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Efficient Olefin Epoxidation by Robust Re_4 Cluster-Supported Mn^{III} Complexes with Peracids: Evidence of Simultaneous Operation of Multiple Active Oxidant Species, Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OOC(O)R

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Abstract: Two new tetranuclear chalcocyanide cluster complexes, $[\{Mn(saloph)H_2O\}_4Re_4Q_4(CN)_{12}]\cdot 4CH_3OH\cdot 8H_2O$ (saloph = *N*,*N*′-*o*-phenylenebis(salicylidenaminato), Q = Se (**1**-Se), Te (**2**-Te)), have been synthesized by the diffusion of a methanolic solution of $[PPh_4]_4[Re_4Q_4(CN)_{12}]$ into a methanolic solution of $[Mn(saloph)]^+$. The structure of **2**-Te has been determined by X-ray crystallography. These rhenium cluster-supported $[Mn^{III}(saloph)]$ complexes have been found to efficiently catalyze a wide range of olefin epoxidations under mild experimental conditions in the presence of *meta*-chloroperbenzoic acid (*m*CPBA). Olefin epoxidation by these catalysts is proposed to involve the multiple active oxidants Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OOC(O)R. Evidence in support of this interpretation has been derived from reactivity and Hammett studies, $H_2{}^{18}O$-exchange experiments, and the use of peroxyphenylacetic acid as a mechanistic probe. Moreover, it has been observed that the participation of Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OOC(O)R can be controlled by changing the substrate concentration. This mechanism provides the greatest congruity with related oxidation reactions that employ certain Mn complexes as catalysts.

Keywords: cluster compounds · epoxidation · manganese · rhenium

Introduction

The Mn-containing complexes [Mn(salen)], [Mn(porphyrin)], and [Mn(nonheme)] are well known as efficient catalysts for olefin epoxidation and alkane hydroxylation.[1] An understanding of the mechanism of O–O bond activation and a characterization of the reactive intermediates are crucial in designing better catalysts for these manganese(III)-complex-catalyzed oxygenation reactions. In most cases, Mn^{V}=O, Mn^{IV}=O, and/or Mn^{III}–OOR are invoked as reactive intermediates during the catalytic cycles,[2] with another intermediate, Mn^{III}–O–Mn^{IV}, being catalytically inactive.[3] The exact nature of the oxygenating species and the mechanism of oxygen transfer to the substrate remain unclear, although the participation of multiple active oxidants has been proposed to account for the experimental results.[4]

Several cyano-bridged rhenium cluster frameworks resembling Prussian blue have been prepared in the hope that their larger cavities might function as molecular sieves or supporting matrices for catalysts.[5] We have previously synthesized new rhenium clusters containing [Mn(OEP)] and [Mn(TPP)] (OEP = octaethylporphinato dianion; TPP = tetraphenylporphinato dianion) complexes, in which manganese(III) porphyrin units are linked to cyano-rhenium clusters to form discrete molecules rather than extended frameworks.[6] Interestingly, the [Mn(TPP)]-containing rhe-

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nium cluster showed high catalytic activity in olefin epoxidation with iodosylbenzene (PhIO).[6]

To develop efficient, selective, readily available, and stable catalysts, to discover new [Mn(salen)]-type-containing Re clusters with novel magnetic properties, and to prevent the formation of catalytically inactive dinuclear μ-oxo complexes (Mn^{IV}–O–Mn^{III}), we designed and synthesized the title clusters starting from Re clusters and the [Mn^{III}(saloph)] complex (saloph = *N*,*N*′-*o*-phenylenebis(salicylidenaminato)).[7] We present here new molecular complexes containing $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions surrounded by [Mn^{III}(saloph)] complexes through bridging CN ligands, $[Mn(saloph)H_2O]_4[Re_4Q_4(CN)_{12}]\cdot 4CH_3OH\cdot 8H_2O$ (Q = Se(**1**), Te(**2**)), among which the compound **1**-Se exhibits paramagnetic behavior with an effective magnetic moment of 9.60 BM. Moreover, **1**-Se and **2**-Te have been found to be stable, efficient, and selective catalysts for olefin epoxidation with *meta*-chloroperbenzoic acid (*m*CPBA) as an oxidant. Most significantly, mechanistic studies of the olefin epoxidation reactions promoted by these catalysts have provided evidence that multiple active oxidants, Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OOC(O)R, operate simultaneously in the epoxidation. Furthermore, it has been observed that the participation of Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OOC(O)R can be controlled by changing the substrate concentration.

Results and Discussion

The new tetranuclear chalcocyanide cluster compounds, $[\{Mn(saloph)H_2O\}_4Re_4Q_4(CN)_{12}]\cdot 4CH_3OH\cdot 8H_2O$ (Q = Se (**1**-Se), Te (**2**-Te)), were synthesized by the direct diffusion technique, in which a methanolic solution of $[PPh_4]_4[Re_4Q_4(CN)_{12}]$ (Q = Te or Se) was accurately layered with a methanolic solution of $[Mn(saloph)]^+$. The structure of **2**-Te was determined by X-ray crystallography. In the new compound **2**-Te, each Re is connected to one $[Mn(saloph)]^+$ unit through one cyano group, and the remaining two cyano groups are dangling (Figure 1). Each cluster-supported [Mn(saloph)]$^+$ unit is axially linked to a water molecule. The overall size of the molecule is about 12.290 Å (the Mn···Mn distance through the rhenium cluster). The coordination geometry about Mn is best described as elongated octahedral. The two N atoms and two O atoms from the tetradentate organic ligand define the equatorial plane and one N atom from the cyano group and one O atom of the solvent H_2O are at the vertices of the pyramids (Table 1). These are the first examples of Re_4 cyano-bridged cluster compounds with a ligand of this type, although a number of such complexes have been described for Re_6 octahedral cyanide clusters.[8] The powder X-ray pattern of **1**-Se is the same as that of **2**-Te (Figure S1; see the Supporting Information), indicating that they share a common structure. Compound **1**-Se exhibits paramagnetic behavior, obeying the Curie–Weiss law $X = X_0 + C/(T-\theta)$ (Figure S2). At room temperature, its effective magnetic moment is 9.60 BM, which is close to the spin-only value of 9.798 BM expected for four Mn^{3+} cations with four unpaired electrons in d^4 configuration. There is no evidence of magnetic exchange coupling between the Mn^{III} units via the central Re_4 cluster. Since [Mn^{III}(salen)]-type complexes are well known as versatile catalysts in a variety of oxygenation reactions,[1,9] the reactivities of the cluster-supported [Mn^{III}(saloph)] compounds **1**-Se and **2**-Te as cata-

