

# Robust and Efficient Amide-Based Nonheme Manganese(III) Hydrocarbon Oxidation Catalysts: Substrate and Solvent Effects on Involvement and Partition of Multiple Active Oxidants

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**Abstract:** Two new mononuclear nonheme manganese(III) complexes of tetradentate ligands containing two deprotonated amide moieties, [Mn(bpc)Cl(H<sub>2</sub>O)] (**1**) and [Mn(Me<sub>2</sub>bpb)Cl(H<sub>2</sub>O)]·CH<sub>3</sub>OH (**2**), were prepared and characterized. Complex **2** has also been characterized by X-ray crystallography. Magnetic measurements revealed that the complexes are high spin ( $S=5/2$ ) Mn<sup>III</sup> species with typical magnetic moments of 4.76 and 4.95  $\mu_B$ , respectively. These nonheme Mn<sup>III</sup> complexes efficiently catalyzed olefin epoxidation and alcohol oxidation upon treatment with MCPBA under mild experimental conditions. Olefin epoxidation by these catalysts is proposed to involve the multiple active oxidants Mn<sup>V</sup>=O, Mn<sup>IV</sup>=O, and Mn<sup>III</sup>–

OO(O)CR. Evidence for this approach was derived from reactivity and Hammett studies, KIE ( $k_H/k_D$ ) values, H<sub>2</sub><sup>18</sup>O-exchange experiments, and the use of peroxyphenylacetic acid as a mechanistic probe. In addition, it has been proposed that the participation of Mn<sup>V</sup>=O, Mn<sup>IV</sup>=O, and Mn<sup>III</sup>–OOR could be controlled by changing the substrate concentration, and that partitioning between heterolysis and homolysis of the O–O bond of a Mn-acylperoxo intermediate (Mn–OOC(O)R) might be significantly affected by the nature of solvent, and that the O–O

bond of the Mn–OOC(O)R might proceed predominantly by heterolytic cleavage in protic solvent. Therefore, a discrete Mn<sup>V</sup>=O intermediate appeared to be the dominant reactive species in protic solvents. Furthermore, we have observed close similarities between these nonheme Mn<sup>III</sup> complex systems and Mn(saloph) catalysts previously reported, suggesting that this simultaneous operation of the three active oxidants might prevail in all the manganese-catalyzed olefin epoxidations, including Mn(salen), Mn(nonheme), and even Mn(porphyrin) complexes. This mechanism provides the greatest congruity with related oxidation reactions by using certain Mn complexes as catalysts.

**Keywords:** high-valent species • hydrocarbon oxidation • manganese • olefin epoxidation • solvent effects

## Introduction

The design of hydrocarbon oxidation catalysts that are rapid, inexpensive, and selective with a wide range of organic substrates remains an important goal.<sup>[1]</sup> While synthetic biomimetic systems containing manganese porphyrins and related Schiff base complexes have been shown to be efficient catalysts for hydroxylation and epoxidation reactions,<sup>[1,2]</sup> the development of other planar tetradentate ligands, such as amido ligands has been less explored.<sup>[3]</sup> These types of ligands are highly desirable owing to their easy and inexpensive preparation and ease of modification.

An understanding of the mechanism of the O–O bond activation and characterization of the reactive intermediates is also crucial in designing better catalysts for these manganese(III) complex catalyzed oxygenation reactions. In most cases, Mn<sup>V</sup>=O, Mn<sup>IV</sup>=O, and Mn<sup>III</sup>–OOR are, independently, invoked as reactive intermediates during the catalytic cycles.<sup>[2]</sup> However, in a few cases, the participation of multiple active oxidants has been proposed to account for the experimental results.<sup>[4]</sup>

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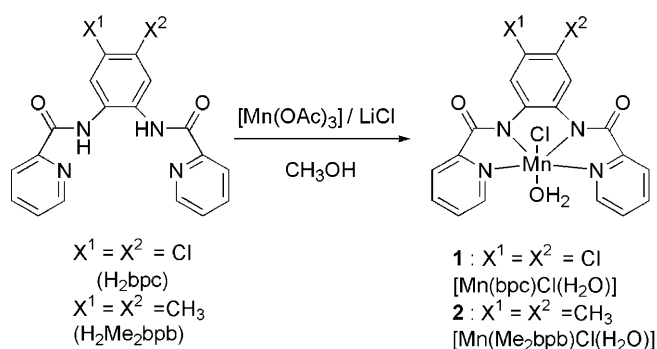
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We have recently reported on the catalytic reactivity of  $\text{Re}_4$  cluster-supported  $\text{Mn}(\text{saloph})$  complexes that are capable of rapidly catalyzing the epoxidation of a variety of olefins using MCPBA as an oxidant under mild experimental conditions.<sup>[5]</sup> Olefin epoxidation by these catalysts was proposed to involve the simultaneous operation of the multiple active oxidants  $\text{Mn}^{\text{V}}=\text{O}$ ,  $\text{Mn}^{\text{IV}}=\text{O}$ , and  $\text{Mn}^{\text{III}}-\text{OO}(\text{O})\text{CR}$ . This discovery has prompted us to explore the development of novel nonheme manganese catalysts and to extend the concept of multiple oxidants to nonheme manganese complex systems.

To develop efficient, selective, readily available, and stable catalysts, to extend the concept of the simultaneous operation of multiple active oxidants to nonheme manganese complexes, and to study the solvent effect on heterolytic versus homolytic O–O bond cleavage of  $\text{Mn}^{\text{III}}-\text{OO}(\text{O})\text{CR}$  species, we have synthesized and characterized amide-based nonheme Mn complexes and applied them to hydrocarbon oxidations with peracids as oxidants. We have found that these Mn complexes efficiently and selectively catalyze olefin epoxidations and operate in the same pathway (multiple active oxidants operating simultaneously) as shown in the previous study with  $\text{Mn}(\text{saloph})$  complexes. Evidence in support of this interpretation is based on reactivity and Hammett studies, KIE ( $k_{\text{H}}/k_{\text{D}}$ ) values,  $\text{H}_2^{18}\text{O}$ -exchange experiments, and the use of peroxyphenylacetic acid as a mechanistic probe. Moreover, it has been proposed that the participation of  $\text{Mn}^{\text{V}}=\text{O}$ ,  $\text{Mn}^{\text{IV}}=\text{O}$ , and  $\text{Mn}^{\text{III}}-\text{OO}(\text{O})\text{CR}$  could be controlled by changing substrate concentration and that the O–O bond of  $\text{Mn}^{\text{III}}-\text{OO}(\text{O})\text{CR}$  species might proceed predominantly by heterolytic cleavage in protic solvents to produce a  $\text{Mn}^{\text{V}}=\text{O}$  species as the dominant epoxidizing intermediate.

