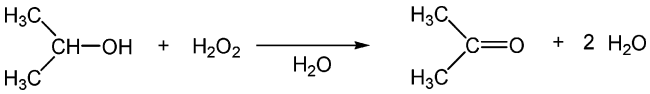


Figure 8. Stereoselectivity in the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane with H_2O_2 to give *cis*- and *trans*-1,2-dimethyl-cyclohexanol catalyzed by *R*,*R*-**1.**

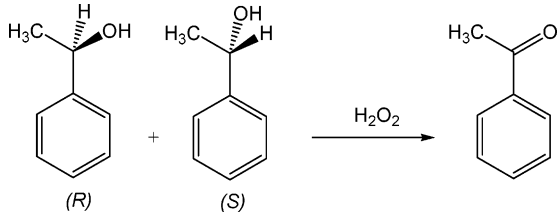
the highest catalytic turnover for epoxidation reaction without cocatalyst reported so far. An exceptional example was reported by De Vos and Bein,[11d] who used a $MnSO_4$/L^{Me3} combination for epoxidation with hydrogen peroxide in acetone solution where solvent acts as a cocatalyst.

The catalytic oxidation of alcohols with hydrogen peroxide was studied using isopropyl alcohol and *rac*-1-phenylethanol as a model substrates. The reaction is carried out with the isolated compounds [*S*,*S*-**1**][PF_6]$_3$ and [*R*,*R*-**1**][PF_6]$_3$ as well as with the in situ prepared complexes in aqueous solution in the absence/presence of ascorbic or oxalic acid as cocatalysts at 20 °C. The results are shown in Table 6−8.



The isolated complexes *S*,*S*-**1** and *R*,*R*-**1** (hexafluorophosphate salts) were tested for the oxidation of isopropyl alcohol with hydrogen peroxide in aqueous as well as in acetonitrile solution at 20 °C. The results are shown in Table 6. Both enantiomers show, within the error limits, the same catalytic activity. In the absence of cocatalyst the complexes are more active in acetonitrile solution; however, in aqueous solution the accelerating effect of the added cocatalyst is more pronounced.

It is interesting to check the enantioselectivity of these two chiral dimanganese complexes in the oxidative kinetic resolution of racemic 1-phenylethanol to give acetophenone. The results are shown in Table 7.



Even at low temperature (2 °C) no enantioselectivity is observed for the oxidation of (*R*)- and (*S*)-1-phenylethanol. This means that both enantiomers are kinetically equivalent in the reactivity toward H-atom abstraction catalyzed by *S*,*S*-**1** and *R*,*R*-**1** both in the absence and in the presence of cocatalyst (including a chiral one − ascorbic acid). On the other hand, in the presence of oxalic and ascorbic acid, the overall catalytic performance increases and attains 145 turnover numbers after 2 h of the reaction (Table 7).

The oxidation of isopropyl alcohol to give acetone catalyzed in aqueous solution was also studied by in situ systems composed of $MnSO_4 \cdot H_2O$ and the appropriate

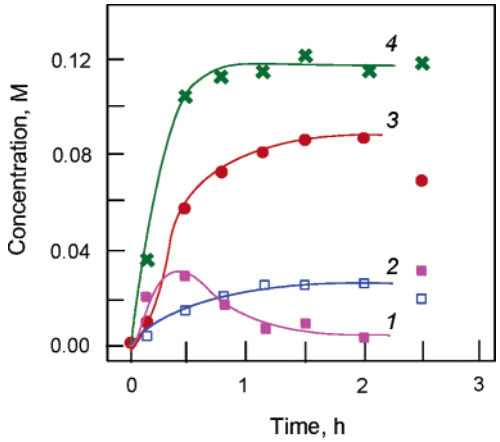


Figure 9. Oxidation of cyclohexane (0.335 M) with H_2O_2 (1.5 M) in acetone at 2 °C catalyzed by the in situ prepared Mn^{2+}/L^{Me3} (1.0/1.5 mM) combination in the presence of disodium oxalate (1.5 mM); the following curves are shown: accumulation of cyclohexyl hydroperoxide (curve *1*), cyclohexanol (*2*), and cyclohexanone (*3*) as well as the sum of the products (*4*) measured using the triphenylphosphine method;[13b,d,g,44] the result after 2.5 h is shown for a separate experiment, when hydrogen peroxide was added dropwise during the first 30 min of the reaction.