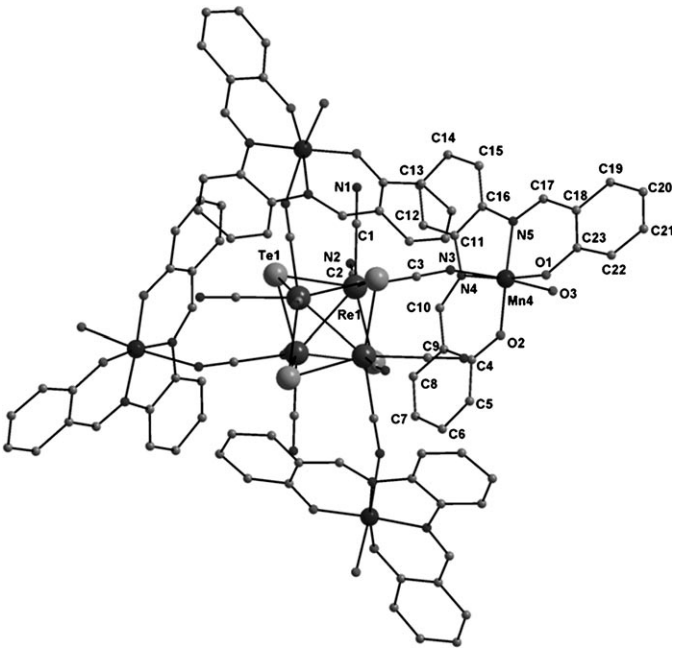


Figure 1. The structure of $[\{Mn(saloph)H_2O\}_4Re_4Te_4(CN)_{12}]$, **2**-Te. All hydrogen atoms are omitted for clarity.

Table 1. Bond lengths [Å] and angles [°] for **2**-Te.

Re1–C3	2.065(16)
Re1–C1	2.075(15)
Re1–C2	2.104(15)
Mn4–O1	1.861(11)
Mn4–O2	1.865(12)
Mn4–N5	1.973(14)
Mn4–N4	2.011(14)
Mn4–O3	2.256(12)
Mn4–N3	2.395(14)
N1–C1	1.183(17)
N2–C2	1.177(16)
N3–C3	1.172(17)
O1-Mn4-O2	91.6(5)
O1-Mn4-N5	92.6(6)
O2-Mn4-N5	172.1(6)
O1-Mn4-N4	172.8(6)
O2-Mn4-N4	95.3(5)
N5-Mn4-N4	80.7(6)
O1-Mn4-O3	92.0(5)
O2-Mn4-O3	89.7(6)
N5-Mn4-O3	83.5(6)
N4-Mn4-O3	90.0(5)
O1-Mn4-N3	94.0(5)
O2-Mn4-N3	87.4(5)
N5-Mn4-N3	98.9(5)
N4-Mn4-N3	84.3(5)
O3-Mn4-N3	173.4(4)
N1-C1-Re1	178.8(14)
N2-C2-Re1	173.4(14)
N3-C3-Re1	173.4(13)

lysts were examined in the epoxidation of olefins by *m*CPBA. To this end, *m*CPBA (0.05 mmol) was added to a mixture of substrate (0.035 mmol), **1**-Se or **1**-Te (2.96×10^{-5} mmol), and solvent (1 mL; CH_3CN/CH_2Cl_2 1:1). The mixture was stirred for 10 min at room temperature. We confirmed that direct substrate oxidation by *m*CPBA was negligible under comparable conditions (occurring over a period of 10–60 min),[10a] whereas oxygen-transfer reactions catalyzed by **1**-Se and **2**-Te occurred in less than two minutes after the addition of the peroxybenzoic acid. UV/Vis spectrophotometry showed that **1**-Se and **2**-Te remained stable during the catalytic reactions. Reactions with olefins in the presence of **1**-Se resulted predominantly in the formation of epoxides (Table 2). For example, the cyclic olefins cyclopentene, cycloheptene, and cyclooctene were oxidized to the corresponding epoxides in good yields (entries 1–3), with conversions ranging from 85 to 100%. In the reaction involving cyclohexene (entry 4), small amounts of the allylic oxidation products cyclohexenol (2.9%) and cyclohexenone (3.5%) were formed along with the major product cyclohexene oxide (77.2%). With cyclohexene under anaerobic conditions (entry 5), almost identical yields of the products were obtained, indicating that free-radical oxidation processes were only minimally involved in the olefin epoxidation reaction.[10] Moreover, terminal alkenes, which usually tend to be the least reactive olefins in metal-catalyzed epoxidations,[11] were readily epoxidized with *m*CPBA and **1**-Se (entries 6 and 7). *cis*-2-Octene was used to probe the stereochemistry of the reaction, which gave *cis*-2-octene oxide as the major product (80.0%) along with some *trans*-2-octene oxide (15.1%). This result indicated that the catalytic epoxidation reaction occurred with approximately 70% stereochemical retention (entry 8). *trans*-2-Octene was oxidized exclusively to *trans*-2-octene oxide. In a competition experiment involving *cis*- and *trans*-2-octenes, *cis*-2-octene was found to be 3.4 times more reactive than *trans*-2-octene, implying a reactivity preference for *cis* over *trans* (entry 10). This value is larger than that obtained with peracids ($k_{cis}/k_{trans}=1.2$–2.2),[12] but somewhat smaller than those observed with the PhIO/[Fe(TPP)Cl] ($k_{cis}/k_{trans}=5.8$)[13] and NaOCl/[Mn(porph)] ($k_{cis}/k_{trans}=5.0$) systems.[14] *cis*-2-Hexene and *trans*-2-hexene showed the same reaction preference as the 2-octenes with **1**-Se. *cis*-Stilbene was oxidized rapidly under the reaction conditions (entry 14), giving *cis*-stilbene oxide (47.9%) as the major product, along with some *trans*-stilbene oxide (6.7%) and benzaldehyde (11.6%), indicating that either a peroxyl radical or an oxomanganese(IV) species was involved as the epoxidizing agent, since these species would be expected to oxidize *cis*-stilbene to nonstereospecific or radical-induced rearranged products.[14] The oxidation of *trans*-stilbene by **1**-Se produced *trans*-stilbene oxide and benzaldehyde (entry 15). The lower overall yield (40.5%) of products from *trans*-stilbene is best explained in terms of steric constraint at the activating site.[15] Styrene was oxidized to styrene oxide (56.5%), benzaldehyde (5.7%), and phenylacetaldehyde (19.8%), again indicating that either a peroxyl radical or an oxomanganese(IV) species was involved as the epoxidizing agent. Analogous re-

Table 2. Olefin epoxidations by *m*CPBA with the catalysts **1**-Se and **2**-Te in CH_2Cl_2/CH_3CN 1:1 at room temperature.[a]