## Results and Discussion

The manganese complexes **1** and **2** were synthesized by reacting equimolar amounts of  $[\text{Mn}(\text{OAc})_3] \cdot 2\text{H}_2\text{O}$  and the ligands  $\text{H}_2\text{bpc}$  or  $\text{H}_2\text{Me}_2\text{bpb}$  in  $\text{CH}_3\text{CN}$  (Scheme 1).<sup>[6]</sup> Slow evaporation solution of **2** in methanol gave dark brown crystals suitable for X-ray analysis. The crystal structure of **2** re-



Scheme 1. Synthesis of manganese(III) complexes.

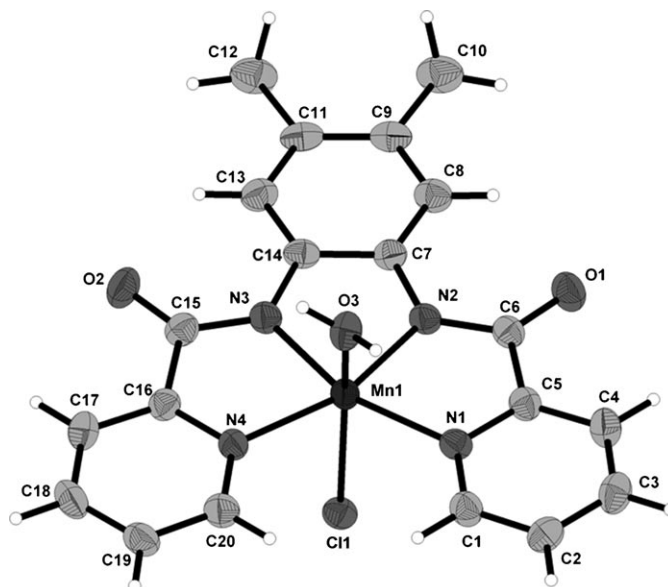


Figure 1. The crystal structure of **2**.

veals a coordination mode around the distorted octahedral metal center (Figure 1) similar to the structures of Fe and Mn bpb analogues.<sup>[7]</sup> The selected bond distances and angles are listed in Table 1. The magnetic moments at room temperature of **1** and **2** were found to be 4.76 and 4.95  $\mu_{\text{B}}$ , respectively, indicating a high-spin ( $S=5/2$ )  $\text{Mn}^{\text{III}}$  species. Complexes **1** and **2** were easily prepared, stable to air and moisture, inexpensive, and readily amenable to diverse reaction conditions.

Table 1. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **2**.

Bonds	[ $\text{\AA}$ ]	Angles	[ $^\circ$ ]
Mn1–N3	1.941(3)	N3–Mn1–N2	81.52(12)
Mn1–N1	2.068(3)	N2–Mn1–N1	80.39(11)
Mn1–O3	2.261(3)	N2–Mn1–N4	161.87(12)
O1–C6	1.238(4)	N3–Mn1–O3	96.43(11)
Mn1–N2	1.944(3)	N1–Mn1–O3	81.27(11)
Mn1–N4	2.076(3)	N3–Mn1–Cl1	99.99(9)
Mn1–Cl1	2.5025(11)	N1–Mn1–Cl1	88.02(8)
O2–C15	1.223(4)	O3–Mn1–Cl1	157.04(8)
		N3–Mn1–N1	161.37(12)
		N3–Mn1–N4	80.68(11)
		N1–Mn1–N4	117.02(11)
		N2–Mn1–O3	96.47(11)
		N4–Mn1–O3	82.16(11)
		N2–Mn1–Cl1	101.71(9)
		N4–Mn1–Cl1	84.78(9)

We investigated the oxidative reactivity of **1** and **2** with olefins and alcohols in the presence of *m*-chloroperbenzoic acid (MCPBA). MCPBA (0.07 mmol) was added to a mixture of substrate (0.035 mmol), manganese complex (0.001 mmol), and solvent (1 mL;  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2 = 1:1$ ; see the Experimental Section). This mixture was stirred for 10 minutes at room temperature, although the epoxidation

reactions were completed within 1 minute. We confirmed that direct substrate oxidation by MCPBA was negligible by control experiments,<sup>[8]</sup> and UV/Vis spectrophotometry showed that the complexes were robust enough during the catalytic reactions (data not shown). Moreover, they did not form a dinuclear  $\mu$ -oxo complex ( $\text{Mn}^{\text{IV}}\text{-O-Mn}^{\text{III}}$ ), known to be catalytically inactive.<sup>[9]</sup>

The results of the epoxidation reactions are summarized in Table 2. With complex **1**, the cyclic olefins cyclopentene, cycloheptene, and cyclooctene were oxidized to the corre-

This result indicates that the catalytic epoxidation reaction occurs with approximately 94% stereochemical retention. *trans*-2-Octene was oxidized exclusively to *trans*-2-octene oxide (Table 2, entry 8). The stereochemistry of *cis*-2-hexene was found to be somewhat low (61.0%; Table 2, entry 10). In the competitive epoxidations of *cis*- and *trans*-2-octene and *cis*- and *trans*-2-hexene, the ratios of *cis*- to *trans*-2-octene oxide and *cis*- to *trans*-2-hexene oxide were determined to be 2.1 (Table 2, entry 9) and 3.4 (Table 2, entry 12), respectively, indicating the preference of *cis*-olefin

Table 2. Olefin epoxidations by MCPBA with Mn complexes **1** and **2** in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:1) at room temperature.<sup>[a]</sup>