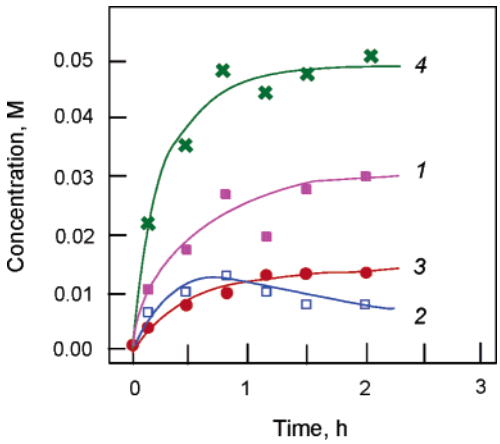
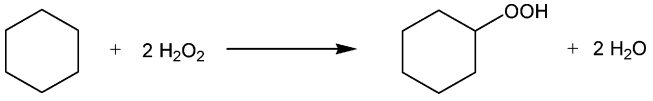


Figure 10. Oxidation of cyclohexane (0.335 M) with H_2O_2 (1.5 M) in acetonitrile at 2 °C catalyzed by the in situ prepared Mn^{2+}/L^{Me3} (1.0/1.5 mM) combination in the presence of disodium oxalate (1.5 mM); the following curves are shown: accumulation of cyclohexyl hydroperoxide (curve *1*), cyclohexanol (*2*), and cyclohexanone (*3*) as well as the sum of the products (*4*) measured using the triphenylphosphine method.[13b,d,g,44]

ligand. Despite the low activity in the absence of a cocatalyst, the introduction of a pendent carboxylato arm into the L^{Me2} structure significantly increases both stability and performance of the catalyst (Table 8). This effect is more pronounced in the case of $L^{Me2R'}$, in line with mechanistic investigations.[13c,e] According to the MS-ESI spectra, the oxidation activity can be tentatively ascribed to the dinuclear manganese complexes with two carboxylato arms bridging two manganese centers. Indeed, the substitution of only one hydrogen atom in the 1,4,7-triazacyclononane ring (by, e.g., methyl group) inhibits the tri- and tetranuclear complex formation.[17,55] However, upon addition of 3 equiv of hydrogen peroxide to the in situ prepared manganese complex containing $L^{Me2R'}$, all the fragments in the MS-ESI spectrum represent di-, tri-, and tetranuclear manganese complexes (*m*/*z* 1196, 1007, 976 (35%, tetranuclear); 945, 914, 685 (50%, trinuclear); 663, 584 (10%, dinuclear). Thus, in the case of $L^{Me2R'}$ ligand the pendent propionato group has a strong tendency to bridge neighboring manganese centers and even at high hydrogen peroxide concentration to keep them in the active dinuclear form (one of the principles of the carboxylate-promoted mechanism).[13c,e,h] In the case of L^{Me2Ac}, the MS-ESI spectrum consists of di- and mononuclear manganese fragments (*m*/*z* 594, 556, 548, 515 (60%, dinuclear); 331, 300, 269 (30%, mononuclear). Therefore, we can assume that in L^{Me2Ac} three nitrogen atoms and the pendent acetato group are preferentially coordinated to the same manganese center and at high hydrogen peroxide concentration these dinuclear complexes are more subjected to the cleavage. However, we were not able to isolate these high-valent species which decomposed during crystallization even at low temperatures (−18 °C, 0 °C, decoloration). In general, as in all cases using 1,4,7-triazacyclononane-type ligands in manganese-catalyzed oxidations, the catalysts activity decreases after some hours, and the manganese-containing solids recovered from the mixture cannot be reused. As the Mn(III)-Mn(IV) complexes *S*,*S*-**1** and *R*,*R*-**1** catalyze the oxidation of alcohols with H_2O_2 (vide supra), the OH functions in these complexes are likely to be unstable in the presence of hydrogen peroxide. This may be the reason for the complex degradation observed at the end of the catalytic reaction.

