# JOC Article

Trimanganese Complexes Bearing Bidentate Nitrogen Ligands as a Highly Efficient Catalyst Precursor in the Epoxidation of Alkenes[†]

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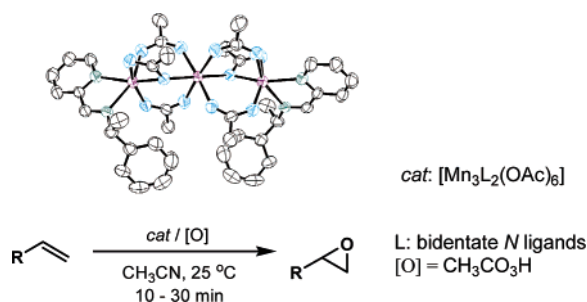
A series of trinuclear manganese complexes coordinated with neutral bidentate nitrogen ligands, [Mn_3L_2-$(OAc)_6$], were prepared from manganese acetate and the corresponding ligands. Using peracetic acid as the oxidant, the air- and moisture-stable manganese clusters exhibited excellent catalytic activity and selectivity in the epoxidation of olefins under mild conditions. The highest activity was observed with a trinuclear complex containing a 2-pyridylimino ligand, [$Mn_3(ppei)_2(OAc)_6$] (ppei = 2-pyridinal-1-phenylethylimine). With this system, the substrate scope was extremely wide to include terminal and electron-deficient double bonds of both aliphatic and aromatic alkenes. The high activity was undiminished under the reaction conditions even directly using a mixture of the pyridylimino ligands and manganese acetates, making this process more convenient. It was also observed that analogous trinuclear complexes, such as [$Mn_3(bipy)_2(OAc)_6$] and [$Mn_3(phen)_2(OAc)_6$], displayed excellent activities. While radical intermediacy was inferred from the product distribution, kinetic data revealed that the epoxidation is roughly first-order in manganese cluster precursor and oxidant, respectively, and zero-order in olefin. These results led us to propose that the trinuclear complexes [$Mn_3L_2(OAc)_6$] serve as catalyst precursors that dissociate into monomeric species with the formulation of [$MnL_2(OAc)_2$] under the reaction conditions.

Introduction

Metal-catalyzed oxidation is one of the most fundamental transformations in chemistry and biology.[1] Detailed understanding of oxidation pathways has led to the development of efficient catalytic procedures potentially viable for large-scale production of valuable compounds from raw materials.[2] Among those, olefin epoxidation has received considerable interests from both academics and industry because epoxides are frequently employed as important building blocks in organic synthesis and materials science.[3] Although numerous procedures have been developed,[4] there is still an increasing demand for more efficient

[†] Dedicated to Professor Sunggak Kim on the occasion of his 60th birthday.

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and selective routes using readily available and stable catalysts. While these reactions are known to proceed via oxo-, peroxo-, or peroxide metal intermediates, efficiency of the oxygen transfer step is dramatically influenced in common by the coordination environment on the metal center. We report herein the utility of highly stable trinuclear manganese complexes[5] bearing neutral bidentate nitrogen ligands (e.g., 2-pyridylimine, bipyridine, and phenanthroline) in the olefin epoxidation reactions using commercial peracetic acid. On the basis of kinetic measurements and site-isolation studies of the catalyst system, some mechanistic aspects and the nature of active catalyst species are also proposed.

Results and Discussion

Among various transition metal complexes, iron and manganese species have been investigated most extensively as catalysts in combination with suitable ligands in the epoxidation reactions mainly due to the fact that the corresponding complexes are easily prepared, generally stable to air and moisture, inexpensive, and readily amenable to diverse reaction conditions. It was shown that a cationic iron complex coordinated with a tetradentate ligand, $[Fe^{II}(mep)(CH_3CN)_2](SbF_6)_2$ (mep = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-diaminoethane), self-assembles in situ to form a carboxylate-bridged μ-oxo diiron(III) complex that carries out efficient epoxidation reactions using 50% aqueous H_2O_2.[6] Although the catalyst system displayed good activities on aliphatic olefins, reactions with electron-deficient olefins as well as styrene derivatives turned out to be rather inefficient. More recently, Stack and co-workers reported a notable catalyst system, $[Mn^{II}(R,R$-mcp)(CF_3SO_3)_2]$ (mcp = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-diaminocyclohexane),[7] a chiral variant of the above-mentioned iron system. Using peracetic acid, scope of olefin substrates was significantly expanded to include terminal and electron-deficient double bonds despite the fact that some sensitive olefins, such as styrene derivatives, are still problematic. Later studies revealed that monomeric manganese catalysts bearing more robust bidentate nitrogen ligands, such as $[Mn^{II}(bipy)_2(CF_3SO_3)_2]$, display even higher activities than the initial $[Mn^{II}(R,R$-mcp)(CF_3SO_3)_2]$ system.[8]