Entry	Substrate	Product	<b>1</b>		<b>2</b>	
			Conversion [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>	Conversion [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>
1	cyclopentene	epoxide	100	73.0 ± 1.9	80.2 ± 1.1	56 ± 1.0
2	cycloheptene	epoxide	100	100	67.1 ± 1.5	73.1 ± 0.8
3	cyclooctene	epoxide	96.1 ± 0.6	85.9 ± 1.6	76.7 ± 2.1	65.0 ± 2.7
4	cyclohexene	epoxide	93.2 ± 3.0	74.5 ± 1.4	72.9 ± 2.1	59.4 ± 0.6
		2-cyclohexene-1-ol		2.8 ± 0.6		3.2 ± 0.2
		2-cyclohexen-1-one		2.1 ± 0.5		2.3 ± 0.4
5	1-octene	epoxide	38.0 ± 0.2	25.3 ± 0.1	28.0 ± 0.3	17.3 ± 0.1
6	1-hexene	epoxide	34.2 ± 3.5	53.7 ± 1.2	20.7 ± 0.7	46.2 ± 0.2
7	<i>cis</i> -2-octene	<i>cis</i> -oxide	88.1 ± 2.3	73.2 ± 0.5	70.5 ± 0.7	56.9 ± 3.2
		<i>trans</i> -oxide		2.4 ± 0.2		2.0 ± 0.0
8	<i>trans</i> -2-octene	<i>trans</i> -oxide	68.8 ± 0.8	41.0 ± 0.1	54.9 ± 0.0	27.9 ± 0.4
9	<i>cis</i> -/ <i>trans</i> -2-octene	<i>cis</i> / <i>trans</i> -oxide		2.1		1.8
10	<i>cis</i> -2-hexene	<i>cis</i> -oxide	89.5 ± 1.3	79.7 ± 0.3	66.7 ± 1.7	61.4 ± 0.3
		<i>trans</i> -oxide		19.2 ± 0.1		18.7 ± 0.1
11	<i>trans</i> -2-hexene	<i>trans</i> -oxide	63.3 ± 0.6	50.7 ± 0.1	40.9 ± 1.2	40.7 ± 0.4
12	<i>cis</i> -/ <i>trans</i> -2-hexene	<i>cis</i> / <i>trans</i> -oxide		3.4		3.3
13	styrene	epoxide	88.7 ± 1.1	53.1 ± 0.2	72.8 ± 2.1	43.3 ± 2.6
		benzaldehyde		4.1 ± 0.0		3.2 ± 0.1
		phenylacetaldehyde		21.2 ± 1.8		13.1 ± 0.2
14	<i>cis</i> -stilbene	<i>cis</i> -oxide	82.2 ± 0.0	32.0 ± 0.2	66.3 ± 1.3	26.0 ± 0.2
		<i>trans</i> -epoxide		23.6 ± 0.6		16.2 ± 0.1
15		benzaldehyde		7.9 ± 0.0		8.5 ± 0.1
	<i>trans</i> -stilbene	<i>trans</i> -oxide	72.9 ± 2.8	54.4 ± 5.8	51.2 ± 4.5	39.0 ± 4.9
		benzaldehyde		7.8 ± 0.0		7.2 ± 0.4
16	1-phenylethanol	acetophenone	33.4 ± 1.0	39.5 ± 1.0	31.8 ± 3.5	32.9 ± 1.0
17	cyclohexanol	cyclohexanone	28.4 ± 1.6	26.7 ± 0.4	29.3 ± 2.8	20.7 ± 0.3
18	benzyl alcohol/ [D <sub>7</sub> ]benzyl alcohol	benzaldehyde ( <i>k</i> <sub>H</sub> / <i>k</i> <sub>D</sub> )		3.2 ± 1.4		3.3 ± 0.3

[a] Reaction conditions: olefin (0.035 mmol), catalyst ( $1.0 \times 10^{-3}$  mmol), MCPBA (0.07 mmol), solvent (1 mL,  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2 = 1:1$ ). [b] Based on substrate.

sponding epoxides in good yields (73–100%; Table 2, entries 1–3), with conversions ranging from 96 to 100%. The reaction of cyclohexene produced mainly the epoxidation product, along with small amounts of cyclohexenone (2.1%) and cyclohexenol (2.8%), indicating that free radical oxidation reactions were only a minor pathway for oxidation.<sup>[10]</sup> The terminal olefins 1-octene and 1-hexene were less efficiently oxidized to 1-octene and 1-hexene epoxides, respectively, under these conditions (Table 2, entries 5 and 6). *cis*-2-Octene was used to examine the percent retention of stereochemistry of the reaction (Table 2, entry 7), with *cis*-2-octene oxide being produced as the major species (73.2%) along with a small amount of *trans*-2-octene oxide (2.4%).

epoxidation to *trans*-olefin epoxidation. These values are similar to or somewhat smaller than those observed with the  $\text{Re}_4$  cluster-supported Mn(saloph) ( $k_{\text{cis}}/k_{\text{trans}} = 3.4\text{--}4.5$ )<sup>[5]</sup> and NaOCl/Mn(porph) ( $k_{\text{cis}}/k_{\text{trans}} = 5.0$ ) systems.<sup>[11]</sup>

With styrene (Table 2, entry 13), the dominant reaction involved the formation of epoxide, yielding styrene oxide (53.1%) with some amounts of phenylacetaldehyde (21.2%) and benzaldehyde (4.1%). *cis*-Stilbene produced both *cis*-stilbene oxide (32.0%) and *trans*-stilbene oxide (23.6%) with minor amounts of benzaldehyde (7.9%; Table 2, entry 14). *trans*-Stilbene was oxidized to *trans*-stilbene oxide (54.4%) and small amounts of benzaldehyde (7.8%; Table 2, entry 15). Product distribution of these aromatic olefins indicates that either the peroxy radical or oxomanganese(IV) is partly involved as the epoxidizing agent as these species should oxidize the substrates to nonstereospecific or radical-induced rearranged products.<sup>[11,12]</sup> However, the minimal portion of free radical oxidation reactions and a high degree of stereospecificity observed in our catalytic systems imply that two different oxidants,  $\text{Mn}^{\text{V}}=\text{O}$  and  $\text{Mn}^{\text{IV}}=\text{O}$ , are produced in these catalytic reactions and that the  $\text{Mn}^{\text{IV}}=\text{O}$  complex is responsible for the nonstereoretentive portion of the epoxidation reaction.<sup>[12]</sup>

Analogous but somewhat lower efficiency was obtained for **2**, thus indicating that the substitution of an electron-withdrawing group -Cl for an electron-donating group -CH<sub>3</sub> on the ligand enhances its reactivity, as observed in Mn(salen) and Mn(porphyrin) systems.<sup>[13]</sup> Importantly, to the best of our knowledge, **1** is the most effective nonheme manganese catalyst that affords high olefin conversions and

epoxide yields in the epoxidation of olefins by MCPBA.<sup>[1–2]</sup> In addition, these Mn<sup>III</sup> complexes are much more robust and exhibited much higher catalytic ability than the Fe<sup>III</sup> analogues.<sup>[14]</sup>

