

Hydrocarbon oxidation with hydrogen peroxide and pentafluoroiodosylbenzene catalyzed by unusually distorted macrocycle manganese complexes

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Abstract

The highly distorted aza macrocycle manganese complexes as the oxidation catalyst were synthesized newly to achieve more green hydrocarbon oxidation; macrocycle **1** ringed by two bipyridine moieties and macrocycle **3** with two bipyridine and two amide bonds in the ring were prepared, and the catalytic abilities of these macrocycle manganese complexes **2** and **4** were examined. A remarkable result is that the unusually distorted manganese complex **4** coordinated by two nitrogen and two oxygen atoms of the macrocyclic ring is capable of catalyzing efficient oxidation of various alkanes and aromatic compounds with hydrogen peroxide. Catalyzed by this complex **4**, a variety of alkenes can be oxidized by hydrogen peroxide and their epoxides are formed in high yields. In contrast, complex **2** shows the failure to catalyze efficient oxidation of hydrocarbons with hydrogen peroxide. To evaluate the catalytic abilities of new complexes **2** and **4** strictly, the alkene oxidation was conducted by employing **2** and **4** as the catalyst and pentafluoroiodosylbenzene as the terminal oxidant, and as a result, these complexes **2** and **4** were capable of converting various types of alkenes to their oxidation products with high yields. Moreover, the following new results were found. (A) Norbornene oxidation catalyzed by complexes **2** with different length of side chains indicates that the yield and exo/endo of epoxide depend on the side chains, suggesting that the side chain could control the catalytic ability. (B) The product distribution of styrene oxidation catalyzed by complex **2** differs greatly from that by complex **4**, suggesting that the macrocyclic structure and coordinated atom affect the alkene oxidation.

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1. Introduction

The activation of C–H bonds of saturated hydrocarbons and aromatic compounds catalyzed by the metal complexes is an important goal for basic and industrial chemistry [1,2]. This transformation using environmentally benign oxidants has aroused much interests [3], because recent chemical industry continues to require the cleaner oxidation, which is an advance over environmentally unfavored oxidations and a step up from more costly organic peroxides. The development of catalysts for the functionalization of hydrocarbons has been therefore

carried out, and a wide variety of metal complexes have been synthesized for this purpose and their catalytic properties have been extensively studied [1–6]. In particular, the hydrocarbon oxidation system based on cleaner oxidants such as hydrogen peroxide holds the promise of advancing today's oxidation system to the green chemistry, which minimizes the waste and the use of toxic chemicals while using a minimum of energy and renewable raw materials. However, the utilization of oxidation systems employing these metal complexes has been limited. New synthetic strategy for better metal complexes meeting for future requirements is still a subject of debate.

The aza macrocycles have been known to show a variety of functionalities, and various macrocycles have been prepared to investigate a wide variety of applications [7]. We have synthesized a new class of aza macrocycles [8–13], which exhibits

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the chemically fascinating properties such as the color switching [9], the high selectivity of binding for Li^+ due to the small ring structure (stability constant $\text{Li}/\text{Na} = 5000$) [6,12,13], and the great enhancement of fluorescence by metal complexation [10,11]. The features which these macrocycles exhibit would arise from their unique structures; these macrocycles have non-planar, unsymmetrical, small, and highly strained ring structure [9,12].

Since the sterically hindered metal complexes [14,15] and aza macrocycle metal complexes [4–6] have been known to be capable of employing as the active catalyst for the hydrocarbon oxidation, we have been intrigued with the possibility that the new class of aza macrocycle metal complexes [8–13] might participate in catalytic processes. Furthermore, two types of macrocycles **1** and **3** we present in this paper seem to be a good selection to explore some factors that could contribute greatly to the ability as the oxidation catalyst. That is, macrocycle **1** includes two bipyridine moieties and has the nonplanar cyclic structure [12]. Manganese complex **2** of macrocycle **1** is coordinated by four pyridine moieties, and the redox property of complex **2** is expected to be changed by the structural variation of macrocyclic skeleton, that could be controlled by the length of side chains [24,25]. In contrast, macrocycle **3** includes two bipyridine moieties and two amide bonds in the macrocyclic ring, and the unique feature of this Mn complex **4** is unusually strained ring structure; manganese atom is bound by two nitrogen atoms with the coordinate bond and two oxygen atoms with the covalent bond in the small macrocyclic ring. These facts have stimulated our effort to use new metal complexes **2** and **4** to catalyze the hydrocarbon oxidation. We have therefore carried out **2** and **4**-catalyzed oxidations of hydrocarbons in the hope that, if the efficient hydroxylation of alkanes with hydrogen peroxide occurs, this more green oxidation system fits into the pursuit of sustainability and there would be the possibility of making industrial debut.

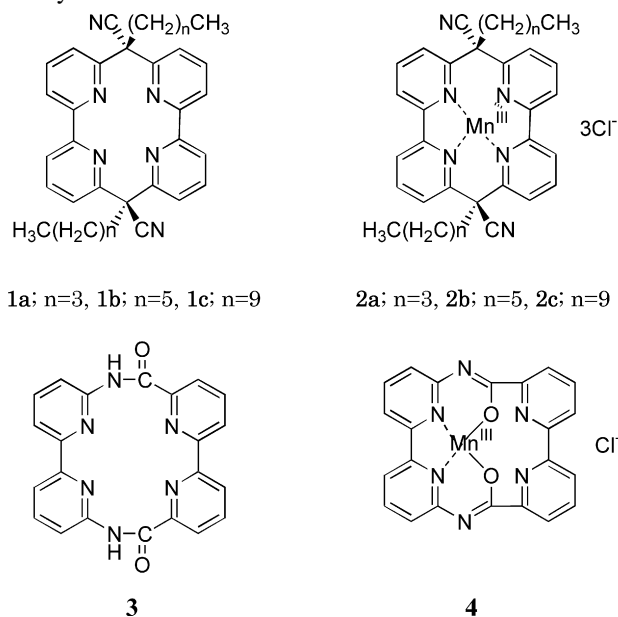
A noticeable result is that the H_2O_2 -oxidation system employing complex **4** is capable of catalyzing efficient oxidation of a wide range of alkanes and aromatic compounds. In addition, this complex **4** is capable of converting various alkenes to their oxidation products with the selectivity by using hydrogen peroxide.