The addition of oxalate buffer (pH 3.5) causes an increase of the oxidation activity in the case of alkyl and hydroxyalkyl *N*-substituted ligands (L^{Me2}, *SS*-L^{BMe3}, *S*-L^{Me2R}, and *S*-$L^{Me2R''}$) but a significant decrease in the case of the ligands containing pendent carboxylato arms (L^{Me2Ac}, $L^{Me2R'}$), see Table 8. This can be explained by the competition of the bidentate oxalate ligand and hydrogen peroxide for the place in the coordination sphere of the manganese center, which is still occupied by three nitrogen atoms of the 1,4,7-triazacyclononane ring and an oxygen atom of the carboxylato pendent arm. The best catalytic performance was shown by the manganese complex containing trialkyl *N*-substituted *S*-$L^{Me2R''}$ ligand, and a TON of 1140 was observed after 1 h of the reaction. However, the manganese complex with trimethyl *N*-substituted *SS*-L^{BMe3} ligand is significantly less effective due to the coordination problems imposed by the rigid bicyclic structure of the macrocyclic ligand.

With the isolated compound [*R*,*R*-**1**][PF_6]$_3$, we also studied the oxidation of cyclohexane with hydrogen peroxide in acetonitrile solution at 25 °C. The oxidation of cyclohexane takes place only in the presence of a cocatalyst such as oxalic acid, and cyclohexyl hydroperoxide is formed as the major product (measured by using the triphenylphosphine method,[13b,d,g,44] (Figure 7). The total catalyst turnover number attains 68 after 5 h of the reaction.



In order to shed light on the nature of the oxidizing species generated from *R*,*R*-**1** upon addition of hydrogen peroxide,

(55) Dubé, C. E.; Mukhopadhyay, S.; Bonitatebus Jr., P. J.; Staples, R. J.; Armstrong, W. H. *Inorg. Chem.* **2005**, *44*, 5161−5175.

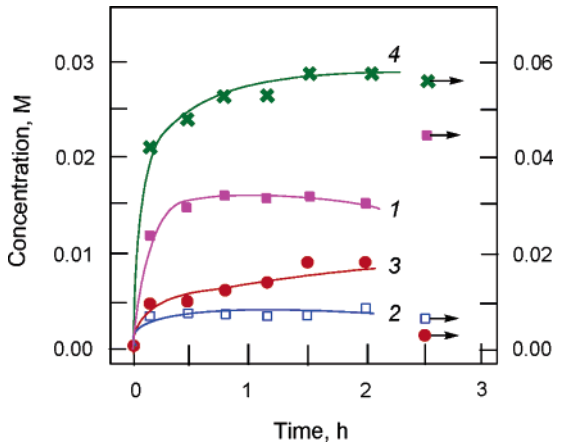


Figure 11. Oxidation of cyclohexane (0.335 M) with H_2O_2 (1.5 M) in acetone at 2 °C catalyzed by the in situ prepared $Mn^{2+}/L^{Me2R''}$ (1.0/1.5 mM) combination in the presence of disodium oxalate (1.5 mM); the following curves are shown: accumulation of cyclohexyl hydroperoxide (curve *1*), cyclohexanol (*2*), and cyclohexanone (*3*) as well as the sum of the products (*4*) measured using the triphenylphosphine method.[13b,d,g,44] The result after 2.5 h is shown for a separate experiment, when hydrogen peroxide was added dropwise during the first 30 min of the reaction.

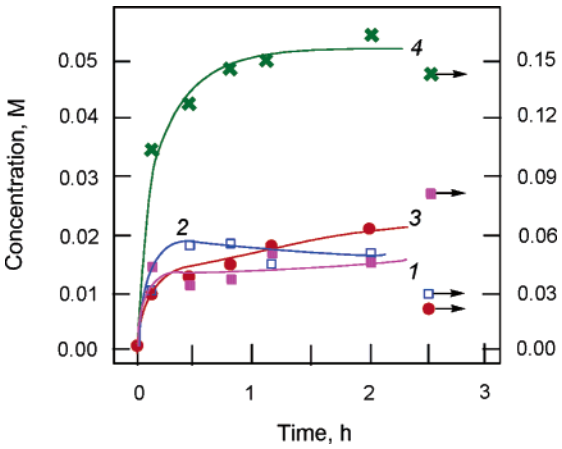


Figure 12. Oxidation of cyclohexane (0.335 M) with H_2O_2 (1.5 M) in acetonitrile at 2 °C catalyzed by the in situ prepared $Mn^{2+}/L^{Me2R''}$ (1.0/1.5 mM) combination in the presence of disodium oxalate (1.5 mM); the following curves are shown: accumulation of cyclohexyl hydroperoxide (curve *1*), cyclohexanol (*2*), and cyclohexanone (*3*) as well as the sum of the products (*4*) measured using the triphenylphosphine method.[13b,d,g,44] The result after 2.5 h is shown for a separate experiment, when hydrogen peroxide was added dropwise during the first 30 min of the reaction.