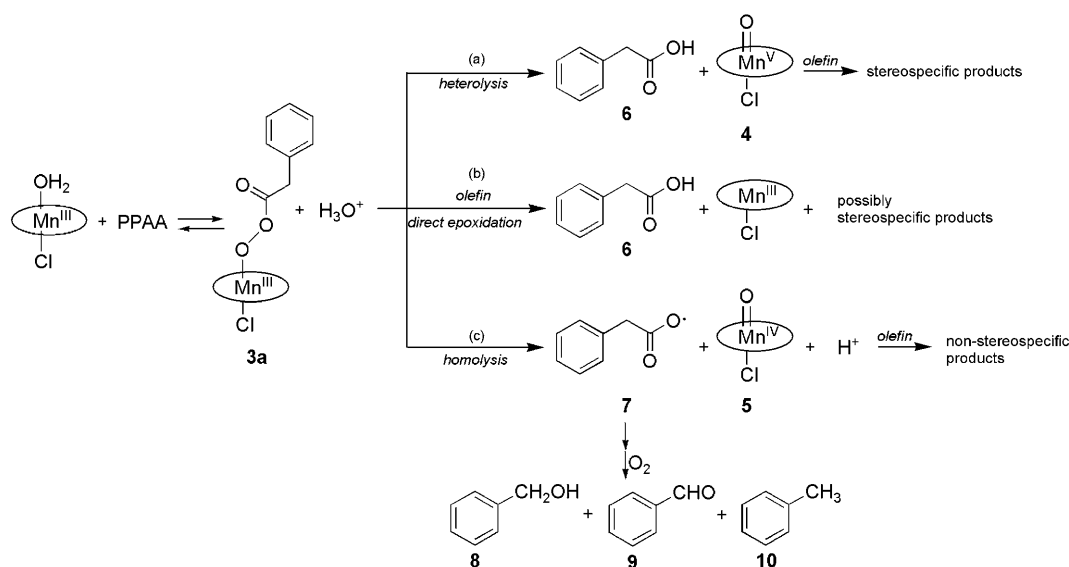
Alcohols were converted less efficiently to the corresponding carbonyl compounds (Table 2, entries 16 and 17) than the olefins were to epoxides. Kinetic isotope effect (KIE) studies have been carried out to gain insight into the nature of the oxidizing species in the alcohol oxidation reactions catalyzed by **1** and **2**. We performed the intermolecular competition reaction involving the excess of benzyl alcohol and [D<sub>7</sub>]benzyl alcohol to prevent further oxidation of the product benzaldehyde to benzoic acid. The kinetic isotope effects for benzaldehyde formation by **1** and **2** were determined to be 3.2 and 3.3 (Table 2, entry 18), respectively, which are almost identical to those of a hydrogen abstraction reaction catalyzed by Fe analogues (3.0 for [Fe(bpc)Cl<sub>2</sub>]<sup>+</sup> and 3.3 for [Fe(Me<sub>2</sub>bpb)Cl<sub>2</sub>]<sup>+</sup>).<sup>[14]</sup> These values indicate that cleavage of the C–H bond is involved in the rate-determining step. Moreover, this result suggests that one of the reactive species responsible for the alcohol oxidation in these catalytic systems might be a high-valent manganese-oxo species.

To obtain further information about the nature of the reactive intermediates, competition experiments were carried out between styrene and equivalent amounts of *p*-substituted styrene derivatives. A significant electronic effect on the reaction rates was observed, showing that more electron-rich olefins react faster than electron-deficient substrates. The rate data gave good linear Hammett plots against  $\sigma$  with  $\rho$  values of  $-1.4$  for **1** and  $-1.8$  for **2** (Figure S1 and S2 in the Supporting Information). This confirms the expected electrophilic character of the oxidant. The values are higher than those reported for the epoxidation of styrenes using Mn<sup>III</sup> tetraphenylporphyrin ( $\rho = -0.41$ ),<sup>[15]</sup> Mn(salen) ( $\rho =$

$-0.3$ ),<sup>[12c]</sup> and Re<sub>4</sub> cluster-supported Mn(saloph) ( $\rho = -0.66$ ).<sup>[5]</sup>

Isotopically labeled water, H<sub>2</sub><sup>18</sup>O, is commonly used in reaction mechanism studies to address the origin of oxygen atoms found in oxidation products. When <sup>18</sup>O labeled oxygen is found in the epoxide product, it is generally concluded that a metal-oxo species performs the oxygen-transfer process.<sup>[16]</sup> We have examined the epoxidation of cyclohexene by **1** and MCPBA in the presence of approximately a 25-fold excess of H<sub>2</sub><sup>18</sup>O relative to the substrate. As shown in Table S1 in the Supporting Information, no <sup>18</sup>O was incorporated from H<sub>2</sub><sup>18</sup>O into cyclohexene oxide (Table S1, entry 1). However, when the amounts of H<sub>2</sub><sup>18</sup>O increased to approximately a 100-fold excess (Table S1, entry 3), the epoxide product had small amounts of <sup>18</sup>O incorporation (3%). A further increase of labeled water resulted in more <sup>18</sup>O incorporation (10%) in the epoxide product (Table S1, entry 5). The results of the labeled-water experiments demonstrate that high-valent Mn=O species are involved in the reactions of the catalysts with MCPBA at a very low concentration of substrate. The dependence of <sup>18</sup>O-incorporation on the concentration of labeled water could be explained by two possibilities: 1) the relative rate difference of oxygen-atom transfer and oxygen exchange as previously reported,<sup>[16]</sup> and 2) an acylperoxo species (Mn–OOC(O)R **3a**; Scheme 2) might be able to directly epoxidize the olefin at the high concentration of substrate, resulting in no <sup>18</sup>O incorporation. Complex **2** with the electron-donating groups ( $-\text{CH}_3$ ) did not show any <sup>18</sup>O-incorporation even in approximately a 100-fold excess of H<sub>2</sub><sup>18</sup>O (Table S1, entry 3).