Entry	Substrate	Product	**1**-Se		**2**-Te	
			Conversion [%][b]	Yield [%][b]	Conversion [%][b]	Yield [%][b]
1	cyclopentene	epoxide	85.4±3.4	84.9±2.3	91.5±1.3	80.7±1.9
2	cycloheptene	epoxide	100	85.5±1.8	100	81.9±0.9
3	cyclooctene	epoxide	84.5±1.1	75.5±2.7	88.2±3.6	82.6±3.4
4	cyclohexene	epoxide	88.3±3.4	77.2±2.5	91.0±2.1	82.1±1.6
		2-cyclohexen-1-ol		2.9±0.2		3.4±0.1
		2-cyclohexen-1-one		3.5±0.3		4.1±0.1
5[c]	cyclohexene	epoxide	89.7±2.5	78.5±2.0	90.0±2.0	83.0±2.8
		2-cyclohexen-1-ol		3.1±0.1		3.6±0.2
		2-cyclohexen-1-one		3.6±0.1		4.3±0.2
6	1-octene	epoxide	75.4±1.7	64.1±2.5	73.5±3.1	68.3±1.4
7	1-hexene	epoxide	70.7±2.7	64.0±1.5	75.0±1.1	65.5±1.4
8	*cis*-2-octene	*cis*-oxide	97.0±1.8	80.0±1.2	100	83.0±3.5
		trans-oxide		15.1±0.7		15.5±0.4
9	*trans*-2-octene	*trans*-oxide	72.5±2.2	68.9±1.3	70.2±1.1	67.1±2.1
10	*cis*-/*trans*-2-octene	*cis*-/*trans*-oxide		3.4		4.5
11	*cis*-2-hexene	*cis*-oxide	90.4±1.8	76.6±1.2	93.0±1.8	81.6±3.5
		trans-oxide		10.6±1.1		10.9±0.4
12	*trans*-2-hexene	*trans*-oxide	57.0±2.2	54.5±1.3	58.7±1.5	52.3±3.1
13	*cis*-/*trans*-2-hexene	*cis*-/*trans*-oxide		7.4		3.4
14	*cis*-stilbene	*cis*-oxide	75.3±2.2	47.9±3.3	64.5±0.1	39.3±0.8
		trans-epoxide		6.7±0.5		4.6±0.3
		benzaldehyde		11.6±1.1		12.2±1.5
15	*trans*-stilbene	*trans*-oxide	45.3±1.2	31.5±2.3	53.0±1.0	35.0±3.1
		benzaldehyde		9.0±0.9		7.9±0.2
16	styrene	epoxide	97.0±2.2	56.5±3.1	98.5±2.3	58.8±1.1
		benzaldehyde		5.7±1.2		5.8±1.5
		phenylacetaldehyde		19.8±1.2		18.6±0.4

[a] Reaction conditions: olefin (0.035 mmol), catalyst (2.96×10^{-5} mmol), *m*CPBA (0.05 mmol), solvent (1 mL, CH_3CN/CH_2Cl_2 1:1). [b] Based on substrate. [c] Under anaerobic conditions in an N_2 atmosphere.

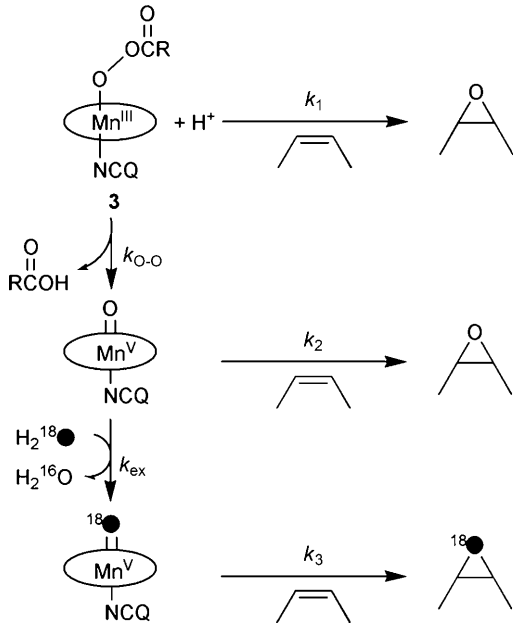
sults were obtained for **2**-Te, indicating that the substitution of Se by Te in the cluster-supported [Mn^{III}(saloph)] compound **1**-Se does not affect the reactivity of the system. On the other hand, for a reactivity comparison between the cluster-supported [Mn^{III}(saloph)] compounds **1**-Se and **2**-Te and the mononuclear [Mn^{III}(saloph)] complex, epoxidation of olefins by the mononuclear [Mn^{III}(saloph)] complex with *m*CPBA was studied under the same reaction conditions. In this case, the formation of a dinuclear μ-oxo complex (Mn^{IV}–O–Mn^{III}) with lower epoxide yields of 10–50% was observed.

Several groups have proposed a [(salen)Mn^{V}=O] intermediate as a reactive species responsible for olefin epoxidation,[16] whereas a [(salen)Mn^{IV}=O] complex, analogous to [(porph)Mn^{IV}=O],[17] has been invoked in radical-type oxidations to account for the formation of ring-opened products in the [Mn^{III}(salen)]-catalyzed epoxidation of a radical probe.[18] Talsi et al. observed that when [(salen)Mn^{IV}=O] was reacted with styrene at 20°C in CH_2Cl_2 the products were benzaldehyde (22% with respect to manganese) and styrene oxide (13%).[4c]

Therefore, the minimal extent of free radical oxidation reactions, the high degree of stereospecificity, and the formation of some *trans*-epoxide and aldehyde from the epoxidation reaction of *cis*-aromatic olefins observed with our catalytic systems imply that two different oxidants, Mn^{V}=O and Mn^{IV}=O, are produced in these catalytic reactions. The results also suggest that the Mn^{IV}=O complex is responsible for the nonstereoretentive portion of the epoxidation reaction.[19]

To obtain more information about the nature of the reactive intermediates, we studied the influence of substituent electronic effects on the rate of epoxidation using styrene and five *para*-substituted styrenes. A significant electronic effect on the reaction rates with **1**-Se was observed, showing that more electron-rich olefins react more rapidly than electron-deficient substrates. This indicates that the reactive intermediates have electrophilic character. As shown in Figure S3, a more precise linear correlation could be obtained by plotting k_{rel} against σ_p^+ ($r=0.97$) rather than against σ_p ($r=0.87$; data not shown). The small negative value of the observed slope ($\rho=-0.66$) compares well with previously reported values for the epoxidation of styrenes obtained using systems based on manganese(III) tetraphenylporphyrin ($\rho=-0.41$),[20] manganese(III) salen ($\rho=-0.3$),[18a] manganese(III) TMTACN ($\rho^-=-0.63$; TMTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane),[21] and manganese(III) ^{H,Me}PyTACN ($\rho^-=-0.67$; ^{H,Me}PyTACN = 1-methyl-4-methyl(2-pyridyl)-1,4,7-triazacyclononane).[1h] **2**-Te showed a similar result ($\rho=-0.47$) to **1**-Se (see Figure S4).