The studies on the alkene oxidation using iodosylbenzene ($\text{C}_6\text{H}_5\text{IO}$) as the oxidant have affected in a fundamental way our understanding of the metal complex-catalyzed oxidation reactions, and their knowledge bases have been established [2,16–20]. The detailed studies on the alkene oxidation with $\text{C}_6\text{H}_5\text{IO}$ catalyzed by new Mn complexes **2** and **4** is needed to evaluate the catalytic abilities of **2** and **4** strictly. The oxidation of a wide variety of alkenes with pentafluoroiodosylbenzene ($\text{C}_6\text{F}_5\text{IO}$) as the terminal oxidant was therefore carried out, and complexes **2** and **4** were found to be capable of catalyzing the oxidation of various alkenes with high yields and turnovers, and to have desirable characteristic as the epoxidation catalyst. Moreover, this evaluation about **2** and **4** afforded notable aspects such as (1) the side chain effect and (2) the effect of the macrocyclic structure and the coordinated atom.

We report here the details of oxidation of various saturated hydrocarbons and aromatic compounds with hydrogen peroxide catalyzed by complex **4**, and the catalytic abilities of **2** and **4** that are evaluated by the alkene oxidation with $\text{C}_6\text{F}_5\text{IO}$ as the terminal oxidant.

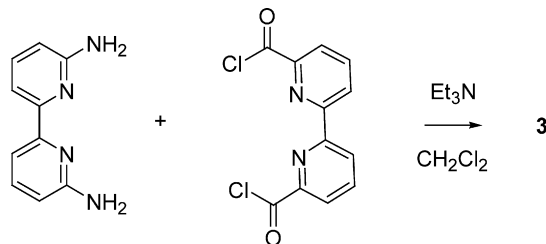
2. Results and discussion

The structures of macrocycles **1**, manganese complexes **2** of macrocycles **1**, macrocycle **3**, and manganese complex **4** of macrocycle **3** are shown in below.



The synthetic method of aza macrocycle **1a** was published already by us [12] and aza macrocycles **1b** and **1c** with two longer side chains were synthesized newly. The assignment of metal complex **2a** using the spectroscopic data has been published [12].

Macrocycle **3** was synthesized by the coupling reaction of 6,6'-diamino-2,2'-bipyridine with 2,2'-bipyridine-6,6'-dicarboxylic acid chloride under high dilution using a syringe pump as shown in below.



Complex **4** was prepared by the reaction of macrocycle **3** with manganese chloride, and the UV–vis spectra of macrocycle **3** and complex **4** in MeOH were shown in Fig. 1. The elemental analysis and UV–vis spectrum measurements of complex **4** in acetonitrile indicated that the composition of macrocycle **3** and manganese atom is 1:1 in solid state and in solution. Mass data indicated the existence of this complex.

Initially the manganese atom in complex **4** was expected to be coordinated by four nitrogen atoms of four pyridine moi-

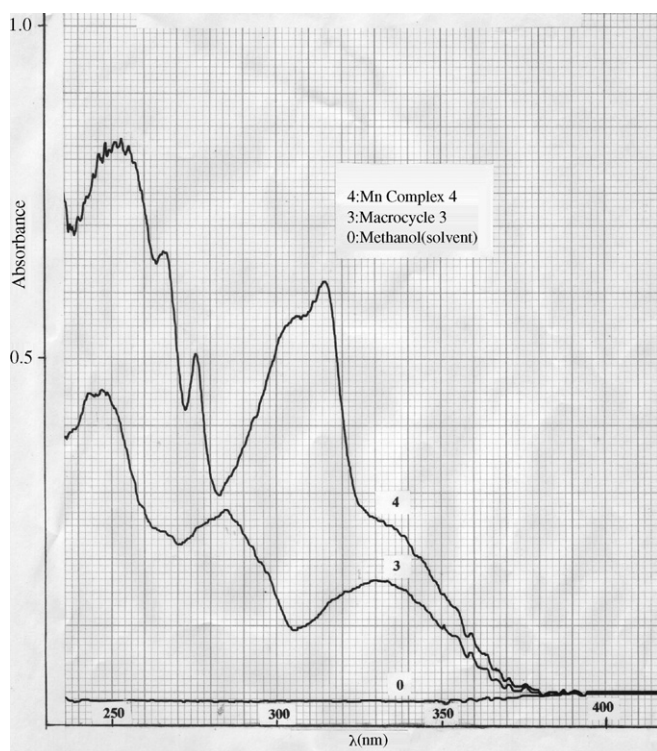


Fig. 1. UV-vis spectra of macrocycle **3** and its Mn complex **4** in MeOH.

eties as shown in the structure of macrocycle **3**. However, the C=O stretching band was not observed in the infrared spectrum of complex **4**, though the infrared spectrum of macrocycle **3** showed a strong C=O stretching band at 1738 cm^{-1} , that means the highly strained ring structure of macrocycle. This result indicates the manganese atom in complex **4** to be coordinated by two nitrogen atoms with the coordinate bond and two oxygen atoms with the covalent bond as shown above structure. This coordination structure would probably arise from the high distortion between two bipyridine moieties due to two amide bonds of bridges and small size of macrocyclic ring, providing a rare ring system; that is, manganese atom is unable to be coordinated by four pyridine moieties due to unusually distorted cyclic structure, and it becomes much easy to form the NNMnOO coordination system. The NNMnOO coordination system found in this complex **4** is similar to that of the salen derivatives which have been known to function as the useful and efficient catalyst [15]. The salen analogues which were prepared from ethylenediamine and salicylaldehydes in 1933 have the acyclic structure ($\text{C}_8\text{N}_2\text{O}_2$ macrocyclic system), affording more freedom for metal coordination, while macrocycle **3** synthesized by us has the rigid cyclic structure ($\text{C}_6\text{N}_4\text{O}_2$ macrocyclic system).

As described above, this macrocycle **3** is supposed to have the higher distortion, and the CPK model of complex **4** supports the structure of highly strained macrocyclic ring. Since the redox property of macrocycle metal complex has been known to be affected greatly by the distortion of macrocyclic ring [24,25], this distortion could play a significant role in controlling the catalytic ability. Thus, there is the possibility that this distorted effect could lead to higher catalytic ability of complex **4**.