We envisioned that metal complexes of 2-pyridylalkylidine ligands might afford notable benefits, such as ease of preparation and facile tuning of both steric and electronic nature in the complexes. Accordingly, a series of 2-pyridylimino derivatives were prepared by the reaction of 2-pyridinecarboxaldehyde derivatives with primary amines.[9] Subsequent complexation of these ligands with manganese acetates was carried out giving
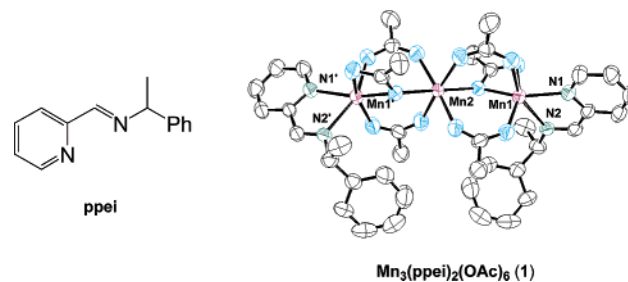

FIGURE 1. Structure of ppei and an ORTEP diagram of $[Mn_3(ppei)_2(OAc)_6]$ (**1**).

neutral manganese complexes in high yields. For example, a manganese complex of 2-pyridinal-1-phenylethylimine (ppei)[10] was obtained through a condensation of 2-pyridinecarboxaldehyde with α-methylbenzylamine followed by metal complexation using $Mn(OAc)_2\cdot4H_2O$ to afford the corresponding manganese complex in 95% overall yield. Although this two-step procedure provides the manganese complexes in satisfactory yields, the same species can be also obtained in situ with similar efficiency, in which the complexes are prepared by the tandem reaction of primary amines with pyridinecarboxaldehyde followed by complexation *in one-pot without isolation of Schiff base ligands* (see the Experimental Section for detail). The resultant manganese complexes are highly stable to air and moisture such that those compounds can be stored more than a few months in air without loss of catalytic activity.

The structure of the prepared complexes was characterized unambiguously by a single-crystal X-ray diffraction study which shows a configuration of trinuclear species bearing six acetates and two ppei ligands (Figure 1).[11] Each metal is positioned in a center of an octahedral geometry, and two different coordination patterns exist with regard to six acetates. Specifically, the four carboxylate groups span the central metal and terminal manganese in a bidentate [Mn−O−C(Me)−O−Mn] fashion, while the remaining two acetate groups involve a monatomic oxygen [Mn−O−Mn] bridge. The separation between the central Mn and neighboring Mn is 3.59 Å, which is within the range of known manganese cluster complexes.[12]

Catalytic activity of the resulting manganese cluster was next investigated in the epoxidation of representative terminal and internal double bonds of aliphatic and aromatic alkenes (Table 1). A dramatic ligand effect was observed with regard to catalytic activity using commercial peracetic acid (32%) as an

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TABLE 1. Effects of the ppei Ligand on Olefin Epoxidation[a]

	$Mn(OAc)_2 \cdot 4H_2O$	**1**		$Mn(OAc)_2 \cdot 4H_2O$ with *rac*-ppei		$Mn(OAc)_3 \cdot 2H_2O$ with *rac*-ppei	
alkene	conv (%)	conv (%)	yield (%)	conv (%)	yield (%)	conv (%)	yield (%)
1-octene	<1	>98	96	96	96	96	95
cyclohexene	<5	>98	95	96	89	>98	87
styrene	0	>98	93	>98	92	>98	90
trans-β-methylstyrene	<1	>98	91	>98	93	>98	94

[a] Reaction conditions: alkene (0.5 mmol), **1** (1.2 mol % with aliphatic and 2.0 mol % with aromatic olefins), $Mn(OAc)_2 \cdot 4H_2O$ (2.0 mol %) or $Mn(OAc)_3 \cdot 2H_2O$ (2.0 mol %), 32% CH_3CO_3H (0.6 mmol), CH_3CN (1.0 mL) either in the absence or presence of *rac*-ppei (5.0 mol %), 25 °C, 18 min. Conversion and yield were determined by GC analyses using biphenyl as an internal standard on the basis of an average of three runs.

oxidant. While almost negligible conversion was observed with simple manganese (II or III) complexes, such as $Mn(OAc)_2 \cdot 4H_2O$ or $Mn(OAc)_3 \cdot 2H_2O$ (2 mol %), in the absence of external ligands,[13] the use of ligated Mn complex **1** (1.2 or 2 mol %) led to almost complete conversion and selectivity in all cases examined, usually achieving >95% conversion and >90% selectivity for the formation of epoxides within 10 min at room temperature.[14] It should be mentioned that highly comparable results could be obtained using in situ conditions, in which simple manganese acetate precursors (2 mol %) are directly employed in combination with *rac*-ppei (5 mol %). This offers a notable and practical advantage in that *no preformed metal complex is required to achieve the high efficiency in the epoxidation reactions*. It turned out that the oxidation state of the manganese acetate precursors has little effects on the resulting catalysts' activities, affording almost identical results from either a Mn(II) or Mn(III) precursor. It is especially noteworthy that styrene can also be employed as a high yielding substrate with this catalyst system, which is markedly in contrast to the [$Mn^{II}(R,R$-mcp)]$^{2+}$ case that results in significant amounts of side products when styrene was examined.[7] With the present catalyst system, the use of oxidants other than peracetic acid, such as NaOCl, Oxone, *N*-methylmorpholine oxide (NMO), or H_2O_2,[15] gave much reduced yields of epoxide.