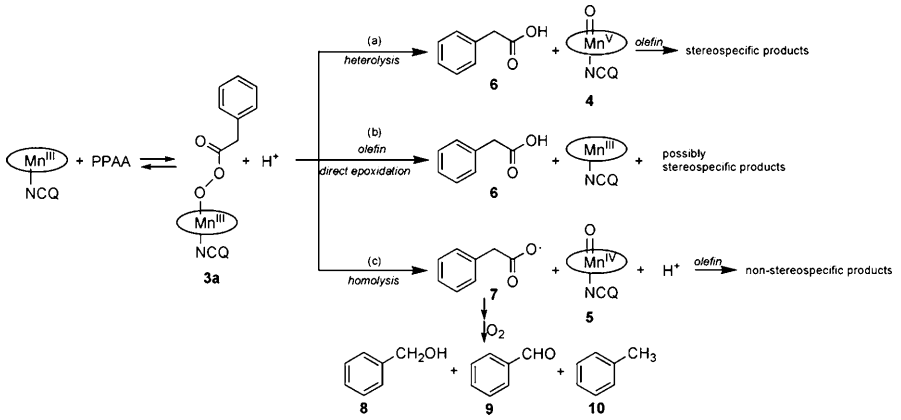
We carried out ^{18}O-labeling experiments, which are commonly used in studies of reaction mechanisms, to test for the involvement of a high-valent metal-oxo intermediate in the metal-mediated oxygen atom transfer reactions.[10a,22] We examined the epoxidation of cyclohexene by **1**-Se and *m*CPBA in the presence of an approximately 28-fold excess of $H_2{}^{18}O$ relative to the substrate in a mixture of anhydrous CH_2Cl_2/CH_3CN 1:1 (Table S1). As the results in Table S1 show, no ^{18}O from the $H_2{}^{18}O$ was incorporated into the cyclohexene oxide (entry 1). Even in an approximately 440-fold excess of $H_2{}^{18}O$ (entry 3), the epoxide product showed no ^{18}O incorporation. This suggests that the oxygen of the active intermediate derived from **1**-Se and *m*CPBA did not exchange with $H_2{}^{18}O$. Analogous results were also obtained for **2**-Te, as shown in Table S1 (entry 4). The lack of oxygen exchange might be explained in one of three ways,[22–24] as shown in Scheme 1: 1) direct epoxidation by Mn–OOC(O)R



Scheme 1.

(**3**) may be much faster than its O–O bond cleavage ($k_1 \gg k_{O-O}$); 2) although Mn=O may be formed, the rate of oxygen exchange may be much slower than the rate of oxygen transfer from the Mn=O intermediate to the substrate ($k_2 \gg k_{ex}$); or 3) as Meunier, Nam, and co-workers proposed,[22b,24] the axial NCQ ligand of the Mn=O intermediate may inhibit oxygen exchange of the Mn=O with bulk $H_2{}^{18}O$ because the six-coordinated metal-oxo intermediate does not have an appropriate binding site for water. Any one of these situations might account for the results obtained with our catalytic systems.

To gain a clearer insight into the reactive oxidants that are involved in olefin epoxidation, we used peroxyphenylacetic acid (PPAA) as a mechanistic probe. The use of PPAA to distinguish homolytic versus heterolytic cleavage of the peracid O–O bond is well established.[10a,23,25] When the O–O bond of the coordinated anion of PPAA (**3a**) is cleaved homolytically (Scheme 2, pathway c), an acyloxyl radical (**7**) is generated. This acyloxyl radical undergoes rapid β-scission (diffusion-controlled rate $\sim 10^9\ s^{-1}$) to give benzyl alcohol (**8**), benzaldehyde (**9**), and toluene (**10**). In contrast, heterolytic O–O bond cleavage of **3a** (pathway a) or direct oxidation by **3a** (pathway b) yields phenylacetic acid (PAA, **6**).



Scheme 2.

First, a control experiment with PPAA as oxidant under the same reaction conditions as used for *m*CPBA was carried out in the absence of substrate (Table 3, entry 1). Interestingly, the heterolytic cleavage product, phenylacetic acid (53.5% based on PPAA), and the homolytic cleavage products, benzaldehyde (54.7%) and benzyl alcohol (2.9%), were formed in a ratio of 48:52. These results indicate that heterolytic (48%) and homolytic (52%) O–O bond cleavage of **3a** occur simultaneously to produce high-valent Mn^{V}=O and Mn^{IV}=O species in the reactions involving the Mn complex and peracids. Next, we varied the concentration of the substrate to examine the concentration dependence of the ratio of heterolysis to homolysis. Surprisingly, the ratio of heterolysis to homolysis varied from 0.93 (48:52) for 0 mM cyclohexene to 1.64 (62:38) for 35 mM cyclohexene to 2.45 (71:29) for 140 mM cyclohexene, as shown in Table 3 (entries 1, 3, and 5). Analogous results were obtained for **2**-Te (entries 6–10). These results suggest that Mn–OOC(O)R (**3**) might also be a possible reactive species in the epoxidation, as previously proposed for [Mn(salen)]- and [Fe(porph)]-catalyzed epoxidations with *m*CPBA as oxygen donor.[26] Moreover, these results demonstrate that both heterolysis and homolysis of the O–O bond of PPAA occur in the Mn–peroxy acid system if the substrate is less active or the concentration of the substrate is very low. In contrast, when the substrate is active or the concentration of the substrate increases, the species Mn–OOC(O)R (**3**) gradually becomes involved in the epoxidation reaction, as proposed for the iron porphyrin/*m*CPBA system by van Eldik et al.[26a] As a result, the multiple oxidants Mn^{III}–OOC(O)R, Mn^{V}=O, and Mn^{IV}=O act simultaneously as the key active intermediates in the epoxidation reaction. This simultaneous operation of the three oxidants might also apply to other metal-catalyzed olefin epoxidations, including those employing [Mn(salen)], [Mn(porphyrin)], and [Mn(nonheme)] complexes.

In order to observe the proposed reactive intermediates Mn^{III}–OOC(O)R, Mn^{V}=O, and Mn^{IV}=O, we carried out UV/Vis spectrophotometric measurements at low temperatures (−40 °C and −70 °C, respectively). Following the addition of 1.2 equiv of *m*CPBA to a solution of **1**-Se in the absence or presence of the substrate cyclohexene, UV/Vis spectra were recorded within 3 s and at intervals of 30 s for 20 min. As shown in Figure S5, no spectral changes were observed, neither at −40 °C nor at −70 °C (the spectral change below 330 nm is attributed to *meta*-chlorobenzoic acid), suggesting that the above reactive intermediates might not be spectroscopically observable. Similar results were also obtained with **2**-Te.