we studied also the oxidation of higher linear and branched alkanes (*n*-hexane, *n*-heptane, *n*-octane, and isooctane). The selectivity parameters are given in Table 9. All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before the GC analysis and calculated based on the ratios of isomeric alcohols. The parameter C(1):C(2):C(3):C(4) indicates the relative normalized reactivities of hydrogen atoms at carbons 1, 2, 3, and 4 of the chain of unbranched alkanes (i.e., calculated taking into account the number of hydrogen atoms at each carbon). The parameter 1°:2°:3° indicates the relative normalized reactivities of hydrogen atoms at primary, secondary, and tertiary carbons of isooctane.

As compared to the known catalytic systems $[(L^{Me3})_2Mn_2(O)_3]^{2+}$/oxaH$_2$ or $[(L^{Me3})_2Mn_2(O)_3]^{2+}$/AcOH,[12,13] which are believed to proceed via abstraction of hydrogen atoms from the alkane by a reactive Mn=O species,[8d] the selectivity parameters are similar, suggesting that also in the case of *R,R*-**1** the oxygenation occurs via reactive manganese-oxo species capable of discriminating between primary and secondary hydrocarbon bonds.

In the isooctane molecule, the secondary C−H bonds are surrounded by bulky *tert*-butyl and isopropyl groups; therefore, the selectivity parameter 2°/1° reflects the sterical hindrance for the oxidizing species. Given the parameter (C(2):C(1))/(2°:1°) for *R,R*-**1** to be in the range from 12 to 18 (3−4 in the case of hydroxyl radicals[58]), we can assume that the oxidizing species generated from *R,R*-**1** have the pronounced sterical restrictions.

The oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane is a simple test for the reaction stereoselectivity (Figure 8). While retention of the stereochemical configuration is characteristic of a concerted reaction mechanism (in enzymes, however, the retention can be imposed by the active site geometry), loss of the stereochemical configuration is indicative of a nonconcerted mechanism, going through an intermediate. The selectivity parameters for the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane with H_2O_2, catalyzed by *R,R*-**1** in acetonitrile, are given in Table 9. The parameter trans/cis indicates the ratio of trans- and cis-isomers of *tert*-alcohols formed in the reaction.

In the oxidation of *trans*-1,2-dimethylcyclohexane the retention of configuration is unambiguous and is more pronounced in the case of acetic acid used as cocatalyst. In the oxidation of *cis*-1,2-dimethylcyclohexane, the retention of configuration is also observed, the cis-isomers of 1,2-dimethyl-1,2-cyclohexyldiol being preferentially formed; however, in the case of acetic acid as cocatalyst a significant amount of trans-isomers is also detected. Thus, we can assume that the oxidation occurs by a concerted reaction mechanism (hydrogen atom abstraction and hydroperoxydation taking place in a single step without formation of an intermediate).

The catalytic oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane with H_2O_2 in acetone was found to be highly stereoselective (retention of the stereochemical configuration up to 99%) using in situ prepared system $MnSO_4/L^{Me3}$ combined with disodium oxalate.[59] However, we found that after reduction of the reaction mixture with solid triphenylphosphine the real trans/cis ratio shows a decrease in stereoselectivity (entries 4 and 5, Table 9) and reflects the presence of the corresponding *tert*-hydroperoxides. Cyclohexyl hydroperoxide is the primary oxidation product in the catalytic oxidation of cyclohexane under the same conditions

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(Figure 9 , curve *1*). In acetonitrile solution cyclohexyl hydroperoxide becomes the major reaction product (Figure 10, curve *1*); however, the overall catalytic performance of the $MnSO_4/L^{Me3}$ system in this solvent is lower.