As mentioned above, complex **4** is expected to have the desirable properties as the active catalyst of oxidation reaction. Since the studies on the alkene oxidations with iodosylbenzene ($\text{C}_6\text{H}_5\text{IO}$) catalyzed by a wide variety of metal complexes have been reported by many research groups [16], the catalytic effectiveness of complex **4** can be evaluated by comparing the oxidation reaction with $\text{C}_6\text{H}_5\text{IO}$ catalyzed by **4** with that by the previously studied metal complexes. Accordingly, the alkene oxidation using **4** as the catalyst and $\text{C}_6\text{F}_5\text{IO}$ as the oxidant was carried out to examine its ability as the catalyst. In this study, the reason why pentafluoroiodosylbenzene ($\text{C}_6\text{F}_5\text{IO}$) is used instead of $\text{C}_6\text{H}_5\text{IO}$ is to compare with our studies on hemin-catalyzed epoxidations [20]. Complex **2** with the strained cyclic structure was also found to be capable of catalyzing the oxidation of various alkenes with $\text{C}_6\text{F}_5\text{IO}$. Thus, more detailed catalytic ability of complex **4** is expected to be elucidated by the comparison of the alkene oxidation by **4** with that by **2**, because the coordination system of **4** including cyclic structure and coordinated atoms differs greatly from that of **2** as shown in above scheme.

For this reason, at first, the alkene oxidation with $\text{C}_6\text{F}_5\text{IO}$ catalyzed by complexes **2** and **4** was carried out, and the catalytic abilities of **2** and **4** were investigated, and it is followed by the studies of the detailed properties of **2** and **4** using a wide variety of reactions and measurements. Second, the oxidation reactions of various alkenes, alkanes, and aromatic compounds with $\text{C}_6\text{F}_5\text{IO}$ catalyzed by **4** were examined.

Finally, the oxidation using various alkanes and aromatic compounds as the substrate and hydrogen peroxide as the oxidant, that is a key of this research, was conducted by using **4** as the catalyst. These results are as follows.

2.1. Catalytic abilities of complexes **2** and **4** in alkene oxidation with pentafluoroiodosylbenzene ($\text{C}_6\text{F}_5\text{IO}$)

Typical reaction conditions employed in these reactions were $1 \times 10^{-3}\text{ M}$ catalyst, 1 M substrate, and $6 \times 10^{-2}\text{ M}$ oxidant [18,19], that is the same as the experiments of hemin-catalyzed epoxidations [20,32]. We can therefore study the catalytic abilities of complexes **2** and **4** in comparison to previously reported porphyrin metal complexes. Under this reaction condition, we verified that the use of simple Mn salts as the catalyst results in no epoxidation.

At first, styrene and norbornene oxidations were carried out by using **2** ringed by four pyridine moieties as the catalyst. The heterogeneous reaction mixture using dichloromethane as the solvent was shaken under an argon atmosphere until all of $\text{C}_6\text{F}_5\text{IO}$ was dissolved, and this solution stood at room temperature. After oxidation reaction for 30 min, the reaction products in the homogeneous solution were analyzed by gas chromatography. As a result, the formation of epoxides of high yields (80–90%) was observed at room temperature. All of $\text{C}_6\text{F}_5\text{IO}$ added was reduced to pentafluoroiodobenzene ($\text{C}_6\text{F}_5\text{I}$) and $\text{C}_6\text{F}_5\text{I}$ formed was used as an internal standard to obtain the yield. The epoxide cycle was repeated by the addition of more $\text{C}_6\text{F}_5\text{IO}$. Eventually, high turnover were obtained [36], and its value was determined as >1000 , because the UV-vis spectrum of the final solution showed no decomposition of **2** after this

Table 1
Styrene and norbornene oxidations with pentafluoriodosylbenzene (C₆F₅IO) Catalyzed by Complexes **2b**, **c**, and **4**

Product ratio (%)					
Complex	Total yield (%) ^a	Epoxide	PhCH ₂ CHO	PhCHO	
(a) Substrate = Styrene					
2b ^b	85	82	13	5	
4 (no Im) ^c	73	61	27	12	
4 (Im) ^c	95	85	10	5	
Product ratio (%)					
Complex	Total yield (%) ^a	Epoxynorbornane	Cyclohexene-4-carboxaldehyde	Norcamphore	Exo/endo
(b) Substrate = Norbornene					
2b ^b	90.5	95.0	3.5	1.5	55
2c ^b	80.3	89.0	5.5	5.5	76
4 (no Im) ^c	88.0	24.0	66.0	10.0	
4 (Im) ^c	100.0	55.0	35.0	10.0	

^a The yields were based on integration of the product vs. that of F₅PhI formed.

^b The reaction conditions; [complex] = 1 × 10⁻³ M, [substrate] = 1 M, [pentafluoriodosylbenzene (C₆F₅IO)] = 6 × 10⁻² M, solvent; CH₂Cl₂ (0.1 mL), reaction time = 30 min. Spectroscopic data such as UV–vis spectrum showed no decomposition of catalysts after oxidation reaction. In the cases of complexes **2b** and **c**, the possibility that the alkyl groups are oxidized under this condition is extremely low, because the concentration of alkenes as the substrates is 1000 times higher than that of catalysts and the reactivity of alkenes is higher than that of alkyl groups.

^c The reaction conditions; [complex **4**] = 1 × 10⁻³ M, [substrate] = 1 M, [C₆F₅IO] = 6 × 10⁻² M, solvent; CH₂Cl₂ (0.2 mL) + CH₃CN (0.1 mL). Im = Imidazole (1 × 10⁻² M) is added as the donor ligand. No Im = Imidazole is not contained in the reaction solution. Ref. [33].

epoxidation. Thus, further epoxidation cycle will be able to be repeated by the addition of more substrate and oxidant, meaning much higher turnover. Table 1 lists the yields and the product distribution observed under above condition with styrene and norbornene. Second, the oxidation reactions of styrene and norbornene catalyzed by **4** were also carried out, and high yields of oxidation products and high turnover (>1000) were also obtained [36]. The UV–vis spectrum of the final solution is also consistent with that of the original solution of **4**. This result is summarized in Table 1.

¹⁸O-labeling studies of complexes **2** and **4** were carried out to trace the source of oxygen in the product of oxidation. ¹⁸O-labeling oxidant was prepared from the oxidant with ¹⁸O-enriched H₂O [21,22]. From these experiments including mass data, the epoxide oxygen was found to be derived from oxidants within experimental error.

These results indicate complexes **2** and **4** to have enough ability as the catalyst of alkene oxidation compared with a wide variety of metal complexes which have been studied previously [1–6,18–20].