Scheme 2 shows the competing reaction pathway mechanism, which may well explain our present epoxidation reactions and other oxidation reactions reported previously.[2,4,26] For example, an appropriate mixture of the Mn^{III}–OOC(O)R, Mn^{V}=O, and Mn^{IV}=O species might account for the stereochemical data[27] and the increase in enantioselectivity in the low-temperature epoxidation of styrene reported for [Mn(salen)]/oxidant systems.[28] The amount of each oxidant in solution would be sensitive to solvent polarity, axial ligands, ligand structures, metal ions, temperature, and oxidant structures that influence the lifetime of Mn^{III}–

Table 3. Yields of products derived from peroxyphenylacetic acid (PPAA) mediated by the catalysts **1**-Se and **2**-Te in the presence of cyclohexene.[a]

Entry	Catalyst	Cyclohexene	Heterolysis[b]	Homolysis[b]			Hetero (**6**)/Homo (**8**+**9**+**10**)	Oxidation products[c]		
			6	**8**	**9**	**10**		oxide	-ol	-one
1	**1**-Se	0	53.5±2.4	54.7±3.0	2.9±0.1	–	48/52 (0.93)	–	–	–
2	**1**-Se	20	55.1±2.1	34.2±1.6	2.3±0.1	–	60/40 (1.51)	58.9±2.5[d]	4.6±0.3[d]	3.2±0.2[d]
3	**1**-Se	**35**	**58.2±1.7**	**33.9±1.6**	**1.6±0.0**	**–**	**62/38 (1.64)**	**46.5±3.4**[d]	**6.2±1.2**[d]	**1.9±0.5**[d]
4	**1**-Se	70	75.2±10.3	31.0±1.9	1.6±0.1	–	70/30 (2.31)	63.1±8.8[e]	6.2±1.2[e]	4.1±1.2[e]
5	**1**-Se	140	75.3±9.7	29.4±6.3	1.4±0.1	–	71/29 (2.45)	74.7±10.0[e]	11.9±0.2[e]	8.5±0.7[e]
6	**2**-Te	0	51.9±2.0	57.7±2.5	3.5±0.2	–	46/54 (0.85)	–	–	–
7	**2**-Te	20	56.3±1.9	28.3±1.8	2.9±0.1	–	64/46 (1.79)	42.9±2.0[d]	4.7±0.2[d]	4.4±0.2[d]
8	**2**-Te	**35**	**73.1±3.1**	**35.0±2.0**	**1.7±0.1**	**–**	**67/33 (1.99)**	**48.3±2.4**[d]	**3.2±0.3**[d]	**2.0±0.2**[d]
9	**2**-Te	70	75.8±9.8	30.7±0.3	1.7±0.1	–	70/30 (2.34)	62.1±9.0[e]	5.7±0.7[e]	4.6±0.4[e]
10	**2**-Te	140	80.3±2.3	25.2±5.5	1.5±0.2	–	75/25 (2.97)	78.1±8.2[e]	9.3±0.6[e]	8.6±2.3[e]

[a] Reaction conditions: cyclohexene (0–0.14 mmol), catalyst (2.96×10^{-5} mmol), PPAA (0.05 mmol), solvent (1 mL, CH_3CN/CH_2Cl_2 1:1); values in bold were obtained under the same reaction conditions as used for *m*CPBA. [b] Based on PPAA. [c] oxide, -ol, and -one indicate cyclohexene oxide, cyclohexenol, and cyclohexenone, respectively. [d] Based on substrate, cyclohexene. [e] Based on oxidant, PPAA.

OOC(O)R and the ratio of heterolysis versus homolysis.[2,4,16a,26,28,29] Therefore, these factors may influence the reaction pathway shown in Scheme 2, resulting in the various product partitions, *cis*-epoxide versus *trans*-epoxide, epoxide versus aldehyde, and so on.[27] More detailed mechanistic studies on the factors that influence heterolysis versus homolysis, the lifetime of Mn^{III}–OOC(O)R (**3**), and the various product partitions, are in progress in our laboratory.

Conclusion

We have successfully synthesized discrete molecules of rhenium cluster-supported [Mn^{III}(saloph)] complexes, which catalyze a wide range of olefin epoxidations with excellent efficiencies, even with terminal olefins, while retaining their integrity under mild experimental conditions. Reactivity and Hammett studies, $H_2{}^{18}O$ exchange experiments, and the use of PPAA as a mechanistic probe suggest that the multiple oxidants Mn^{III}–OOC(O)R, Mn^{V}=O, and Mn^{IV}=O operate simultaneously as the key active intermediates in the epoxidation reactions. However, an attempt to observe the proposed reactive intermediates Mn^{III}–OOC(O)R, Mn^{V}=O, and Mn^{IV}=O by UV/Vis spectrophotometry at low temperatures (−40 °C and −70 °C) proved unsuccessful. Nonetheless, the present results provide important clues for a resolution of the long-standing dichotomy of views pertaining to the nature of the active oxidants in [Mn(salen)]-catalyzed reactions, and even in those catalyzed by [Mn(porphyrin)] and [Mn(nonheme)] complexes.[1–4]

Experimental Section

General: Olefins, epoxides, cyclohexenol, cyclohexenone, ethanol, methanol, acetone, *o*-phenylenediamine, salicylaldehyde, dichloromethane, acetonitrile, $Mn(OAc)_2{\cdot}4H_2O$, *m*CPBA (65%), and $H_2{}^{18}O$ (95% ^{18}O enrichment) were purchased from Aldrich Chemical Co. and were used without further purification. $[PPh_4]_4[Re_4Se_4(CN)_{12}]$[30] and peroxyphenylacetic acid (PPAA)[10a] were synthesized according to literature methods. Product analyses following olefin epoxidations, partition reactions of PPAA, and ^{18}O incorporation reactions of cyclohexene oxide were performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with a Hewlett–Packard model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with an FID detector using a 30 m capillary column (Hewlett–Packard DB-5 or HP-FFAP). XRD data were obtained on a Rigaku X-ray diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer from samples in $CDCl_3$ solution, with TMS as an internal standard. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C instrument. Magnetic susceptibility measurements on powder samples were carried out in the temperature range from 5 to 300 K in an applied magnetic field of 1000 G using a Quantum Design MPMS-5 SQUID magnetometer.

Preparation of H_2saloph: The ligand *N*,*N*′-disalicylidene-1,2-phenylenediamine (H_2saloph) was prepared by the condensation reaction of *o*-phenylenediamine and salicylaldehyde according to the previously published procedures[7b,31–34] with some modification. A solution of salicylaldehyde (10 mmol) in ethanol (10 mL) was added to a stirred solution of *o*-phenylenediamine (5 mmol) in ethanol (15 mL). After refluxing for 2.5 h and then leaving the mixture to stand overnight, the orange-yellow product was collected by filtration and washed with cold ethanol. The reaction was performed under N_2. ^1H NMR ($CDCl_3$): $\delta = 12.97$ (2H), 8.65 (2H), 7.41–6.93 ppm (12H).

Preparation of Mn^{III}(saloph) complex: The complex was prepared according to the previously reported literature method[7] with a small modification. $Mn(OAc)_2{\cdot}4H_2O$ (1 mmol) was added to a stirred solution of H_2saloph (1 mmol) in ethanol (20 mL). After refluxing for several minutes and then stirring overnight at room temperature, a dark-brown solid was collected by filtration and washed with acetone.

Preparation of $[Mn(saloph)H_2O]_4[Re_4Q_4(CN)_{12}]{\cdot}4CH_3OH{\cdot}8H_2O$ (Q = Se (1-Se) and Te (2-Te)): The cluster compounds were prepared by a direct diffusion technique in which a methanolic solution of $[PPh_4]_4[Re_4Q_4(CN)_{12}]$ (0.05 mmol; Q = Se or Te) containing a trace amount of H_2O was carefully layered with a methanolic solution of [Mn^{III}(saloph)] (0.25 mmol). Dark-violet crystals of **2**-Te suitable for X-ray analysis were obtained after three weeks. The powder X-ray pattern of **1**-Se was found to be the same as that of compound **2**-Te, indicating that they share a common structure. Elemental analysis calcd (%) for $C_{96}H_{88}Mn_4N_{20}O_{24}Re_4Te_4$ (**2**-Te) (3380.82): C 34.11, H 2.62, N 8.29; found: C 34.06, H 2.65, N 8.34; elemental analysis calcd (%) for $C_{96}H_{88}Mn_4N_{20}O_{24}Re_4Se_4$ (**1**-Se) (3186.26): C 36.19, H 2.79, N 8.79; found: C 36.12, H 2.73, N 8.81.