Peroxyphenylacetic acid (PPAA) has often been used as a mechanistic probe to distinguish homolytic versus heterolytic cleavage of the peracid O–O bond.<sup>[14,17]</sup> When the O–O bond of the coordinated anion of PPAA (**3a**) undergoes heterolytic O–O bond cleavage (Scheme 2; pathway a) or di-



Scheme 2. Product distribution of O–O bond cleavage of PPAA with manganese complexes.

rectly oxidizes the substrate (pathway b), phenylacetic acid (PAA, **6**) is formed. In contrast, the homolytic cleavage of the O–O bond of **3a** generates an acyloxyl radical (**7**; pathway c) that undergoes a rapid  $\beta$ -scission (diffusion-controlled rate ca.  $10^9 \text{ s}^{-1}$ ) to give benzyl alcohol (**8**), benzaldehyde (**9**), and toluene (**10**). First, a control experiment with PPAA as an oxidant under the same reaction conditions as MCPBA was carried out in the absence of substrate (Table S2 in the Supporting Information, entry 1). As previously shown for the Mn(saloph) system,<sup>[5]</sup> the heterolytic cleavage product, phenylacetic acid (45.5% based on PPAA), and the homolytic cleavage products, benzaldehyde (39.5%) and benzyl alcohol (3.1%), were formed in a ratio of 52:48. These results suggest that heterolytic (52%) and homolytic (48%) O–O bond cleavage of **3a** occur simultaneously to produce high valent  $\text{Mn}^{\text{V}}=\text{O}$  (**4**) and  $\text{Mn}^{\text{IV}}=\text{O}$  (**5**) species even in the reactions involving the nonheme Mn complexes and peracids. Next, we increased the concentration of substrate to examine concentration dependence on the ratio of heterolysis to homolysis. Importantly, the ratio of heterolysis to homolysis varied from 1.07 (52:48) for 0 mm cyclohexene to 1.92 (66:34) for 35 mm cyclohexene to 4.14 (80:20) for 140 mm cyclohexene (Table S2, entries 1, 3, and 5). Analogous results were obtained for **2** (Table S2, entries 6–10). These results, again, suggest that the  $\text{Mn}-\text{OOC}(\text{O})\text{R}$  (**3**) might be a potent reactive species for epoxidation as previously proposed in Mn(salen)-, Fe(porph)-, and  $\text{Re}_4$  cluster-supported Mn(saloph)-catalyzed epoxidation with MCPBA as oxygen donor.<sup>[5,18]</sup> Moreover, these results confirm the facts observed in Mn(saloph)/MCPBA system<sup>[5]</sup> that both heterolysis and homolysis of the O–O bond of PPAA occur simultaneously in the Mn-peracid systems if the substrate is less active or the concentration of the substrate is very low. However, when the substrate is active or the concentration of the substrate is increased, the species  $\text{Mn}-\text{OOC}(\text{O})\text{R}$  (**3**) might be gradually involved in the epoxidation reaction.<sup>[18a]</sup> Therefore, even in our nonheme  $\text{Mn}^{\text{III}}$ -catalyzed epoxidation reaction, the multiple oxidants,  $\text{Mn}^{\text{III}}-\text{OOC}(\text{O})\text{R}$ ,  $\text{Mn}^{\text{V}}=\text{O}$ , and  $\text{Mn}^{\text{IV}}=\text{O}$ , might act simultaneously as the key active intermediates. More significantly, our previous and present re-

sults suggest that this simultaneous operation of the three oxidants might prevail in all the manganese-catalyzed olefin epoxidations, including Mn(porphyrin) complexes.

Furthermore, we were interested to find conditions to generate only one reactive species (e.g.; generation of  $\text{Mn}^{\text{V}}=\text{O}$ ). Therefore, we have changed the solvent components from a mixture of  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  to that of  $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ , because it has been demonstrated previously that protic solvents facilitate the O–O bond heterolysis to produce metal(V) oxo species.<sup>[19]</sup> With complex **1**, the reaction condition with 0.035 mmol of cyclohexene was chosen to examine the product distribution of the oxidant PPAA. As shown in Table 3, entries 1–6, when an amount of the protic solvent  $\text{CH}_3\text{OH}$  was gradually increased from 0% to 90%, the heterolysis was dramatically increased up to approximately 90% to produce a possible reactive  $\text{Mn}^{\text{V}}=\text{O}$  species. These results suggest that partitioning between the heterolytic and homolytic O–O bond cleavage of PPAA is significantly affected by the nature of the solvent, and that the O–O bond of PPAA proceeds predominantly by heterolytic cleavage in protic solvent to produce a discrete  $\text{Mn}^{\text{V}}=\text{O}$  intermediate as the dominant reactive species. Therefore, a certain reaction condition could be established in which only one reactive species among the multiple active oxidants is generated. Analogous results were obtained for **2** (Table 3, entries 7–12).

To further test the possibility that the Mn-oxo species performs the oxygen-transfer process in the protic solvents, we have, again, carried out  $^{18}\text{O}$ -labeling studies by **1** and MCPBA with a gradual increase of the protic solvent  $\text{CH}_3\text{OH}$  in the presence of approximately a 450-fold excess of  $\text{H}_2^{18}\text{O}$  relative to the substrate. As shown in Table 4, amounts of  $^{18}\text{O}$  incorporation of the epoxide product (Table 4, entries 2–6) gradually increased from 10% (10% MeOH) to 25% (90% MeOH). These results also suggest that high-valent  $\text{Mn}=\text{O}$  species might be involved in the reactions of the catalysts with MCPBA at a very low concentration of substrate in protic solvents. Moreover, this seems to be consistent with the results of the product distribution of the oxidant PPAA in protic solvent as shown in Table 3.

Table 3. Yield of products derived from peroxyphenylacetic acid (PPAA) mediated by Mn complexes **1** and **2** in the presence of cyclohexene in protic solvent<sup>[a]</sup>.