2.2. Evidence for the formation of reactive intermediate

Clearly, complexes **2** and **4** generate active species upon reaction with C₆F₅IO, because these complexes can participate efficient epoxidation as described above. However, the structure of active oxidant generated in this reaction is still unknown. Most of the previously reported papers about the oxidation reaction catalyzed by manganese complexes have emphasized the formation of an oxo-Mn intermediate by the reaction of manganese complexes with iododisylbenzene [16]. In the case of this study, spectroscopic studies on the reactions of **2** and **4** with C₆F₅IO also indicate the possibility that

the oxo-Mn species are formed. After addition of C₆F₅IO to the dichloromethane solution of complex **2c**, a yellow brown solution including **2c** immediately turned dark brown. The maximum absorption in its UV–vis spectrum shifted from 272 to 259 nm. A new peak at 703 cm⁻¹ appeared in the infrared spectrum of this new compound in dichloromethane, and this observed value is close to that (712 cm⁻¹) of the previously reported tetrakis(2,4,6-trimethylphenyl)porphyrin Mn^{IV}(O) complex [17]. Thus, these results suggest the formation of oxo-manganese complex as the intermediate in this system [16]. However, it leaves unanswered the question of whether the oxo-Mn complex is Mn^V=O or Mn^{IV}=O. The spectrum using C₆F₅IO as the oxidant was very similar to that using tert-butyl hydroperoxide being structurally diverse oxidant, but the difference between the absorption spectra of Mn^V and Mn^{IV} would be difficult to distinguish [23]. Although the ESR measurements were tried to obtain the information about this question, the definite conclusion was not obtained.

In the case of complex **4**, after addition of C₆F₅IO to the solution of **4** (λ_{max} 315 nm), the UV–vis spectrum showed the new absorption band centered at 480 nm, the maximum of which is obscured by the tail of strongly absorbing species at λ > 450 nm. This new transient species with the absorption at 480 nm disappeared by the addition of alkenes such as styrene and norbornene; that is, the decay of the absorption at 480 nm with time was observed. It seems that the trend of spectral changes and the position of absorption are similar to that of the previously reported salen Mn complexes. The formation of oxo-Mn species may be postulated by the suggestion arisen from these facts and by analogy with other possible intermediates, though the precise structure of intermediate is still unknown [21,34,41].

2.3. Styrene oxidation by complexes **2** and **4** with C₆F₅IO

The noticeable fact observed in Table 1 is that the product distribution (epoxide, PhCH₂CHO, and PhCHO) by complex **2** is very different from that by complex **4**; **4** produces more side products (PhCH₂CHO and PhCHO) than **2b**. There are many factors that contribute to this result. One of such factors seems to be the difference in the stereochemical and electronic structures created by the ring strain and the heteroatoms, because the manganese atom of **2b** is coordinated by four nitrogen atoms, while that of **4** is coordinated by two nitrogen and two oxygen atoms. Additionally, we may be unable to ignore the solvent effect.

On the other hand, the coordination system (NNMnOO) of **4** is similar to that of the previously reported acyclic salen metal complexes [21,22], though **4** has cyclic and highly strained structure. Accordingly, there is the possibility that the information to understand the difference in the product distribution between complexes **2b** and **4** is obtained by the comparison of styrene oxidation catalyzed by **4** with that by the salen metal complexes. It was reported that a considerable amount of phenylacetaldehyde and benzaldehyde as side products in the styrene oxidation by the salen Cr complexes are arisen from the instability of styrene oxide under this reaction condition, and the formation of these side products is markedly suppressed by the presence of the donor ligand [21a]. To confirm the instability of styrene oxide under the oxidation reaction using **4**, a large excess of styrene oxide was added to the final solution after completion of styrene oxidation catalyzed by **4** and this reaction mixture was shaken. The analyses of this solution by means of gas chromatography indicated the increase of side products (phenylacetaldehyde and benzaldehyde) and the decrease of styrene oxide with time. Thus, one of the reasons why **4** provides more side products compared with **2b** would be the conversion from the first formed styrene oxide to side products after completion of styrene oxidation reaction with C₆F₅IO by **4**.

The effect of the donor ligand as the cocatalyst on the catalytic epoxidation of alkenes by **4** is also evident. The addition of imidazole to the reaction solution led to a dramatic change of product distribution (the increased yield of epoxide) as well as to an enhancement in the rate of oxidation reaction as shown in Table 1. That is, when styrene oxidation with C₆F₅IO was carried out in the presence of imidazole, the ratio of styrene oxide and the total yield of the oxidation products increased from 61 to 85% and from 73 to 95%, respectively [33]. This property of **4** is similar to the salen Cr complexes [21].

2.4. Norbornene oxidation by complex **2** with C₆F₅IO

As seen in Table 1 including the results of alkene oxidation with C₆F₅IO, the following interesting facts for affecting this oxygen transfer emerged from results of norbornene oxidation catalyzed by complexes **2b** and **c** with different length of side chains. That is, the yields and the product distribution in norbornene oxidation depend on the length of side chains of these complexes. For example, total yields by **2b** and **c** are 90.5 and 80.3%, respectively. Moreover, their exo/endo ratios of

epoxynorbornanes are 55 and 76, respectively. This difference in norbornene oxidation would be explained by the clarification of the reaction mechanism. As described above section, spectroscopic data suggest the formation of the oxo-Mn intermediate in this system. Several research groups have reported the alkene oxidation via this oxo-metal intermediate [16–22]. One of typical examples is the norbornene oxidation with C₆F₅IO catalyzed by porphyrin Fe (III) complexes; it was reported that the mechanism of hemin-catalyzed norbornene oxidation is explained as an electron transfer from norbornene to oxo-porphyrin iron (III) complex followed by radical collapse to give a carbocation rather than direct attack [18,19]. Exo- and endo-epoxynorbornane, cyclohexene-4-carbaldehyde, and norcamphore, which are produced by the hemin-catalyzed norbornene oxidation, can be explained by this mechanism. Despite the divergences in macrocycle **1** ringed by four pyridines and porphyrins ringed by four pyrroles, they share in common the production of substantial amount of endo-2,3-epoxynorbornane (exo/endo = 55) [18]. That is, the result in Table 1 suggests the mechanism of electron transfer from norbornene to oxo-Mn complex to be reasonable as the explanation of complex **2**-catalyzed norbornene oxidation. The mechanism of electron transfer from the olefin to high valent nickel oxo compound has also been reported for the olefin oxidation catalyzed by nickel cyclam complexes (cyclam = 1,4,8,11-tetraazacyclo-tetradecane) [22]. As a whole, these nickel cyclam complexes are the same macrocyclic system (C₁₀N₄ macrocyclic system) as **2** has, though four nitrogen atoms of **2** are included in four pyridine moieties. This fact also suggests above mechanism that norbornene oxidation by **2b** and **c** proceeds by the electron transfer from the olefin to oxo-Mn complex.