It was observed that handedness of the coordinating ppei ligand has little effects on the enantio- and diastereoselectivities as well as reactivity in the epoxidation. In fact, all manganese complexes showed the same conversion and selectivity in the epoxidation reactions irrespective of the stereochemistry of the

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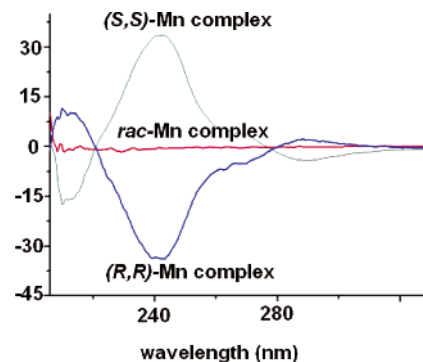

FIGURE 2. ORD spectrum of *rac*-**1**, (*R,R*)-**1**, and (*S,S*)-**1** in methanol (2.0 × 10^{-5} M).

employed ligand: *rac*-ppei, *R*-ppei, or *S*-ppei. When optical rotatory dispersion (ORD) was measured for two complexes [$Mn_3(ppei)_2(OAc)_6$] bearing either *R*-ppei or *S*-ppei, the pair appeared to be optical antipodes, while a complex of *rac*-ppei did not show any optical behavior as anticipated (Figure 2).[16] A manganese complex prepared from *R*-ppei displays a peak and a trough at wavelengths of 243 and 210 nm, respectively, thus showing a positive Cotton effect.[17]

Under the optimized conditions, a wide range of double bonds of internal, terminal, and conjugated aliphatic alkenes was cleanly epoxidized with the catalyst **1** (1.2−2 mol %) using commercial peracetic acid (Table 2). In general, the epoxidation reactions were completed within 30 min at room temperature, and selectivity for the formation of epoxides was generally excellent enough to afford epoxides in high yields almost irrespective of electronic and/or steric variation on substrates. Epoxidation of *cis* aliphatic olefins proceeds with a high stereoselectivity to afford predominantly *cis*-epoxides (*cis/trans*, >20:1) as demonstrated in entry 4. Labile functional groups, such as acetate or a free hydroxyl group, were tolerated under the reaction conditions (entries 9 and 10, respectively). In addition, a conjugated enone was selectively epoxidized in high yield (entry 11), albeit requiring slightly higher loading of catalyst **1** (2 mol %). However, selectivity in a diene epoxidation turned out to be rather low. For example, reaction of (*R*)-(−)-carvone and 4-vinylcyclohexene resulted in an almost nonselective epoxidation (entries 13 and 14). The reaction was readily applicable to a gram scale process giving isolated yields almost comparable to those in the small scale reactions. It should be

(16) Interestingly, when *rac*-ppei was employed as a ligating ligand to react with Mn(II) sources, homochiral manganese clusters of [$Mn_3(R$-ppei)-(*R*-ppei)(OAc)$_6$] and [$Mn_3(S$-ppei)(*S*-ppei)(OAc)$_6$] were isolated separately from the reaction mixture, whose structures were determined by X-ray crystallographic analyses.

(17) For a previous example of CD spectra of chiral Pd(ppei) complexes, see ref 10e.

TABLE 2. Epoxidation of Aliphatic Olefins Using Isolated Catalyst 1 and under in situ Conditions[a]

entry	alkene	condition	GC yield (%) (isolated yield)[b]	Mn(OAc)$_2$·4H$_2$O with rac-ppei[c]
1	1-decene	A	96 (92)	
2	1-octene	A	96 (86)	
3	trans-2-octene	A	94 (87)	93
4	cis-2-octene	A	97 (91)[d]	
5	2-methyl-1-heptene	A	97 (90)	95
6	2-methyl-2-hexene	A	92 (83)	94
7	cyclohexene	A	95 (79)	
8	cyclooctene	A	90 (81)	94
9	allyl acetate	B	97	
10	9-decen-1-ol	A	89 (82)	
11	2-cyclohexen-1-one	B	95 (85)	
12	norbornene	B	72[e]	
13	R-(−)-carvone	A	93[f]	
14	4-vinylcyclohexene	A	77[g]	

[a] Condition A: alkene (0.5 mmol), **1** (1.2 mol %), 32% CH$_3$CO$_3$H (0.6 mmol), CH$_3$CN (1.0 mL), 25 °C, 18 min. Condition B: alkene (0.5 mmol), **1** (2.0 mol %), 32% CH$_3$CO$_3$H (1.0 mmol, added in two portions), CH$_3$CN (1.0 mL), 25 °C, 28 min. [b] GC yields were determined using biphenyl as an internal standard on the basis of an average value of three runs. Isolated yields were based on the reactions performed on a 1.0 g scale. [c] 2.0 mol % of Mn(OAc)$_2$·4H$_2$O and 5.0 mol % of rac-ppei. [d] cis/trans-Isomer, >20:1. [e] exo-2,3-Epoxynorbornane. [f] Mixture of 1,2-epoxide and 8,9-epoxide (1: 1.2). [g] Equal mixture of internal and terminal epoxide.