Entry	Catalyst	Solvent (MeCN/MeOH)	Heterolysis <sup>[b]</sup>		Homolysis <sup>[b]</sup>		Hetero ( <b>6</b> )/ Homo ( <b>8</b> + <b>9</b> + <b>10</b> )	Oxidation products <sup>[c,d]</sup>		
			<b>6</b>	<b>8</b>	<b>9</b>	<b>10</b>		oxide	ol	one
1	<b>1</b>	10:0	58.0±0.6	1.8±0.2	30.4±0.2	–	64/36(1.80)	31.6±0.5	3.5±0.1	1.8±0.1
2	<b>1</b>	9:1	59.6±2.6	1.6±0.2	24.8±0.4	–	70/30(2.26)	26.5±0.5	3.0±0.7	1.7±0.2
3	<b>1</b>	7:3	69.7±3.0	1.5±0.2	16.8±0.2	–	79/21(3.81)	21.3±0.3	3.4±0.1	1.4±0.2
4	<b>1</b>	5:5	71.0±0.2	1.1±0.2	11.9±0.4	–	85/15(5.46)	17.5±0.2	3.2±0.0	1.3±0.0
5	<b>1</b>	3:7	78.2±1.2	1.6±0.2	9.7±0.2	–	87/13(6.92)	14.2±1.1	3.1±0.1	1.2±0.0
6	<b>1</b>	1:9	74.8±3.6	1.1±0.2	7.9±0.2	–	89/11(8.31)	13.2±0.9	3.0±0.1	1.2±0.0
7	<b>2</b>	10:0	46.4±0.2	1.6±0.2	33.9±0.6	–	57/43(1.31)	21.4±1.2	3.3±0.2	1.9±0.2
8	<b>2</b>	9:1	60.7±4.3	2.0±0.2	24.3±0.6	–	70/30(2.31)	18.1±1.1	3.0±0.2	1.4±0.1
9	<b>2</b>	7:3	72.7±1.4	1.6±0.2	17.4±0.4	–	79/21(3.83)	17.1±0.9	3.0±0.1	1.3±0.1
10	<b>2</b>	5:5	70.8±1.8	1.2±0.2	12.1±0.6	–	84/16(5.32)	12.7±1.7	2.9±0.1	1.2±0.1
11	<b>2</b>	3:7	70.2±1.4	1.1±0.2	9.7±0.4	–	87/13(6.50)	10.3±1.3	2.8±0.0	1.1±0.0
12	<b>2</b>	1:9	74.9±3.1	1.2±0.2	8.7±0.2	–	88/12(7.57)	8.3±0.3	2.8±0.1	1.1±0.1

[a] Reaction conditions: cyclohexene (0.035 mmol), catalyst ( $1.0 \times 10^{-3}$  mmol), PPAA (0.07 mmol), solvent (1 mL). [b] Based on PPAA. [c] Oxide, ol, and one indicate cyclohexene oxide, cyclohexenol, and cyclohexenone, respectively. [d] Based on substrate, cyclohexene.



Table 4. Percentage of  $^{18}\text{O}$ -incorporated from  $\text{H}_2^{18}\text{O}$  into cyclohexene oxide formed during cyclohexene oxidation by MCPBA and Mn complexes **1** and **2** in protic solvent.<sup>[a]</sup>

Entry	Catalyst	Solvent ( $\text{CH}_3\text{CN}/\text{MeOH}$ )	$^{18}\text{O}$ in cyclohexene oxide [%]
1	<b>1</b>	10:0	$13.0 \pm 2.0$
2	<b>1</b>	9:1	$10.0 \pm 2.0$
3	<b>1</b>	7:3	$11.0 \pm 1.0$
4	<b>1</b>	5:5	$17.0 \pm 3.0$
5	<b>1</b>	3:7	$21.0 \pm 2.0$
6	<b>1</b>	1:9	$25.0 \pm 1.0$
7	<b>2</b>	10:0	$5.0 \pm 1.0$
8	<b>2</b>	5:5	$3.0 \pm 1.0$
9	<b>2</b>	1:9	$7.0 \pm 3.0$

[a] Reaction conditions: cyclohexene (0.005 mmol), catalyst ( $1.0 \times 10^{-3}$  mmol), MCPBA (0.005 mmol),  $\text{H}_2^{18}\text{O}$  (2.222 mmol), solvent (1 mL, a mixture of anhydrous  $\text{CH}_3\text{CN}$  and  $\text{MeOH}$ ).

Complex **2** showed less  $^{18}\text{O}$  incorporation compared with complex **1** under the same reaction conditions (Table 4, entries 7–9).

Based on the results of  $^{18}\text{O}$  incorporation in protic solvents, we have tried to carry out hydrocarbon oxidations in the protic but non-oxidizable solvent  $\text{H}_2\text{O}$ , since methanol used as a protic solvent is oxidizable to formaldehyde, thus resulting in the reduction of the yields as shown in Table 3. Unfortunately, however, catalysts **1** and **2** are not soluble in the solvent systems that contains more than 4% of water. Therefore, we plan to prepare some water-soluble bpb derivative ligands.

Next, we have carried out UV/Vis spectroscopic measurements at low temperature ( $-40$  and  $-70^\circ\text{C}$ , respectively) to observe the proposed reactive intermediates,  $\text{Mn}^{\text{III}}\text{--OOC(O)R}$ ,  $\text{Mn}^{\text{V}}\text{=O}$ , and  $\text{Mn}^{\text{IV}}\text{=O}$ . As soon as 1.2 equivalents of MCPBA were added to a solution of **1** in the absence of and in the presence of cyclohexene, UV/Vis spectra were taken within 3 seconds and every 30 seconds for 20 minutes. As shown in Figure S3 in the Supporting Information, there is no spectral change at  $-40^\circ\text{C}$  and even at  $-70^\circ\text{C}$  (data not shown), suggesting that those reactive intermediates might be spectroscopically not observable or present in a too low concentration to be detected. The same results were also obtained with **2**. A further effort to detect the possible reactive species was carried out by EPR spectroscopy at low temperature ( $-40^\circ\text{C}$ ). Figure S4 in the Supporting Information shows the EPR spectra of frozen complex **1** solution (dotted line) and an intermediate state (solid line), frozen at 5 seconds after mixing complex **1** and MCPBA at  $-40^\circ\text{C}$  in a mixture of  $\text{MeCN}$  and  $\text{CH}_2\text{Cl}_2$  (1:1) (see the Supporting Information). Two spectra show weak, background EPR signals without any significant change, suggesting that it is difficult to detect the possible reactive intermediates with these spectroscopic instruments. Further efforts to observe the possible reactive species are currently under investigations.