The possibility of procession of oxidation reaction by this mechanism leads an answer to the question about the yields and product distribution as shown in Table 1. That is, the degree of electron transfer which occurs between norbornene and oxo-Mn complex might be explained in a qualitative way in terms of electron density on the Mn complex, that is evaluated by its redox potential [21b]. The redox properties of Mn complexes used in this study are expected to depend on the length of side chains of macrocycle, because the side chain dependence of the redox potential has been reported previously for the dodeca-substituted porphyrins, which exhibit the distortion changes of macrocyclic ring with the variation of side chains [24,25]. To see whether the length of side chains perturb the redox properties of these complexes, the redox potentials of **2b** and **c** were measured in dichloromethane solution containing tetra-*n*-butyl ammonium bromide by cyclic voltammetry. These voltammograms show the reversible redox process, and the oxidation halfwave potentials (1st oxidation, V versus SEC) of **2b** and **c** in dichloromethane are 1.17 and 0.91 V, respectively, and the value of **2c** is lower than that of **2b** ($\Delta E = 0.26$ V) [35]. This result indicates the electron density of these complexes with different length of side chains to decrease in order **2c** > **2b**.

It was reported that the exo-epoxynorbornane/endo-epoxynorbornane ratio decreases in hemin-catalyzed norbornene oxidation as the electron density in the porphyrin Fe(III) decreases, and the yields of oxidation products and the ratio of

epoxide for aldehyde and keton increases with the decrease of electron density of porphyrin Fe(III) [18,19]. In addition, these results were explained by the electron transfer mechanism as stated above. As seen in Table 1, the trend of oxidation products catalyzed by **2b** and **c** is consistent with those reported for hemin-catalyzed norbornene oxidation; when the electron density decreases (**2c** > **2b**), the *exo/endo* ratio decreases from 76 to 55 and the yield of oxidation products increases from 80.3 to 90.5% and the ratio of epoxide increases from 89 to 95%. Eventually, the fact that **2b** provides higher yield of epoxide and lower *exo/endo* ratio is interpreted as arising from higher oxidation potential of **2b**. The relationship between the yield of epoxide and the redox potential of salen Mn(III) complex has been examined already [21b] and the trend of oxidation products catalyzed by the salen Mn(III) complex is similar to that by **2**; the fact that the decreasing electron density of metal complex provides higher yield of epoxide is observed.

One of the reasons why the redox potential changes with the length of side chains on the macrocyclic ring is as follows. As is stated above, the X-ray structure determination of macrocycle **1** showed the nonplanarity of macrocyclic ring [12]. The X-ray data of dodeca-substituted porphyrins reported previously indicated the degree of planarity of macrocyclic skeleton to change with the variation of the length of side chains [24]. Moreover, since the cyclic voltammetry studies on dodeca-substituted porphyrins provide definite evidence that the degree of planarity of macrocyclic skeleton is closely related to the redox potential [25], the redox potential of **2** is supposed to change with the length of side chains.

The competitive epoxidation of alkene pairs was also conducted by using styrene and *trans*-stilbene to examine the substrate selectivity of alkene oxidation. The epoxide ratio (styrene oxide/stilbene oxide) in epoxidation by **2b** and **c** were 1.5 and 3.7, respectively, and this indicates that **2b** and **c** show the substrate selectivity in the alkene oxidation. The observed difference in the substrate selectivity would probably come from the interaction between two side chains and substrates or their macrocyclic structures.

The result described above is a new finding that alkene oxidation can be controlled by two side chains of macrocycle which changes the conformational structure of ring accompanied by the variation of the redox properties.

2.5. Hydrocarbon oxidation by complex **4** with C₆F₅IO

As described in above section, the distorted, unsymmetrical macrocycle Mn complex **4** showed the ability as the catalyst of alkene oxidation, though the yield of styrene oxidation by **4** in CH₂Cl₂–CH₃CN is lower than that by **2b** in CH₂Cl₂ as shown in Table 1. We need to know whether the C₆F₅IO-based system using **4** can oxidize various alkanes and aromatic compounds with high efficiency and high selectivity, because the oxidation efficiency of these compounds by C₆F₅IO–CH₂Cl₂ system using **2** is extremely low. The oxidation of a wide range of hydrocarbons with C₆F₅IO was therefore carried out by using **4** in CH₂Cl₂–CH₃CN and their results were summarized in Table 2, indicating efficient oxidation of these substrates. It is one of

Table 2

Hydrocarbon oxidation with pentafluoriodosylbenzene (C₆F₅IO) catalyzed by complex **4**

Substrate	Product	Yield (%) ^a	Total yield (%)
Cyclohexene	Epoxide	88	100
	Cyclohexenol	7	
	Cyclohexenone	5	
Cyclooctene	Epoxide	100	100
1-Octene	Epoxide	85	85
Cyclohexane	Cyclohexanol	75	75
<i>n</i> -Hexane	2-Hexanol	30	36
	1-Hexanol	6	
Benzene	Phenol	15	46
	1,4-Benzoquinone	31	

The reaction conditions; [complex **4**] = 1×10^{-3} M, [substrate] = 1 M, [C₆F₅IO] = 6×10^{-2} M, solvent; CH₂Cl₂ (0.2 mL) + CH₃CN (0.1 mL), reaction time = 30 min.

^a The yields were based on C₆F₅I formed by the reaction.

surprises that the C–H bonds activation of saturated hydrocarbons and aromatic compounds can be achieved with this aza macrocycle Mn complex **4**, that is similar to the results in the previous papers using the porphyrin Mn complexes [26]. It is also noteworthy that the yield (85%) of 1-octene oxide from 1-octene is very high, though terminal alkenes have been known to be much less reactive in the reaction with Mn complex catalysts. As seen in Tables 1 and 2, there is much discrimination between the electron-rich styrene, the strained norbornene, and normal olefins, because the attack of **4** with highly distorted ring structure on the substrates would become highly selective. The oxidation of cyclohexene by **4** produced both epoxidation products and only small amounts of allylic oxidation products, suggesting the possibility that radical reactions were not involved.

As shown in Table 1, the trend of norbornene oxidation by **4** is similar to that of styrene oxidation described in above section; that is, the yields of side products (cyclohexene-4-carboxaldehyde and norcamphore) become higher compared to **2**. Specifically, it is noticeable that the ratio of side products is higher than epoxide (epoxynorbornane), indicating the formation of carbocation and subsequent rearrangements. The addition of imidazole to this reaction mixture led the increase of yield from 88% to 100% [33]. However, no change of cyclohexene-4-carboxaldehyde and norcamphore with time was detected, and then the side products would be the product of direct oxidation. Thus, the rearrangements to cyclohexene-4-carboxaldehyde and norcamphore would probably proceed easily via carbocation under the reaction condition employed in this study [18,19]. This point is quite different from the case of styrene oxidation by **2**.