Olefin epoxidations by the cluster-supported Mn complexes (1-Se and 2-Te) with *m*CPBA: a) Aerobic conditions: *m*CPBA (0.05 mmol) was added to a mixture of substrate (0.035 mmol), the cluster-supported Mn complex (2.96×10^{-5} mmol), and solvent (CH_3CN/CH_2Cl_2 1:1; 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction mixture was applied to a column of silica gel and the organic products were eluted; the eluent was monitored by subjecting periodically withdrawn 20 μL aliquots to GC/MS analysis. Dodecane as an internal standard was used to quantify the products and conversions of substrates. All reactions were run at least in triplicate and the average product yields are presented. The product yields are based on substrate consumed. In the competitive reaction of *cis*-2-octene and *trans*-2-octene, the amount of each substrate was 0.035 mmol. b) Anaerobic conditions: Substrate (0.035 mmol), the cluster-supported Mn complex (2.96×10^{-5} mmol), and solvent (CH_3CN/CH_2Cl_2 1:1; 1 mL) were placed in a vial that could be sealed with a rubber septum. N_2 was then bubbled into the vial containing the reaction solution for 10 min. Thereafter, *m*CPBA (0.05 mmol) was added to the solution. The rest of the procedure was the same as above.

Competitive reactions of styrene and *para*-substituted styrenes for the construction of a Hammett plot: *m*CPBA (0.018 mmol) was added to a mixture of styrene (0.01 mmol) and *para*-X-substituted styrene (0.01 mmol, X = -OCH_3, -CH_3, -Cl, and -CN), the cluster-supported Mn complex (2.96×10^{-5} mmol), and solvent (CH_2Cl_2/CH_3CN 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 equation $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$, 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.[22a]

$H_2{}^{18}O$ experiments: *m*CPBA (0.005 or 0.01 mmol) was added to a mixture of cyclohexene (0.005–0.02 mmol), the cluster-supported Mn complex (2.96×10^{-5} mmol), and $H_2{}^{18}O$ (10–40 μL, 95% ^{18}O-enriched, Aldrich Chemical Co.) in a dried solvent mixture (CH_3CN/CH_2Cl_2 1:1; 1 mL). The reaction mixture was stirred for 3 min at room temperature and then directly analyzed by GC/MS. The ^{16}O and ^{18}O compositions were determined from the relative abundances of the mass peaks at *m*/*z* 99 for [^{16}O]-cyclohexene oxide and *m*/*z* 101 for [^{18}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 cluster-supported Mn complexes with PPAA: PPAA (0.05 mmol) was added to a mixture of cyclohexene (0–0.14 mmol), the cluster-supported Mn complex (2.96×10^{-5} mmol), and solvent (CH_3CN/CH_2Cl_2 1:1; 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least in tripli-

cate and the average product yields are presented. Product yields are based on PPAA consumed.

UV/Vis spectrophotometric studies: UV/Vis spectrophotometric studies were carried out as follows. Solutions of **1**-Se (1.0×10^{-5} mmol) in CH_2Cl_2/CH_3CN 1:1 (3 mL) were first cooled to −40 °C or −70 °C in 1 cm UV cells. *m*CPBA (1.2 equiv, diluted with CH_2Cl_2 (30 μL)) was then injected into each UV cell in a single portion, whereupon the spectral changes were directly monitored within 3 s and at intervals of 30 s for 20 min by UV/Vis spectrophotometry. Analogous studies with **2**-Te gave similar results. In addition, the same results were obtained with both **1**-Se and **2**-Te in the presence of cyclohexene (0.01 mmol).

Crystallography: Single-crystal X-ray diffraction data for **2**-Te were collected at 170 K on a Bruker SMART AXS diffractometer.[35] Graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) was used. Crystal decay was monitored by re-collecting 50 initial frames at the end of the data collection. Cell refinement and data reduction were carried out with the program SAINT.[35] Absorption corrections were applied using the SADABS program.[35] The crystal structure was solved by direct methods and was refined by full-matrix least-squares techniques, with anisotropic thermal parameters for non-hydrogen atoms except O3S and C3S in the solvent molecule, using the SHELX package.[36] Hydrogen atoms (except those connected to O3 in the solvent H_2O) were placed in calculated positions with C−H distances of 0.93–0.96 Å and isotropic thermal parameters and were included in the refinement in a riding motion approximation with $U_{iso}=1.2\,U_{eq}$(C) or $U_{iso}=1.5\,U_{eq}$(C), where C is the parent C atom to which the H atom is attached. The crystal data, experimental, and refinement results are summarized in Table 4.

Table 4. Crystal data and structure refinement for **2**-Te.

Empirical formula	$C_{96}H_{88}Mn_4N_{20}O_{24}Re_4Te_4$
formula weight	3380.82
T [K]	170(2)
λ [Å]	0.71073
crystal system	tetragonal
space group	$P4_2/n$
unit cell dimensions	
a [Å]	19.220(9)
b [Å]	19.220(9)
c [Å]	14.420(14)
α [°]	90.000
β [°]	90.000
γ [°]	90.000
V [Å^3]	5327(6)
Z	2
ρ_{calcd} [Mg m^{-3}]	2.108
absorption coefficient [mm^{-1}]	6.137
F(000)	3208
crystal size [mm^3]	$0.06\times0.05\times0.03$
2θ range for data collection [°]	1.77 to 26.00
reflections collected	29240
independent reflections	5238 ($R_{int}=0.2499$)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5238/6/347
goodness-of-fit on F^2	0.869
final R indices [$I>2\sigma(I)$]	$R_1=0.0637$, $wR_2=0.1170$
R indices (all data)	$R_1=0.1502$, $wR_2=0.1355$
largest diff. peak and hole [e Å^{-3}]	1.715 and −1.680