## Conclusion

We have synthesized and characterized the nonheme  $\text{Mn}^{\text{III}}$  complexes **1** and **2** with two deprotonated amide moieties, which efficiently catalyze a wide range of olefin epoxidation with excellent stability under mild experimental conditions. These results may provide guidance in the design of new oxidation catalysts: 1) High activity and stability with these simple complexes can be achieved without resorting to more extreme strategies such as very electron-deficient or complicated ligands, 2) These amide-based catalysts are easily synthesized and show the possibility for ligand modification to design practical amide-based catalysts, and 3) these  $\text{Mn}^{\text{III}}$  complexes are much more robust and exhibit much higher catalytic ability than the  $\text{Fe}^{\text{III}}$  analogues,<sup>[14]</sup> thus suggesting that  $\text{Mn}^{\text{III}}$  complexes could be better catalysts than the analogous  $\text{Fe}^{\text{III}}$  complexes. On the other hand, reactivity and Hammett studies, KIE ( $k_{\text{H}}/k_{\text{D}}$ ) values,  $\text{H}_2^{18}\text{O}$  exchange experiments, and the use of PPAA as a mechanistic probe suggest that the multiple oxidants,  $\text{Mn}^{\text{III}}\text{--OOC(O)R}$ ,  $\text{Mn}^{\text{V}}\text{=O}$ , and  $\text{Mn}^{\text{IV}}\text{=O}$ , operate simultaneously as the key active intermediates in the epoxidation reactions. Moreover, it has been proposed that the participation of  $\text{Mn}^{\text{V}}\text{=O}$ ,  $\text{Mn}^{\text{IV}}\text{=O}$ , and  $\text{Mn}^{\text{III}}\text{--OOR}$  can be controlled by changing the substrate concentration. Furthermore, partitioning between the heterolytic and homolytic O–O bond cleavage of PPAA is significantly affected by the nature of solvent, and the O–O bond of PPAA proceeds predominantly by heterolytic cleavage in protic solvent, suggesting that a discrete  $\text{Mn}^{\text{V}}\text{=O}$  intermediate appears to be the dominant reactive species in protic solvent. These results presume that  $\text{Mn}^{\text{V}}\text{=O}$  species might become the common reactive intermediate in protic solvents,<sup>[20]</sup> whereas the three active oxidants,  $\text{Mn}^{\text{III}}\text{--OOC(O)R}$ ,  $\text{Mn}^{\text{V}}\text{=O}$ , and  $\text{Mn}^{\text{IV}}\text{=O}$ , operate simultaneously in aprotic solvents. These results also suggest that we will be able to find the certain conditions in which only one reactive species operates, although we could not directly observe the possible reactive species by UV/Vis and EPR methods at low temperature. Finally, we have observed close similarities between these nonheme  $\text{Mn}^{\text{III}}$  complex systems and the previous  $\text{Re}_4$  cluster-supported  $\text{Mn}(\text{saloph})$  systems, suggesting that this simultaneous operation of the three active oxidants might prevail in all the manganese-catalyzed olefin epoxidations, including  $\text{Mn}(\text{salen})$ ,  $\text{Mn}(\text{nonheme})$ , and even  $\text{Mn}(\text{porphyrin})$  complexes. Therefore, the present results provide important information for the design of new oxidation catalysts and for the resolution of the long-standing dichotomy of views pertaining to the nature of the active oxidants in  $\text{Mn}(\text{nonheme})$ - and  $\text{Mn}(\text{salen})$ -, and even  $\text{Mn}(\text{porphyrin})$ -catalytic reactions.<sup>[1,4,21]</sup>

## Experimental Section

**General:** Olefins, alcohols,  $[\text{D}_7]$ benzyl alcohol, epoxides, cyclohexenol, cyclohexenone, methanol, acetone, methylene chloride, acetonitrile,  $[\text{Mn}(\text{OAc})_3] \cdot 2\text{H}_2\text{O}$ , MCPBA (65%) and  $\text{H}_2^{18}\text{O}$  (95%  $^{18}\text{O}$  enrichment) were

purchased from Aldrich Chemical Co. and were used without further purification. Peroxyphenylacetic acid (PPAA) was synthesized according to methods described in the literature.<sup>[5,14]</sup> Product analyses for olefin epoxidation, partition reaction of PPAA, and <sup>18</sup>O incorporation reactions of cyclohexene oxide were performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with Hewlett–Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using a 30 m capillary column (Hewlett–Packard, DB-5 or HP-FFAP). <sup>1</sup>H NMR spectra was recorded on a Bruker 250 in CDCl<sub>3</sub> with TMS as internal standard. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C Instrument. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Low-temperature UV/Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with an Optostat variable-temperature liquid-nitrogen cryostat (Oxford Instruments). EPR spectra were recorded on a Jeol JES-TE300 ESR spectrometer using 100 kHz field modulation. Low temperature spectra were obtained using a Jeol ES-DVT3 variable temperature controller.

**Synthesis of manganese complexes **1** and **2**:** Ligands bpc and Me<sub>2</sub>bpb were synthesized as previously reported.<sup>[14,22]</sup> [Mn(bpc)(H<sub>2</sub>O)Cl] (**1**) and [Mn(Me<sub>2</sub>bpb)(H<sub>2</sub>O)Cl]·CH<sub>3</sub>OH (**2**) were prepared by refluxing [Mn(OAc)<sub>3</sub>]·2H<sub>2</sub>O (0.13 g, 0.5 mmol) with H<sub>2</sub>bpc (0.19 g, 0.5 mmol) or H<sub>2</sub>Me<sub>2</sub>bpb (0.17 g, 0.5 mmol) in 20 mL methanolic LiCl (0.21 g, 5 mmol) for 5–10 min.<sup>[7c]</sup> For **1**, after the reaction the solution was stirred for 30 min, the dark brown microcrystals precipitated were collected by filtration, washed with methanol, and air-dried. The yield was 0.14 g (55.3 %). IR (KBr):  $\tilde{\nu}$  = 1651 cm<sup>-1</sup> (C=O); elemental analysis calcd (%) for C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>MnN<sub>4</sub>O<sub>3</sub> (**1**): C, 43.80; H, 2.45; N, 11.35; found: C, 43.53; H, 2.71; N, 11.56. For **2**, dark brown crystals suitable for X-ray analysis were obtained by slow evaporation from a methanol solution for one week at room temperature. Yield was 0.14 g (60.0 %). IR (KBr):  $\tilde{\nu}$  = 1623 cm<sup>-1</sup> (C=O); elemental analysis calcd (%) for C<sub>21</sub>H<sub>22</sub>ClMnN<sub>4</sub>O<sub>4</sub> (**2**): C, 52.02; H, 4.57; N, 11.56; found: C, 52.13; H, 4.50; N, 11.27.