As described above, there is the possibility that the mechanism of norbornene oxidation by complex **4** differs greatly from that by complex **2**. However, it leaves unanswered the question of why the difference in the mechanism between **2** and **4** occurs.

Eventually, the yields of hydrocarbon oxidation with C₆F₅IO catalyzed by new complex **4** are considered to be considerably high. Most importantly, almost quantitative epoxidation

of alkenes with C₆F₅IO were achieved by this system using **4** [39].

2.6. Hydrocarbon oxidation by complex **4** with hydrogen peroxide: Efficient catalytic hydroxylation of alkanes

The results using C₆F₅IO as the terminal oxidant showed complex **4** to have a good activity as the oxidation catalyst of various hydrocarbons. This suggests that complex **4** is able to generate very active oxidants upon reaction with more unreactive oxidants such as hydrogen peroxide. Additionally, some organic peroxides are a great boon but carry with it the problem of having to deal with environmentally unfavored side products. However, since hydrogen peroxide is very cheap and environmentally safe, this system seems to be very important for the industrial use. Finding out whether complex **4** can oxidize efficiently various alkanes and aromatic compounds with hydrogen peroxide is exactly the point of this research. Thus, the oxidation reactions of various alkanes, aromatic compounds, and alkenes were conducted by using hydrogen peroxide.

First, the alkene epoxidation with hydrogen peroxide catalyzed by **2** was carried out, but efficient epoxidation was not observed. It has been reported that cyclam Mn complexes having the same macrocyclic system (C₁₀ N₄ macrocyclic system) are ineffective as catalysts of either cyclohexene or *cis*-stilbene epoxidation by hydrogen peroxide [5a]. In contrast, complex **4** is capable of catalyzing efficient oxidation of alkanes, aromatic compounds, and alkenes with hydrogen peroxide. The products obtained from reaction of hydrogen peroxide with hydrocarbons in the presence of **4** are summarized in Table 3.

As shown in Table 3, the yields of alkene oxidation using hydrogen peroxide were in the range from 72% to 80%, that is similar to the results reported in the previous paper about the porphyrin Mn complexes [3d]. However, most of the oxidation

system reported previously requires the presence of imidazole as a cocatalyst to obtain high yields. Complex **4** can achieve higher yields of alkene oxidation without the donor ligands such as imidazole or pyridine.

Another noticeable result of alkene oxidations shown in Table 3 is that the side products for the oxidations of styrene, cyclohexene, and *cis*-stilbene are not observed, though other oxidation systems produce a variety of side products. It is well recognized that cyclohexene is prone to allylic oxidation. In fact, the cyclohexene oxidation by **4** with C₆F₅IO afforded cyclohexenol and cyclohexenone as shown in Table 2. However, the fact that only cyclohexene oxide is produced by hydrogen peroxide is notable, suggesting the possibility that the oxidation mechanism depends on the oxidant. Styrene oxidation did not afford PhCH₂CHO and PhCHO, which were found in the oxidations by **2b** and **4** with C₆F₅IO. Though the oxidation of *cis*-stilbene has been known to provide variable products including *trans*-stilbene oxide, only *cis*-stilbene oxide is produced with high yield (76%). Accordingly, the effectiveness of **4** as the oxidation catalyst seems to be unique, and we must find the reason why such reaction occurs in the future.

The selectivity of alkene oxidation reactions by the system using **4** and hydrogen peroxide was examined in order to explore the wider functionality of this complex. To examine the substrate selectivity, the competitive epoxidation of alkene pairs was carried out by using styrene and *trans*-stilbene. The epoxide ratio (styrene oxide/*trans*-stilbene oxide) was 2.5. In addition, the oxidation reaction of isoprene was carried out in order to examine the regioselectivity. The epoxide ratio (1,2-epoxide/3,4-epoxide) was 1.8. These results indicate the alkene epoxidation with hydrogen peroxide catalyzed by **4** to proceed with substrate selectivity (chemo-selectivity) as well as regioselectivity.

Particularly significant is the hydroxylation of alkanes by **4**, that is shown in Table 3. It was reported that the hydroxylation of alkanes with hydrogen peroxide catalyzed by the porphyrin Mn complexes requires the presence of the donor ligands [3]. However, as shown in Table 3, the hydroxylation reaction of alkanes by **4** occurs without the donor ligands such as imidazole and their yields tend to be higher than the values of yield reported in the previous paper [3d].

Since the efficient conversion from benzene to phenol is an important goal in industrial process, this oxidation was carried out by using **4** and hydrogen peroxide. The oxidation of benzene afforded a small amount of phenol (5%), but much more 1,4-benzoquinone (27%) was obtained [40]. This would be produced by the conversion from the first formed phenol into 1,4-benzoquinone with hydrogen peroxide in this homogeneous reaction system, because the reactivity of phenol is much higher than benzene as a starting material under this oxidation condition (homogeneous system). The heterogeneous oxidation system using **4** and hydrogen peroxide provides the possibility of forming more phenol compared to 1,4-benzoquinone, because the system, which is able to prevent the oxidation from phenol to 1,4-benzoquinone, would be devised by using heterogeneous system. The use of ethylbenzene as the substrate gives another interesting aspect; the ethyl group is oxidized easily rather than benzene ring under this reaction condition.

Table 3
Hydrocarbon oxidation with hydrogen peroxide catalyzed by complex **4**

Substrate	Product	Yield (%) ^a	Total yield (%)
Alkenes			
Cyclooctene	Epoxide	80	80
Styrene	Epoxide	72	72
Cyclohexene	Epoxide	78	78
<i>cis</i> -Stilbene	<i>cis</i> -Epoxide	76	76
Alkanes			
Cyclohexane	Cyclohexanol	38	40
	Cyclohexanone	2	
Cyclooctane	Cyclooctanol	41	46
	Cyclooctanone	5	
Aromatic compounds			
Ethylbenzene	1-Phenylethanol	20	35
	Acetophenone	15	
Benzene	Phenol	5	32
	1,4-Benzoquinone	27	

The reaction conditions; [complex **4**] = 1×10^{-3} M, [substrate] = 1 M, [H₂O₂] = 2×10^{-2} M, solvent; CH₂Cl₂ (0.2 mL) + CH₃CN (0.2 mL). Reaction time: 30 min for alkenes, 60 min for alkanes.

^a The yields were based on H₂O₂ added.