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[1] a) E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.* **2005**, *105*, 1563–1602; b) A. Martinez, C. Hemmert, C. Loup, G. Barre, B. Meunier, *J. Org. Chem.* **2006**, *71*, 1449–1457; c) G. Yin, M. Buchalova, A. M. Danby, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper, D. H. Busch, *Inorg. Chem.* **2006**, *45*, 3467–3474; d) S. Y. Liu, J. D. Soper, J. Y. Yang, E. V. Rybak-Akimova, D. G. Nocera, *Inorg. Chem.* **2006**, *45*, 7572–7574; e) D. E. Lansky, A. A. Narducci Sarjeant, D. P. Goldberg, *Angew. Chem.* **2006**, *118*, 8394–8397; *Angew. Chem. Int. Ed.* **2006**, *45*, 8214–8217; f) W. J. Song, M. S. Seo, S. D. George, T. Ohta, R. Song, M. J. Kang, T. Tosha, T. Kitagawa, E. I. Solomon, W. Nam, *J. Am. Chem. Soc.* **2007**, *129*, 1268–1277; g) A. Murphy, T. D. P. Stack, *J. Mol. Catal. A* **2006**, *251*, 78–88; h) I. Garcia-Bosch, A. Company, X. Fontrodona, X. Ribas, M. Costas, *Org. Lett.* **2008**, *10*, 2095–2098; i) B. Kang, M. Kim, J. Lee, Y. Do, S. Chang, *J. Org. Chem.* **2006**, *71*, 6721–6727; j) G. Yin, M. Buchalova, A. M. Danby, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper, D. H. Busch, *J. Am. Chem. Soc.* **2005**, *127*, 17170–17171; k) S. H. Wang, B. S. Mandimutsira, R. Todd, B. Ramdhanie, J. P. Fox, D. P. Goldberg, *J. Am. Chem. Soc.* **2004**, *126*, 18–19.

[2] a) T. Katsuki, *J. Mol. Catal. A* **1996**, *113*, 87–107; b) J. T. Groves, J. Lee, S. S. Marla, *J. Am. Chem. Soc.* **1997**, *119*, 6269–6273; c) S. E. Park, W. J. Song, Y. O. Ryu, M. H. Lim, R. Song, K. M. Kim, W. Nam, *J. Inorg. Biochem.* **2005**, *99*, 424–431; d) R. Zhang, M. Newcomb, *Acc. Chem. Res.* **2008**, *41*, 468–477; e) A. Rosa Silva, C. Freire, B. de Castro, *New J. Chem.* **2004**, *28*, 253–260; f) M. J. Sabater, M. Alvaro, H. Garcia, E. Palomares, J. C. Scaiano, *J. Am. Chem. Soc.* **2001**, *123*, 7074–7080; g) C. Linde, N. Koliai, P. O. Norrby, B. Åkermark, *Chem. Eur. J.* **2002**, *8*, 2568–2573; h) T. Strassner, K. N. Houk, *Org. Lett.* **1999**, *1*, 419–421; i) R. I. Kureshy, N. H. Khan, S. H. R. Abdi, S. T. Patel, P. K. Iyer, P. S. Subramanian, R. V. Jasra, *J. Catal.* **2002**, *209*, 99–104; j) C. G. Miller, S. W. Gordon-Wylie, C. P. Horwitz, S. A. Strazisar, D. K. Peraino, G. R. Clark, S. T. Weintraub, T. J. Collins, *J. Am. Chem. Soc.* **1998**, *120*, 11540–11541; k) I. V. Khavrutskii, D. G. Musaev, K. Morokuma, *Inorg. Chem.* **2005**, *44*, 306–315; l) T. H. Parsell, R. K. Behan, M. T. Green, M. P. Hendrich, A. S. Borovik, *J. Am. Chem. Soc.* **2006**, *128*, 8728–8729; m) N. Jin, J. T. Groves, *J. Am. Chem. Soc.* **1999**, *121*, 2923–2924; n) M. P. Feth, C. Bolm, J. P. Hildebrand, M. Kohler, O. Beckmann, M. Bauer, R. Ramamonjisoa, H. Bertagnolli, *Chem. Eur. J.* **2003**, *9*, 1348–1359; o) C. Mukherjee, A. Stammler, H. Bogge, T. Glaser, *Inorg. Chem.* **2009**, *48*, 9476–9484.

[3] a) K. A. Campbell, M. R. Lashley, J. K. Wyatt, M. H. Nantz, R. D. Britt, *J. Am. Chem. Soc.* **2001**, *123*, 5710–5719; b) K. P. Bryliakov, O. A. Kholdeeva, M. P. Vanina, E. P. Talsi, *J. Mol. Catal. A* **2002**, *178*, 47–53.

[4] a) J. P. Collman, L. Zeng, J. I. Brauman, *Inorg. Chem.* **2004**, *43*, 2672–2679; b) J. P. Collman, L. Zeng, R. A. Decreau, *Chem. Commun.* **2003**, 2974–2975; c) K. P. Bryliakov, D. E. Babushkin, E. P. Talsi, *J. Mol. Catal. A* **2000**, *158*, 19–35.

[5] a) L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772; b) N. G. Naumov, A. V. Virvets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem.* **1998**, *110*, 2043–2045; *Angew. Chem. Int. Ed.* **1998**, *37*, 1943–1945; c) N. G. Naumov, D. V. Soldatov, J. A. Ripmeester, S. B. Artemkina, V. E. Fedorov, *Chem. Commun.* **2001**, 571–572; d) M. V. Bennett, M. P. Shores, L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 6664–6668.

[6] Y. Kim, S. K. Choi, S.-M. Park, W. Nam, S.-J. Kim, *Inorg. Chem. Commun.* **2002**, *5*, 612–615.

[7] a) K. L. Zhang, Y. Xu, C. G. Zheng, Y. Zhang, Z. Wang, X. Z. You, *Inorg. Chim. Acta* **2001**, *318*, 61–66; b) K. L. Zhang, Y. Xu, Y. Song, Y. Zhang, Z. Wang, X. Z. You, *J. Mol. Struct.* **2001**, *570*, 137–143.

[8] a) S.-M. Park, Y. Kim, S.-J. Kim, *Eur. J. Inorg. Chem.* **2003**, 4117–4121; b) Y. Kim, S.-M. Park, W. Nam, S.-J. Kim, *Chem. Commun.* **2001**, 1470–1471; c) Y. Kim, S.-M. Park, S.-J. Kim, *Inorg. Chem. Commun.* **2002**, *5*, 592–595.

[9] a) T. Katsuki, *Coord. Chem. Rev.* **1995**, *140*, 189–214; b) C. M. Che, J. S. Huang, *Coord. Chem. Rev.* **2003**, *242*, 97–113; c) H. Shitama, T. Katsuki, *Chem. Eur. J.* **2007**, *13*, 4849–4858.

[10] a) S. H. Lee, J. H. Han, H. Kwak, S. J. Lee, E. Y. Lee, H. J. Kim, J. H. Lee, C. Bae, S. N. Lee, Y. Kim, C. Kim, *Chem. Eur. J.* **2007**, *13*, 9393–9398; b) T. K. M. Shing, Y. Y. Yeung, P. L. Su, *Org. Lett.* **2006**, *8*, 3149–3151; c) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**, Chapter 2.

[11] K. P. Ho, W. L. Wong, K. M. Lam, C. P. Lai, T. H. Chan, K. Y. Wong, *Chem. Eur. J.* **2008**, *14*, 7988–7996.

[12] a) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella, R. Noyori, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905–915; b) C. Kim, T. G. Traylor, C. L. Perrin, *J. Am. Chem. Soc.* **1998**, *120*, 9513–9516.