**X-ray analysis:** Dark brown plate-like crystals suitable for crystallographic analysis were obtained from CH<sub>3</sub>OH. The diffraction data were collected on a Nonius Kappa-CCD diffractometer using MoK $\alpha$  ( $\lambda$  = 0.71073 Å).<sup>[23]</sup> The crystal was mounted on a glass fiber under epoxy resin. The CCD data were integrated and scaled using the DENZO-SMN software package,<sup>[24]</sup> and the structures were solved by direct methods and refined using SHELXL/PC V5.1.<sup>[25]</sup> The crystallographic data for **2** are listed in Table 5. CCDC-665111 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Catalytic hydrocarbon oxidations by manganese catalysts with MCPBA:** MCPBA (0.07 mmol) was added to a mixture of substrate (0.035 mmol),

manganese catalyst (0.001 mmol), and solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> = 1:1; 1 mL). The mixture was stirred for 10 min at room temperature. The reaction was monitored by GC/mass analysis of 20  $\mu$ L aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average conversion and product yields are presented. Product and conversion yields were based on substrate. In the competitive reactions of *cis*-2-hexene and *trans*-2-hexene and *cis*-2-octene and *trans*-2-octene, the concentration of the substrate was 0.1 mmol.

**Kinetic isotope effect for the benzyl alcohol oxidation by manganese catalysts with MCPBA:** To improve the accuracy for measuring the amount of deuterated benzyl alcohol product, a 1:6 mixture of benzyl alcohol and deuterated benzyl alcohol was used.<sup>[14]</sup> The reaction conditions were as follows: MCPBA (0.05 mmol) was added to a mixture of benzyl alcohol (0.1 mmol), deuterated benzyl alcohol (0.6 mmol), manganese catalyst (0.001 mmol), and solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> = 1:1; 1 mL). Excess benzyl alcohol and [D<sub>7</sub>]benzyl alcohol were used to prevent further oxidation of the product benzaldehyde to benzoic acid. The mixture was stirred for 10 min at room temperature. Reaction was monitored by GC/mass analysis of 20  $\mu$ L aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average KIE values are presented.

**Competitive reactions of styrene and *para*-substituted styrenes for Hammett plot:** MCPBA (0.018 mmol) was added to a mixture of styrene (0.01 mmol) and *para*(X)-substituted styrene (0.01 mmol, X = -OCH<sub>3</sub>, -CH<sub>3</sub>, -Cl, and -CN), Mn complex (0.001 mmol), and solvent (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN = 1:1; 1 mL). The mixture was stirred for 10 min at room temperature. The amounts of styrenes before and after reactions were determined by GC. The relative reactivities were determined using the following equation:  $k_p/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$  where  $X_i$  and  $X_f$  are the initial and final concentrations of substituted styrenes and  $Y_i$  and  $Y_f$  are the initial and final concentrations of styrene.<sup>[16b]</sup>

**H<sub>2</sub><sup>18</sup>O experiments:** MCPBA (0.005 and 0.01 mmol, respectively) was added to a mixture of cyclohexene (0.005–0.02 mmol), Mn complex (0.001 mmol), and H<sub>2</sub><sup>18</sup>O (10–40  $\mu$ L, 95 % <sup>18</sup>O enriched, Aldrich Chemical Co.) in a dried solvent mixture (1 mL) of CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> (1:1). The reaction mixture was stirred for 5 min at room temperature and then directly analyzed by GC/MS. The <sup>16</sup>O and <sup>18</sup>O compositions were determined by the relative abundance of mass peaks at  $m/z$  = 99 for <sup>16</sup>O-cyclohexene oxide and  $m/z$  = 101 for <sup>18</sup>O-cyclohexene oxide. All reactions were run at least in triplicate and the average values are presented. Analysis of the O–O bond cleavage products from the reactions of the Mn complexes with PPAA in a mixture of aprotic solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>) and a mixture of protic solvent (CH<sub>3</sub>CN/CH<sub>3</sub>OH). PPAA (0.07 mmol) was added to a mixture of cyclohexene (0–0.14 mmol), Mn complex (0.001 mmol), and solvent (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> = 1:1; 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/mass analysis of 20  $\mu$ L aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in triplicate and the average product yields are presented. Product yields were based on PPAA. In a mixture of protic solvents (CH<sub>3</sub>CN/CH<sub>3</sub>OH), the same reactions were performed by gradually varying the amount of CH<sub>3</sub>OH from 0 % to 90 %.

**UV/Vis spectroscopic studies:** UV/Vis spectroscopic studies were carried out as follows: Solutions of **1** (0.125 mM) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN = 1:1 (3 mL) were first cooled to –40 °C or –70 °C in an 1 cm UV cell. MCPBA (1.2 equiv, diluted in 30  $\mu$ L of CH<sub>2</sub>Cl<sub>2</sub>) was then injected into the UV cell in a single portion, whereupon the spectral changes were directly monitored within 3 s and at intervals 30 s for 20 min by UV/Vis spectrophotometer. Analogous experiments with **2** gave similar results. In addition, the same results were obtained with both **1** and **2** in the presence of cyclohexene.

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Table 5. Crystal data and structure refinement for **2**.

formula	C <sub>21</sub> H <sub>22</sub> ClMnN <sub>4</sub> O <sub>4</sub>
<i>M</i> <sub>r</sub>	484.82
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> [Å]	15.2357(4)
<i>b</i> [Å]	12.2956(7)
<i>c</i> [Å]	11.2817(8)
$\beta$ [°]	97.476(3)
<i>V</i> [Å <sup>3</sup> ]	2095.5(2)
<i>Z</i>	4
$\rho_{\text{calcd}}$ [Mg m <sup>-3</sup> ]	1.537
$\mu$ [mm <sup>-1</sup> ]	0.794
reflections collected	14823
independent reflections	4684 [ <i>R</i> (int) = 0.0765]
data/restraints/parameters	4684/2/292
goodness-of-fit on <i>F</i> <sup>2</sup>	1.032
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0508, <i>wR</i> <sub>2</sub> = 0.1241
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1042, <i>wR</i> <sub>2</sub> = 0.1496
extinction coefficient	0.0012(5)
largest diff. peak/hole [e Å <sup>-3</sup> ]	0.641/–0.531

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