As is stated above, the yields and the selectivities indicate new complex **4** to be the effective catalyst to mediate the hydrocarbon oxidation using hydrogen peroxide. In contrast, complex **2** coordinated by two bipyridine moieties shows the failure to catalyze efficient oxidation of hydrocarbons with hydrogen peroxide in spite of its cyclic structure. Hence, the highly distorted, cyclic NNOO coordination of **4** may be a key factor to lead the highly active catalysts with hydrogen peroxide. In addition, since this ligand system is air stable for ease of handling, the importance of this complex **4** as the catalyst will be increased greatly by the elaboration of macrocycle with chiral point like ferrocene and salen derivatives.

3. Conclusion

The activation of C–H bonds of alkanes and aromatic compounds can be achieved by the oxidation system using unusually distorted macrocycle Mn complex **4** as the catalyst and hydrogen peroxide as the oxidant. This is one of the excellent hydroxylation systems because it converts very inexpensive alkanes into much higher value compounds without producing any by-products. The ability of **4** as the catalyst of alkene oxidation with hydrogen peroxide has also been demonstrated. This oxidation system employing **4** seems to be able to bridge the gap to the industrial use. In contrast to **4**, complex **2** shows the failure to convert efficiently the hydrocarbons to their oxidation products by hydrogen peroxide. This result indicates that the catalytic ability of complex with hydrogen peroxide could depend on the structure of macrocyclic ring and the atom by which the coordination system is formed.

Complex **2** was found to be effective catalysts (80–90% yields) for alkene oxidation with pentafluoriodosylbenzene (C_6F_5IO), though there are very few metal complexes coordinated by simple bipyridine ligands that are effective enough to allow use in the alkene oxidation. This ability of **2** is also affected by the distortion of macrocycle which would strongly perturb the redox properties. This effect was confirmed by changing the degree of the distortion of macrocycle, that is produced by the variation of the length of the side chains of macrocycle. In other words, this suggests the creation of a new type of catalytic system that the catalytic ability can be controlled. There is the possibility that the mechanism of norbornene oxidation with C_6F_5IO catalyzed by **2** differs greatly from that by **4**, suggesting the effect of cyclic structure and the coordinated atom.

In summary, new Mn complexes with the rare macrocyclic structure show the catalytic ability which functions as the activation and functionalization of various hydrocarbons. Additionally, a new catalytic system capable of probing the structure–function relationships could be created by using these macrocyclic systems.

4. Experimental section

4.1. Reagents

All solvents and reagents were purchased from Tokyo Kasei Kogyo Co. and Wako Chemical Co. The reagents

were used without further purification. Dichloromethane used for the coupling reaction of 2,2'-bipyridyl-6,6'-diamine [12] with 2,2'-bipyridyl-6,6'-diacid chloride was distilled from CaH_2 under an argon atmosphere just before the reaction. Dichloromethane used for the oxidation reactions were stirred over and distilled from CaH_2 , and acetonitrile was distilled from P_2O_5 before use. Other solvents were used as received. Hydrogen peroxide (H_2O_2) was obtained commercially. Pentafluoriodosylbenzene (C_6F_5IO) was prepared from perfluoriodosobenzene-bis-(trifluoroacetate) [31] in a manner similar to that for iododisylbenzene [37] and was dried over P_2O_5 under vacuum. Tetrakis(2,6-dichloro-phenyl)porphyrin used for the confirmation of oxidation experiments was prepared by the collidine method [38].

4.2. Physical measurements

1H -NMR spectra (270 MHz) were measured on a JEOL GX-270 and were recorded in $CDCl_3$ or CD_3CN at 298 K with $SiMe_4$ as an internal standard. The UV–vis spectra were recorded on a Hitachi 340 recording spectrometer with the cell compartment thermostated at 20 °C in 1 cm quartz cell. IR spectra were collected on a Perkin-Elmer FT-IR spectrometer with a KBr method routinely. Mass spectra were taken in a JEOL JMS-700 spectrometer. Cyclic voltammograms of complexes **2b** and **c** were obtained by using a Nikko Keisoku potentiogalvanostat. Cyclic voltammograms were recorded in the three-electrode system, consisting of a glassy carbon working electrode, a platinum wire as a counter electrode, and an $Ag/AgCl$ reference electrode. Complexes **2b** and **c** were measured in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. CH_2Cl_2 was thoroughly degassed with an argon prior to recording cyclic voltammograms, and the reversible voltammograms of complexes **2b** and **c** were obtained [35]. The products of hydrocarbon oxidation catalyzed by new Mn complexes **2** and **4** were analyzed by Shimadzu gas chromatography with capillary column.

4.3. Syntheses

Macrocycle **1a** and its metal complex **2a** were synthesized by the method published by us [12]. The synthetic method of macrocycles **1b** and **c** was almost the same as that of macrocycle **1a**. Dicyano macrocycle **5** with red color was prepared by the reaction of 6,6'-dibromo-2,2'-bipyridine with α -cyanoacetamide and sodium hydride in DMF [12,13]. The synthetic methods of *trans*-dialkylated dicyano macrocycle **1b** and **c** from dicyano macrocycle **5** are as follows.

4.4. Macrocycle **1b**

The dispersion of sodium hydride in mineral oil was placed in a 200 mL three-necked flask fitted with a reflux condenser and pressure compensated dropping funnel, and air in this reaction system was replaced completely by dry argon. The mineral oil was removed by washing of the dispersion with dry light petroleum under an argon atmosphere. The moisture in DMF

was removed completely by the dryness over 3 Å-molecular sieve and subsequent distillation under vacuum. This process to purify the solvent was carried out just before the reaction. This anhydrous DMF (50 mL) was added to sodium hydride, and this mixture was stirred for 1 h under an argon atmosphere. Macrocycle **5** (0.15 g) was added to this mixture and the suspension obtained was stirred for 3 h at room temperature, and then, the temperature was elevated to 70 °C. Hydrogen gas was evolved during this procedure and the reaction mixture was stirred until the generation of hydrogen gas was not observed. The color of the reaction mixture turned to reddish brown with this process. After cooling to room temperature, 1-bromohexane (5 mL) in 30 mL dry DMF which was purified by the method described above was added dropwise to this reaction mixture, and the temperature was raised to 130 °C and this reaction mixture was stirred during 24 h under an argon atmosphere. After cooling to room temperature, the water (50 mL) was added to this reaction mixture, and chloroform (50 mL) was then added. The organic phase was separated and the solvent was removed completely, and the resulting solid was dried under vacuum. This crude product was purified by silica-gel column chromatography using dichloromethane-hexane as eluent. Colorless *trans*-dihexyl dicyano macrocycle (**1b**) was obtained from the first fraction (yield 31%). From the second and third fractions were obtained colorless *cis*-dihexyl dicyano macrocycle and red-colored monohexyl dicyano macrocycle, respectively. *trans*-Dihexyl dicyano macrocycle **1b**; ¹H-NMR (CDCl₃, 298 K) δ 7.98, 7.87, 7.58, 2.45, 1.21, 0.77. UV-vis (CHCl₃) λ_{max} 263 nm.