**TABLE 3. Epoxidation of Aromatic Olefins Using Catalyst 1**[a]

entry	alkene	condition	GC yield (%) (isolated yield)	Mn(OAc)$_2$·4H$_2$O with rac-ppei[c]
1	styrene	A	93 (84)	
2	4-chlorostyrene	A	94 (88)	96
3	4-acetoxystyrene	A	90[b]	85[b]
4	trans-β-methylstyrene	A	91	
5[c]	trans-stilbene	A	94 (91)	93
6	cis-β-methylstyrene	A	80[d]	
7	cis-stilbene	B	89 (86)[e]	
8	ethyl-trans-cinnamate	B	94 (92)	

[a] Same conditions as in Table 2 were used (2.0 mol % of **1** was used in all cases except in entry 8, in which 3.0 mol % of **1** was employed). [b] ^{1}H NMR yield of the crude reaction mixture. [c] Reactions were carried out in a cosolvent (CH$_2$Cl$_2$/CH$_3$CN, 1:1). [d] cis/trans-Isomeric epoxides (4.1:1). [e] cis/trans-Isomeric epoxides (3.2:1).

mentioned that, even under the in situ conditions, highly comparable results were obtained with regard to reactivity and selectivity, in which the epoxidation was carried out with a manganese complex catalyst prepared *in one-pot* without using the isolated trinuclear manganese species. In this procedure, peracetic acid is added into a solution containing an olefin, manganese(II) acetate (2 mol %), and the ppei ligand (5 mol %) in acetonitrile.

We next turned our attention to aromatic olefins because epoxidations of this type of substrate were known to be sluggish, leading to significant amounts of side products especially when the metal systems of Jacobsen[6] or Stack[7,8] were employed. It was observed that epoxidation of styrene derivatives proceeds quite efficiently with **1** (Table 3).[18] Electronic variation on aryl substituents did not affect the efficiency of the reaction (entries 2 and 3). In contrast to aliphatic *cis* olefins, epoxidation of internal aromatic olefins gave the corresponding epoxides as a mixture of *cis*- and *trans*-isomers with a ratio of 4.1:1 and 3.2: 1, respectively (entries 6 and 7). This implies that the epoxidation proceeds via a radical pathway (vide infra) since no

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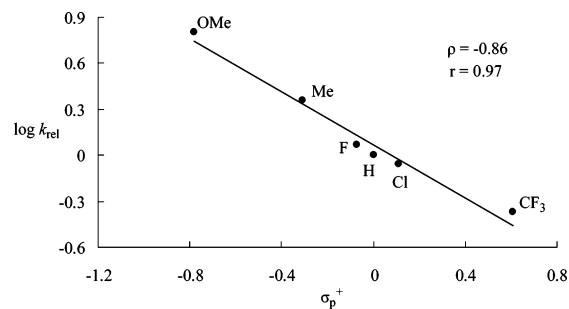
FIGURE 3. Hammett plot of log k_{rel} versus σ_p^+ for the epoxidation of styrene and *p*-substituted styrenes.

isomerization of double bonds takes place under the epoxidation conditions.[19] Conjugated aromatic olefins, such as cinnamic ester, were also efficiently epoxidized to afford epoxy ester (entry 8).

When competition experiments were carried out between styrene and an equivalent amount of *p*-substituted styrene derivatives, a significant electronic effect on the reaction rates was observed to show that the more electron-rich olefins react faster than electron-deficient substrates.[20] Styrenes having a substituent at the *para*-position reacted as the following order: OMe ($k_{rel} = 6.35$) > Me (2.27) > F (1.17) > H (1.0) > Cl (0.87) > CF$_3$ (0.42). A shown in Figure 3, a more precise linear correlation can be obtained when k_{rel} is plotted with σ_p^+ ($r = 0.97$) rather than with σ_p ($r = 0.84$). The small negative value of the observed reaction constant ($\rho = -0.86$) is highly comparable to those in the previously reported epoxidation procedures using porphyrin metal oxo systems.[21]

Dependence of the initial rates on the concentration of catalyst **1**, styrene, and oxidant was next measured to reveal that the reaction is roughly first-order in catalyst **1** (1.10) and the oxidant's concentration (1.24), respectively, and close to zero-order in the olefin concentration (0.06).[22,23] In addition, an induction period was observed during the epoxidation process.[20] In analogy to the previous reports,[24] the present kinetic behavior suggests that the rate-determining step is most likely related to the formation of a putative manganese peroxo species rather than an oxygen atom transfer step from the active manganese intermediates to the double bonds.