With an *N*-alkyl-substituted analogue of L^{Me3}, (*S*)-1-(2-methylbutyl)-4,7-dimethyl-1,4,7-triazacyclononane (*S*-$L^{Me2R''}$), the stereoselectivity in the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane is substantially lower (entries 6 and 7, Table 9). Moreover, the oxidation of cyclohexane with hydrogen peroxide catalyzed by $MnSO_4$/*S*-$L^{Me2R''}$ system is more effective in acetonitrile rather then in acetone solution (Figures 11 and 12). It can be rationalized by the fact that complexation of *S*-$L^{Me2R''}$ containing a bulky chiral substituent with manganese sulfate is less effective then in the case of L^{Me3}; therefore, the catalytic activities and selectivities of both systems are different. The lower degree of complexation in the case of $MnSO_4$/*S*-$L^{Me2R''}$ system can also explain why the catalytic performance is two (in acetone) and even three times higher (in acetonitrile solution), if hydrogen peroxide is added dropwise in the initial reaction period (Figures 11 and 12, separate experiments at 2.5 h). Alternatively, the stability of the active manganese complexes formed in $MnSO_4$/*S*-$L^{Me2R''}$ system in the presence of hydrogen peroxide is lower with respect to the $MnSO_4/L^{Me3}$ catalytic system. Finally, both in situ prepared catalytic combinations are capable of hydroxylation of alkanes under mild conditions.

Conclusion

The manganese complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane-derived ligands are versatile catalysts for the oxidation of a wide range of organic functional groups by the clean oxidant H_2O_2.

Five new 1,4,7-triazacyclononane-derived ligands have been synthesized and characterized. The corresponding manganese complexes prepared in situ show a significant catalytic activity in the oxidation of alcohols and the epoxidation of olefins with H_2O_2. The reactivity and the selectivity of the catalysts can be tuned: (a) using oxalic and ascorbic acids, which act as coligands or/and reducing agents for the manganese centers, and (b) introducing a functionality (carboxylato or hydroxo pendent arm) or/and chirality into the 1,4,7-triazacyclononane macrocycle. The manganese complex containing the 3-(4,7-dimethyl-1,4,7-triazacyclononan-1-yl)propionate ligand **(**$L^{Me2R'}$) shows one of the best performances in the oxidation of alcohols and in epoxidation of alkenes reported so far with H_2O_2; if no cocatalyst is added, the reaction proceeds smoothly in water under mild conditions. The MS-ESI spectra of the reaction mixture show that the propionato pendent arm in $L^{Me2R'}$ has a strong tendency to bind two neighboring manganese centers and is capable of proton transfer during the oxidation. The catalytic activity can be tentatively attributed to dinuclear manganese complexes with two carboxylato pendent arms bridging two manganese centers.

Two dinuclear manganese complexes containing enantiomerically pure (*R*)- and (*S*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane **(***S*,*S*-**1**, *R*,*R*-**1)** ligands have been isolated as the hexafluorophosphate salts. The molecular structures of *S*,*S*-**1** and *R*,*R*-**1** provide the first examples of dinuclear manganese complexes bridged by two chiral pendent arms.

The epoxidation of indene with H_2O_2 using *S*,*S*-**1** and *R*,*R*-**1** as catalyst gives the mixture of (1*R*,2*S*)- and (1*S*,2*R*)-indene oxide with the enantiomeric excess up to 13%. Thus, the catalysts present one more example of the chiral high-valent manganese complexes with enantioselective properties in the catalytic oxidation with H_2O_2. The oxidation of linear and branched alkanes proceeds only in the presence of oxalic or acetic acid. The high degree of regio- and stereoselectivity allow us to assume the oxidation to preferentially proceed via concerted mechanism with participation of high-valent manganese-oxo species. Finally, *S*,*S*-**1** and *R*,*R*-**1** provide additional insights into the oxidation mechanism and can serve as a basic model for the further catalyst design.

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Supporting Information Available: Crystallographic data in CIF format and ORTEP plot for complexes [*S*,*S*-**1**][PF_6]$_3$·0.5(CH_3)$_2$CO and [*R*,*R*-**1**][PF_6]$_3$·0.5(CH_3)$_2$CO. This material is available free of charge via the Internet at http://pubs.acs.org.

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