4.5. Macrocycle **1c**

Macrocycle **1c** (*trans*-didecyl dicyano macrocycle) was synthesized by the same method as macrocycle **1b**, although 1-bromodecane was used in place of 1-bromohexane in this case.

Metal complexes of **2b** and **c** were prepared by the same procedure as metal complex of **2a**.

4.6. Preparation of macrocycle **3**

Macrocycle **3** was synthesized by the coupling reaction of 2,2'-bipyridyl-6,6'-diamine [12] with 2,2'-bipyridyl-6,6'-diacid chloride [27,29]. At first, 2,2'-bipyridyl-6,6'-diacid chloride was synthesized by the reaction of 2,2'-bipyridyl-6,6'-diacid with thionyl chloride in benzene [30]. 2,2'-Bipyridyl-6,6'-diamine (0.186 g, 1 × 10⁻⁴ mol) and triethylamine (0.01 g, 1 × 10⁻⁴ mol) were dissolved in 10 mL of dichloromethane. 2,2'-Bipyridyl-6,6'-diacid chloride (0.0281 g, 1 × 10⁻⁴ mol) was also dissolved in 10 mL of dichloromethane. Both solutions were added to 100 mL dichloromethane in a 300 mL three-necked flask with reflux condenser by using a syringe pump for over 7 h under an argon atmosphere. This reaction mixture was refluxed during the coupling reaction. Furthermore, the reaction solution was refluxed for 2 h after addition of all solutions. After cooling, the solvent was evaporated to dryness. The product was purified by column chromatography on silica-gel (Wako-gel, C-300). The chloroform-hexane system

was used as the eluents. The first fraction eluted is the product (yield, 56%). The second and third fractions were open-chain products. The structures of product was confirmed by UV-vis spectroscopy, infrared spectroscopy, ¹H-NMR (270 MHz) spectroscopy, elemental analysis, and mass spectroscopy. ¹H-NMR (CDCl₃, 298 K) δ 7.90–8.2 (4H, m), 7.61–7.77 (6H, m), 7.20 (2H, d). IR (KBr disk), (cm⁻¹) 3406, 3961, 2925, 2854, 1738, 1640, 1581, 1430, 1393, 1294, 1251, 1145, 1077, 968, 831, 790, 765, 703, 612. UV-vis (MeOH) λ_{max} (nm) 246, 285, 330. Mass. C₂₂H₁₄N₆O₂: *m/z* 394. Anal. Calcd (%) for C₂₂H₁₄N₆O₂: C, 67.01; H, 3.55; N, 21.32. Found (%): C, 66.85; H, 3.63; N, 21.21.

4.7. Preparation of Mn complex **4**

Complex **4** was synthesized by addition of manganese chloride to the CH₂Cl₂ solution of macrocycles **3**. A large excess of manganese chloride was added to the CH₂Cl₂ solution of **3** under an argon atmosphere. After being stirred for 3 h at room temperature, the reaction mixture was exposed to air and stirred under an oxygen atmosphere for 3 h. After filtration to remove the solid, the solvent was evaporated partially by rotary evaporator, and as a result, the reaction mixture was concentrated. This reaction mixture was stood under air for overnight at room temperature, and the product as a precipitate was isolated by filtration. IR (KBr disk) (cm⁻¹) 2925, 2854, 1622, 1456, 1398, 1339, 1270, 1184, 1121, 1080, 1018, 988. UV-vis (MeOH) λ_{max} (nm) 252, 266, 276, 306, 315. Mass, C₂₂H₁₂N₆O₂MnCl: *m/z* 482. Anal. Calcd (%) for C₂₂H₁₂N₆O₂MnCl: C, 54.73; H, 2.49; N, 17.41. Found (%): C, 54.35; H, 2.56; N, 17.32.

4.8. Hydrocarbon oxidation reactions. General procedures

Complex **4**-catalyzed oxidations of hydrocarbons with hydrogen peroxide were carried out as follows. Complex **4** was dissolved in the mixture of 0.2 mL CH₂Cl₂ and 0.2 mL CH₃CN in a 5 mL round bottom flask, which was replaced by argon. The substrate (1 M) were added to this solution (1 × 10⁻³ M) containing **4**. Hydrogen peroxide (2 × 10⁻² M) was slowly added over a period of 3 min to the solution of **4** and substrate while stirring under an argon atmosphere. This reaction mixture was stirred for 60 min for alkanes (30 min for alkenes). The reaction mixture was filtered, and then the products were analyzed directly by gas chromatography or HPLC. The yields of products were based on hydrogen peroxide added.

The hydrocarbon oxidation reactions using **4** as the catalyst and pentafluoroiodosylbenzene (C₆F₅IO) [31] as the oxidant were carried out by the same procedure, but the solvent used was CH₂Cl₂ (0.2 mL) + CH₃CN (0.1 mL) in this case. The reaction time was 30 min. The initial reaction mixture was heterogeneous, but continued stirring of this heterogeneous reaction mixture eventually led to the homogeneous solution.

Complexes **2b** and **c** were dissolved in 0.1 mL dichloromethane in 1 mL test tube [32]. The substrate (1 M) were added to this solution (1 × 10⁻³ M) containing **2**, and the test tube was sealed with a silicon septum. The contents were thoroughly mixed, and C₆F₅IO (6 × 10⁻² M)

was added. This reaction mixture was shaken until all of C_6F_5IO was dissolved. This procedure was carried out under an argon atmosphere. After filtration to remove unresolved materials, this solution was stood for 30 min and was injected directly to gas chromatography by microsyringe. The yields were based on integration of the products versus that of C_6F_5I formed. The trials to analyze the products after several epoxide cycles were carried out. Moreover, to confirm exactness of this experiment, this procedure was applied for alkene oxidation catalyzed by tetrakis-(2,6-dichlorophenyl)porphyrin iron (III) chloride and the results obtained were consistent with the previously reported results [18–20]. Since this reaction condition is the same as the oxidation reaction catalyzed by the porphyrin metal complexes, the data obtained by the Mn complexes used in this work could be compared directly with those by the porphyrin metal complexes which were reported previously.

The blank experiments without **2** or **4** did not afford any oxidation products.

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[41] The trials of structural characterization of X-ray crystallography of the intermediates formed from complexes 2 and 4 were unsuccessful, because these intermediates were too unstable to isolate as a single crystal.