In addition, we were interested in investigating some relevant manganese clusters having certain bidentate ligands, such as

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(22) For detailed kinetic data on the concentration of **1**, styrene, and oxidant, see the Supporting Information.

(23) For some reports on the saturation kinetics behavior in metal-catalyzed oxygenations, see: (a) Bressan, M.; Morvillo, A. *Inorg. Chem.* **1989**, *28*, 950. (b) Amatsu, H.; Miyamoto, T. K.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3193.

(24) For related mechanistic discussions on olefin epoxidation, see: (a) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000. (b) Collman, J. P.; Brauman, J. I.; Hampton, P. D.; Tanaka, H.; Bohle, D. S.; Hembre, R. T. *J. Am. Chem. Soc.* **1990**, *112*, 7980. (c) Norrby, P.-O.; Linde, C.; Akermark, B. *J. Am. Chem. Soc.* **1995**, *117*, 11035. (d) Collman, J. P.; Zeng, L.; Brauman, J. I. *Inorg. Chem.* **2004**, *43*, 2672.

TABLE 4. Epoxidations Catalyzed by [Mn$_3$(bipy)$_2$(OAc)$_6$] (2) and [Mn$_3$(phen)$_2$(OAc)$_6$] (3)[a]

entry	alkene	2 conv (selec %)	3 conv (selec %)
1	1-decene	88 (95)	76 (95)
2	9-decen-1-ol	82 (84)	81 (84)
3	styrene	>98 (88)	96 (80)
4	ethyl-*trans*-cinnamate	>98 (85)	>98 (74)

[a] Same conditions as in Table 2. In entry 1, 1.2 mol % of each catalyst **2** and **3** was used. In entries 2 and 3, 2.0 mol % of each catalyst **2** and **3** was used. In entry 4, 3.0 mol % of **2** and **3** was employed.

2,2′-bipyridine or 1,10-phenanthroline. The corresponding trinuclear complexes, [Mn$_3$(bipy)$_2$(OAc)$_6$][25] (**2**) and [Mn$_3$(phen)$_2$-(OAc)$_6$][26] (**3**), were similarly prepared, and their molecular structures were unambiguously characterized by X-ray diffraction analyses.[27] When the trinuclear manganese complex **2** or **3** was examined as a catalyst using peracetic acid, both species displayed quite comparable reactivity and selectivity when compared to those of the corresponding monomeric catalyst [Mn(bipy)$_2$(CF$_3$SO$_3$)$_2$] or [Mn(phen)$_2$(CF$_3$SO$_3$)$_2$] as reported by Stack and co-workers (Table 4).[8]

These results, in combination with the above-mentioned kinetic measurements and induction period, led us to propose that *the trinuclear manganese complexes, [Mn$_3$L$_2$(OAc)$_6$], work as a catalyst precursor generating in situ an active catalyst [MnL$_2$(OAc)$_2$] and much less active [Mn(OAc)$_2$(solvent)$_n$] species under the reaction conditions*. Indeed, we isolated from the reaction mixture an insoluble manganese species, [Mn(OAc)$_2$-(solvent)$_n$], that shows almost no catalytic reactivity in the epoxidation. As a result, it can be assumed that the ppei-bound monomeric species [Mn(ppei)$_2$(OAc)$_2$] is mainly responsible for the observed catalytic activity of the trimanganese complex precursor. If manganese chloride was employed as a Mn source, the resultant unstable complex exhibited very similar catalytic activity when compared to that of [Mn$_3$(ppei)$_2$(OAc)$_6$].[28]

Although it has been known that dissociation of certain manganese clusters into monometallic moieties readily occurs by a ligand substitution or rearrangement processes,[29] a possibility that the trinuclear species themselves participate in the present catalysis in our system cannot be completely ruled out at present.[30] In fact, Crabtree and co-workers reported that a manganese cluster, [Mn$_3$O$_4$(bipy)$_4$(H$_2$O)$_2$](ClO$_4$)$_4$, shows excellent epoxidation activity using Oxone and that the oxidation takes place through an oxo transfer pathway without dissociation into monomeric manganese moieties.[5b,31]

(25) For the structural determination of **2**, see ref 12b.

(26) For the structural determination of **3**, see ref 12c.

(27) See the Supporting Information for the X-ray crystal structure of complex **3**.

(28) Although we could not characterize the generated complex, formation of a monometallic species can be envisioned as a major complex due to the much less bridging ability of the chloride ligand.

(29) For example, see: Ma, C.; Chen, C.; Liu, Q.; Liao, D.; Li, L. *Eur. J. Inorg. Chem.* **2003**, 1227.