[13] J. T. Groves, T. E. Nemo, *J. Am. Chem. Soc.* **1983**, *105*, 5786–5791.

[14] P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy, *J. Am. Chem. Soc.* **1988**, *110*, 8462–8470.

[15] C. T. Dalton, K. M. Ryan, V. M. Wall, C. Bousquet, D. G. Gilheany, *Top. Catal.* **1998**, *5*, 75–91.

[16] a) K. Srinivasan, P. Michaud, J. K. Kochi, *J. Am. Chem. Soc.* **1986**, *108*, 2309–2320; b) D. Feichtinger, D. A. Plattner, *Angew. Chem.* **1997**, *109*, 1796–1798; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1718–1719; c) M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Guler, T. Ishida, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 948–954; d) L. Kurti, M. M. Blewett, E. J. Corey, *Org. Lett.* **2009**, *11*, 4592–4595.

[17] a) J. T. Groves, M. K. Stern, *J. Am. Chem. Soc.* **1988**, *110*, 8628–8638; b) J. T. Groves, M. K. Stern, *J. Am. Chem. Soc.* **1987**, *109*, 3812–3814.

[18] a) W. Adam, C. Mock-Knoblauch, C. R. Saha-Moller, M. Herderich, *J. Am. Chem. Soc.* **2000**, *122*, 9685–9691; b) C. Linde, M. Arnold, P. O. Norrby, B. Åkermark, *Angew. Chem.* **1997**, *109*, 1802–1803; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1723–1725.

[19] a) J. T. Groves, M. K. Stern, *J. Am. Chem. Soc.* **1987**, *109*, 3812–3814; b) C. Linde, M. F. Anderlund, B. Åkermark, *Tetrahedron Lett.* **2005**, *46*, 5597–5600.

[20] O. Bortolini, B. Meunier, *Perkin Trans. 2* **1984**, 1967–1970.

[21] J. R. Lindsay Smith, B. C. Gilbert, A. M. I. Payeras, J. Murray, T. R. Lowdon, J. Oakes, R. P. I. Prats, P. H. Walton, *J. Mol. Catal. A* **2006**, *251*, 114–122.

[22] a) J. H. Han, S.-K. Yoo, J. S. Seo, S. J. Hong, S. K. Kim, C. Kim, *Dalton Trans.* **2005**, 402–406; b) J. Bernadou, B. Meunier, *Chem. Commun.* **1998**, 2167–2173; c) J. T. Groves, J. Lee, S. S. Marla, *J. Am. Chem. Soc.* **1997**, *119*, 6269–6273; d) W. Nam, M. H. Lim, S. K. Moon, C. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 10805–10809; e) M. S. Seo, J.-H. In, S. O. Kim, N. Y. Oh, J. Hong, J. Kim, L. Que, Jr., W. Nam, *Angew. Chem.* **2004**, *116*, 2471–2474; *Angew. Chem. Int. Ed.* **2004**, *43*, 2417–2420, and references therein.

[23] N. Suzuki, T. Higuchi, T. Nagano, *J. Am. Chem. Soc.* **2002**, *124*, 9622–9628.

[24] K. A. Lee, W. Nam, *J. Am. Chem. Soc.* **1997**, *119*, 1916–1922.

[25] a) T. G. Traylor, S. Tsuchiya, Y. S. Byun, C. Kim, *J. Am. Chem. Soc.* **1993**, *115*, 2775–2781; b) J. T. Groves, Y. Watanabe, *Inorg. Chem.* **1986**, *25*, 4808–4810.

[26] a) A. Franke, C. Fertinger, R. van Eldik, *Angew. Chem.* **2008**, *120*, 5316–5320; *Angew. Chem. Int. Ed.* **2008**, *47*, 5238–5242; b) K. Machii, Y. Watanabe, I. Morishima, *J. Am. Chem. Soc.* **1995**, *117*, 6691–6697; c) Y. Watanabe, K. Yamaguchi, I. Morishima, K. Takehiro, M. Shimizu, T. Hayakawa, H. Orita, *Inorg. Chem.* **1991**, *30*, 2581–2582; d) W. Adam, K. J. Roschmann, C. R. Saha-Moller, D. Seebach, *J. Am. Chem. Soc.* **2002**, *124*, 5068–5073; e) W. Nam, M. H. Lim, H. J. Lee, C. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 6641–6647.

[27] a) T. Linker, *Angew. Chem.* **1997**, *109*, 2150–2152; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2060–2062; b) N. S. Finney, P. J. Pospisil, S. Chang, M. Palucki, R. G. Konsler, K. B. Hansen, E. N. Jacobsen, *Angew. Chem.* **1997**, *109*, 1798–1801; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1720–1723; c) W. Adam, K. J. Roschmann, C. R. Saha-Moller, *Eur. J. Org. Chem.* **2000**, 3519–3521.

[28] a) M. Palucki, P. J. Pospisil, W. Zhang, E. N. Jacobsen, *J. Am. Chem. Soc.* **1994**, *116*, 9333–9334; b) M. Palucki, G. J. McCormick, E. N. Jacobsen, *Tetrahedron Lett.* **1995**, *36*, 5457–5460.

[29] a) H. Sasaki, R. Irie, T. Hamada, K. Suzuki, T. Katsuki, *Tetrahedron* **1994**, *50*, 11827–11838; b) K. Yamaguchi, Y. Watanabe, I. Morishima, *J. Am. Chem. Soc.* **1993**, *115*, 4058–4065.

[30] a) O. A. Efremova, Y. V. Mironov, N. V. Kuratieva, V. E. Fedorov, *Acta Crystallogr. Sect. E* **2004**, *60*, m1817; b) Y. V. Mironov, A. V. Virovets, S. B. Artemkina, V. E. Fedorov, *J. Struct. Chem.* **1999**, *40*, 313–316; c) Y. V. Mironov, A. V. Virovets, W. S. Sheldrick, V. E. Fedorov, *Polyhedron* **2001**, *20*, 969–974; d) Y. V. Mironov, E. Albrecht-Schmitt, J. A. Ibers, *Inorg. Chem.* **1997**, *36*, 944–946.

[31] M. Amirnasr, K. J. Schenk, A. Gorji, R. Vafazadeh, *Polyhedron* **2001**, *20*, 695–702.

[32] T. Joseph, S. B. Halligudi, C. Satyanarayan, D. P. Sawant, S. Gopinathan, *J. Mol. Catal. A Chem.* **2001**, *168*, 87–97.

[33] R. D. Archer, H. Chen, L. C. Thompson, *Inorg. Chem.* **1998**, *37*, 2089–2095.

[34] H. Chen, J. A. Cronin, R. D. Archer, *Inorg. Chem.* **1995**, *34*, 2306–2315.

[35] SMART, Version 5.054 (Data Collection), and SAINT-PLUS, Version 6.19 (Data Processing), Software for the SMART System, Bruker Analytical X-ray Instruments, Inc., Madison, **1997**.

[36] SHELXTL, DOS/Windows/NT, Version 5.10, G. M. Sheldrick, Bruker Analytical X-ray Instruments, Inc., Madison, **1997**.

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