(30) For previous examples of multinuclear manganese complexes being active species, see: (a) Mathur, P.; Crowder, M.; Dismukes, G. C. *J. Am. Chem. Soc.* **1987**, *109*, 5227. (b) Chavan, S. A.; Halligudi, S. B.; Srinivas, D.; Ratnasamy, P. *J. Mol. Catal. A: Chem.* **2000**, *161*, 49. (c) Carrell, T. G.; Cohen, S.; Dismukes, G. C. *J. Mol. Catal. A: Chem.* **2002**, *187*, 3. (d) Larsen, A. S.; Wang, K.; Lockwood, M. A.; Rice, G. L.; Won, T.-J.; Lovell, S.; Sadílek, M.; Tureèek, F.; Mayer, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 10112.

(31) (a) Wessel, J.; Crabtree, R. H. *J. Mol. Catal. A: Chem.* **1996**, *113*, 13. (b) Sarneski, J. E.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H.; Schulte, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7255.

Attachment of metal complexes to a solid support has been frequently utilized as an insightful tool to obtain information on the reaction pathway as well as a means of extending practical advantages of homogeneous catalysis. This approach has turned out to be valid especially in a search for the existence of putative internuclear interactions.[32] With this context, synthesis of an anchored pyridylimino ligand and its manganese(II) complex (**4**) was successfully carried out (Scheme 1). In each step, the pyridyl-containing compounds were detached from the resin, and the chemical structure was fully characterized using spectroscopic tools. In addition, elemental analyses of nitrogen contents were satisfactorily carried out to confirm the validity of each transformation (see the Supporting Information). Inductively coupled plasma (ICP) analysis of **4** revealed that manganese content in the supported complex was 0.329 mmol/g (1.81 wt %), indicating that each synthetic step proceeded with high efficiency (>80% yield).

When the supported manganese complex **4** (2.0 mol %) was employed under the same conditions as with the manganese clusters **1−3**, the reactivity was shown to be significantly attenuated, although selectivity remained still high (Table 5). Considering that the polystyrene-bound pyridylimino group (L) has little flexibility, it is reasonable to regard that a metal coordination of two anchored bidentate ligands (L$_2$) at the same time giving the assumed active manganese species [MnL$_2$-(OAc)$_2$] is not feasible under this environment. Therefore, the decreased reactivity of the site-isolated catalyst can be ascribed mainly to the geometric restraints present in the anchored ligand, although the heterogenization itself may also contribute in part to the decreased catalytic activity. We assume that this result may support our proposal that the active species is the monomeric moieties [MnL$_2$(OAc)$_2$] when we employ the trinuclear complexes [Mn$_3$L$_2$(OAc)$_6$]. On the other hand, catalytic activity of the recovered resin-bound manganese complex dropped sharply, especially more significant with the slow reacting substrates.

Conclusions

Trinuclear manganese complexes, [Mn$_3$L$_2$(OAc)$_6$], bearing certain bidentate nitrogen ligands L, such as 2-pyridylimino or bipyridino groups, displayed excellent catalytic activity in the epoxidation of olefins using commercial peracetic acid. Among those complexes investigated, species bearing 2-pyridylimino (ppei) exhibited especially high reactivity and selectivity. With the present catalyst system, substrate scope is extremely wide such that terminal and electron-deficient double bonds of both aliphatic and aromatic alkenes become now viable substrates. The catalytically active species can be also directly generated under the in situ conditions, in which the use of a preassembled trinuclear manganese complex is not required, thus making this epoxidation procedure operationally attractive. Results from the preliminary mechanistic studies and kinetic measurements led us to propose that the trinuclear manganese clusters, upon addition of peracetic acid oxidant, dissociate into two types of metal species, [MnL$_2$(OAc)$_2$] and [Mn(OAc)$_2$(solvent)$_n$], or their oligomeric species; the former L-bound species is assumed to be mainly responsible for the observed activity. This assumption was further supported both by the observation of an induction

(32) (a) Collman, J. P.; Belmont, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7288. (b) Töllner, K.; Popovitz-Biro, R.; Lahav, M.; Milstein, D. *Science* **1997**, *278*, 2100. (c) Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 4147.

SCHEME 1. Synthesis of the Polymer-Supported Ligand and Its Manganese Complex 4[a]
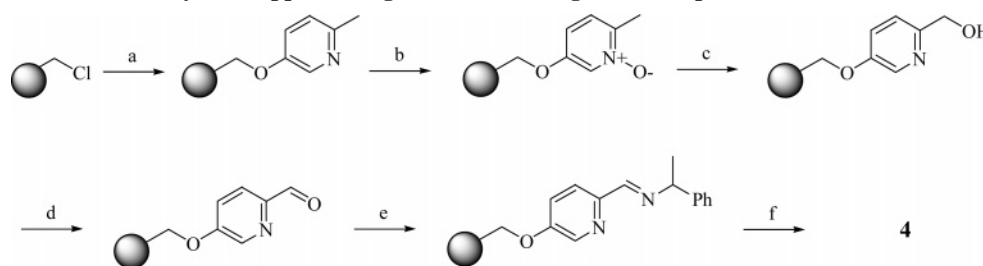
[a] Reagents and conditions: (a) 5-hydroxy-2-methylpyridine (4 equiv), NaI (4 equiv), Cs₂CO₃ (4 equiv), DMF, 80 °C, 12 h; (b) *m*-chloroperoxybenzoic acid (4 equiv), CHCl₃, room temperature, 24 h; (c) trifluoroacetic anhydride (5 equiv), CH₂Cl₂, room temperature, 24 h; (d) SeO₂ (6 equiv), 1,4-dioxane, 90 °C, 20 h; (e) α-methylbenzylamine (6 equiv), EtOH, 80 °C, 12 h; (f) Mn(OAc)₂·4H₂O (5 equiv), EtOH, 80 °C, 12 h.

TABLE 5. Effect of Polymer-Supported Mn (4) on the Epoxidation of Olefins[a]

	1st Run		2nd Run[b]	
alkene	conv (%)	selec (%)	conv (%)	selec (%)
cyclooctene	74 (>98)	99 (90)	64	99
1-decene	50 (>98)	97 (96)	<1	
trans-β-methylstyrene	47 (>98)	94 (91)	29	90

[a] Reaction conditions: olefin (0.5 mmol), polymer-supported Mn complex (30.4 mg, 2.0 mol %), and 32% CH₃CO₃H (0.6 mmol) in CH₃CN (1.0 mL), 25 °C, 18 min. Conversion was determined by GC using dodecane as an internal standard. Selectivity indicates the formation of epoxide, and the numbers in parentheses are the results of epoxidation using catalyst **1** (1.2 mol % with aliphatic and 2.0 mol % with aromatic olefin). [b] Reactions were performed with the filtered resin from the first run.

period in the epoxidation reaction and by the results with the solid-supported catalyst system.

Experimental Section

Preparation of 2-Pyridinal-1-phenylethylimine (ppei) Ligand. Anhydrous magnesium sulfate (4.81 g, 40.0 mmol) and α-methylbenzylamine (2.42 g, 20.0 mmol) were added at 0 °C to a solution of 2-pyridinecarboxaldehyde (2.14 g, 20.0 mmol) in 20 mL of diethyl ether. The reaction mixture was stirred at room temperature for 12 h, and then it was filtered through a pad of Celite. The filtrate was evaporated under reduced pressure to afford the desired ppei ligand in 97% yield (4.08 g) as a yellow oil which was used without further purification: ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, 1H, *J* = 4.7 Hz), 8.44 (s, 1H), 8.07 (d, 1H, *J* = 7.8 Hz), 7.71 (dt, 1H, *J* = 7.6, 1.5 Hz), 7.42 (d, 2H, *J* = 7.5 Hz), 7.32 (t, 2H, *J* = 7.3 Hz), 7.29−7.21 (m, 2H), 4.62 (q, 1H, *J* = 6.6 Hz), 1.60 (d, 3H, *J* = 6.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 154.7, 149.3, 144.5, 136.4, 128.4, 126.9, 126.6, 124.6, 121.4, 69.5, 24.5; IR (neat) 2972, 2862, 1645, 1587, 1567, 1493 cm⁻¹; HRMS (EI) calcd for C₁₄H₁₄N₂ 210.1157 [M+], found 210.1159.

General Procedure for the Synthesis of [Mn₃(ppei)₂(OAc)₆] (1), [Mn₃(2,2′-bipyridine)₂(OAc)₆] (2), and [Mn₃(1,10-phenanthroline)₂(OAc)₆] (3). α-Methylbenzylamine (1.21 g, 10.0 mmol) was added to a solution of 2-pyridinecarboxaldehyde (1.07 g, 10.0 mmol) in absolute ethanol (50 mL). The mixture was heated to reflux for 1 h, and then Mn(OAc)₂·4H₂O (2.45 g, 10.0 mmol) was added in one portion. The yellow solution immediately turned into a pale brown solution, and then a solid began to appear. After 10 min of stirring under the same temperature, the reaction mixture was cooled to 25 °C, and the resulting heterogeneous brown solution was partially evaporated. The pale brown precipitate was isolated by filtration washing with cold ethanol to afford **1** in 92% yield (2.89 g based on Mn). X-ray quality crystals were grown by the vapor diffusion method, where a small vial containing the reaction mixture of **1** was sealed in a large vial containing excess diethyl ether. Anal. Calcd for C₄₀H₄₆N₄O₁₂Mn₃ (**1**): C, 51.13; H, 4.93; N, 5.96. Found: C, 50.63; H, 4.80; N, 6.01.

Synthetic procedure for the preparation of analogous manganese clusters **2** and **3** was identical to that for the synthesis of **1**: **[Mn₃-(bipy)₂(OAc)₆] (2).** Yield was 68% based on Mn content. Anal. Calcd for C₃₂H₃₄N₄O₁₂Mn₃: C, 46.23; H, 4.12; N, 6.74. Found: C, 46.16; H, 4.09; N, 6.73.

[Mn₃(1,10-phenanthroline)₂(OAc)₆] (3). Yield was 70% based on Mn content. Anal. Calcd for C₃₆H₃₄N₄O₁₂Mn₃: C, 49.16; H, 3.90; N, 6.37. Found: C, 48.63; H, 3.94; N, 6.32. X-ray structure and collection data of **3** are presented in Supporting Information.

Representative Procedure for the Epoxidation Reactions. Condition A: To a solution of 1-decene (74.6 mg, 0.5 mmol) and **1** (5.6 mg, 1.2 mol %) in acetonitrile (1.0 mL) was added commercial peracetic acid (32%, 0.13 mL, 0.6 mmol) dropwise via syringe over 3 min, and the reaction mixture was stirred for 15 min at room temperature. After adding diethyl ether (5 mL) and biphenyl (0.5 mmol, an internal standard), the reaction mixture was passed through a pad of silica gel washing with diethyl ether. The oven condition for the GC/MS analysis was 70 °C for 3 min, 10 °C/min to 90 °C holding for 1 min, and 5 °C/min to 150 °C holding for 1.0 min on HP-5MS column, and the retention time of 1,2-epoxydecane was 11.18 min. The reaction proceeded with >98% conversion and in 96% GC yield on the basis of an average of three runs. **CAUTION!** The reaction exotherms if peracetic acid is added too quickly or if heat transfer from the reaction flask is inadequate to maintain the desired temperature.

Gram Scale Epoxidation: To a solution of 1-decene (1.06 g, 7.13 mmol) and **1** (80.4 mg, 0.085 mmol, 1.2 mol %) in CH₃CN (17 mL) was added peracetic acid (32%, 1.80 mL, 8.55 mmol) dropwise via syringe over 5 min. After stirring for 25 min at room temperature, the reaction mixture was quenched with saturated NaHCO₃ solution and was subsequently extracted with *n*-pentane. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Et₂O/*n*-pentane, 1:10) to afford 1,2-epoxydecane as a colorless oil (1.02 g, 92%): ¹H NMR (400 MHz, CDCl₃) δ 2.88 (m, 1H), 2.72 (dd, 1H, *J* = 5.0, 4.0 Hz), 2.43 (dd, 1H, *J* = 5.1, 2.7 Hz), 1.25−1.51 (m, 14H), 0.86 (t, 3H, *J* = 6.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 52.4, 47.1, 32.5, 31.8, 29.5, 29.4, 29.2, 25.9, 22.6, 14.0.

Condition B: A 10 mL round-bottom flask equipped with a stirring bar was charged with *cis*-stilbene (93.8 mg, 0.5 mmol), **1** (9.4 mg, 0.01 mmol, 2.0 mol %), and acetonitrile (1.0 mL). Peracetic acid (32%, 0.10 mL, 0.5 mmol) was added dropwise via syringe over 5 min at the start, and additional portion of peracetic acid (0.5 mmol) was next added after 10 min over 3 min. The reaction mixture was stirred for additional 10 min at room temperature. After addition of diethyl ether (5 mL) and biphenyl (0.5 mmol, internal standard), the reaction mixture was passed through a pad of silica gel washing with diethyl ether. The oven condition for the GC/MS analysis was 110 °C for 3 min, 15 °C/min to 180 °C holding for 1 min, and 5 °C/min to 210 °C holding for 1 min on a HP-5MS column. The retention time of *cis*- and *trans*-stilbene oxide was 9.30 and 10.76 min, respectively. GC analysis indicates that

epoxidation proceeded with >98% conversion and in 89% GC yield (*cis/trans*, 3.2:1) as an average of three runs.

Epoxidation Reactions under the in situ Conditions. A 10 mL round-bottom flask equipped with a stirring bar was charged with olefin (0.5 mmol), ppei (0.025 mmol, 5.0 mol %), $Mn(OAc)_2\cdot4H_2O$ (2.0 mol %) or $Mn(OAc)_3\cdot2H_2O$ (2.0 mol %), and acetonitrile (1.0 mL). The mixture was stirred at room temperature for 6 min, during which time a pale pink color of the mixture solution containing $Mn(OAc)_2\cdot4H_2O$ turned to pale brown, and a heterogeneous solution having $Mn(OAc)_3\cdot2H_2O$ was changed to a homogeneous brown solution. Subsequently, peracetic acid (32%, 0.6 mmol, 1.2 equiv to olefin) was added dropwise to the reaction mixture via syringe over 3 min. After stirring the mixture for 15 min at room temperature, diethyl ether (5 mL) and biphenyl (internal standard) were added. The crude reaction mixture was then passed through a pad of silica gel washing with diethyl ether. Conversion and yield of epoxide were determined by a GC analysis as above.

Supporting Information Available: X-ray crystallographic data of **1** and **3**, data of competition experiments, procedure of radical inhibition experiments, spectroscopic data and GC detection conditions of the produced epoxides, experimental details and data of kinetic studies, procedure and data of induction period experiments, and details for the synthesis of polymer-supported manganese complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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