Heteroatom Chemistry
Volume 12, Number 5, 2001

Synthesis and Properties of Group 15 Element Porphyrin Peroxides

Wataru Satoh, Shuji Masumoto, Yohsuke Yamamoto, and Kin-ya Akiba

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan; Tel./Fax: +81-3-5286-3156; E-mail: akibaky@mn.waseda.ac.jp

Received 10 January 2001; revised 21 March, 2001

ABSTRACT: *[(Por)M(R)(OOR′)]$^+$Y$^-$ (Por: TPP [tetraphenylporphyrin], OEP [octaethylporphyrin]; M: Sb, As, P; R: Me, Et, Ph; R′: H, C(=O)m-ClC$_6$H$_4$, t-Bu) were prepared from [(Por)M(R)(X)]$^+$Y$^-$ (X: OTf, Br). The reactivities of the peroxide porphyrins toward nucleophiles such as triphenylphosphine increased in the order of -OOt-Bu, m-CPBA, and -OOH derivatives. Phosphorus (P-OOH) and arsenic hydroperoxide (As-OOH) were much more reactive than the corresponding antimony hydroperoxide (Sb-OOH). The higher reactivity of phosphorus and arsenic peroxides can be explained by the stability of the M=O (M=P, As) bonding system in the intermediates of the oxidation reactions. An X-ray structural analysis of [(TPP)Sb(Me)(OOt-Bu)]$^+$PF$_6^-$ is presented.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:431–443, 2001

INTRODUCTION

Transition metal porphyrins having oxygen–oxygen bonds have attracted great attention, especially in relation to oxidation reactions by cytochrome P450 [1–29]. In the catalytic oxidation cycle of cytochrome P450, one of the essential steps is protonation of an Fe(III) dianion complex to give an Fe-OOH complex and cleavage of the O–O bond to give a reactive iron–oxo species [6]. However, investigation of these M-OOH porphyrins have been limited, due to instability of the species, although unstable iron porphyrins bearing an OOH group have been investigated at very low temperatures [24,25].

As for main group element porphyrins, some porphyrins having M-OOR (R = alkyl) bonds have been reported to be relatively stable [30,31]. For example, germanium porphyrins with OOEt bonds have been prepared by an oxygen insertion reaction to the germanium alkyl or by substitution with alkyl hydroperoxide [32]. However, to our knowledge, there have been no reports on main group porphyrins bearing an OOH group, which should be of interest because the properties of these compounds could provide an understanding of the iron intermediates in the catalytic cycle of P450. Here, we report synthesis of group 15 element porphyrins containing an OOH group by reactions of [(Por)M(R)(X)]$^+$Y$^-$ [Por: TPP [tetraphenylporphyrin], OEP [octaethylporphyrin]; M: Sb, As, P; R: Me, Et, Ph; X: Br, OTf] with hydrogen peroxide, as shown in Scheme 1 {[(TPP)Sb(Me)(OOR′)]$^+$X$^-$ (**2-X**) is shown

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

Correspondence to: Kin-ya Akiba.

Contract Grant Sponsor: Ministry of Education, Science, Sports, and Culture of Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 09239103.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 09440218.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 11166248.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 11304044.

as an example}. In addition, the reactivity of group 15 element porphyrin peroxides bearing an OOH group toward nucleophiles such as triphenylphosphine have been investigated in light of the difference of porphyrin skeletons, central elements, and axial substituents.

RESULTS AND DISCUSSION

*Preparation of [(TPP)Sb(Me)(OOt-Bu)]$^+PF_6^-$ (**4-PF$_6$**)*

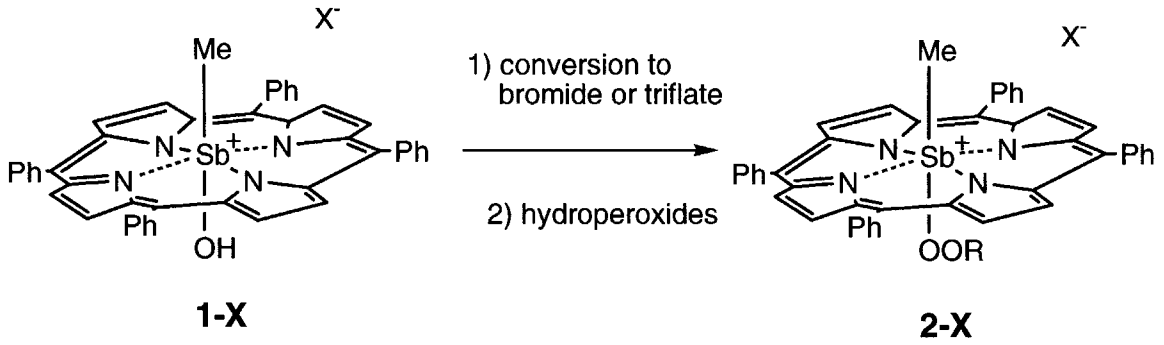
[(TPP)Sb(Me)(OH)]$^+$OH$^-$ (**1-OH**) [33] was converted to a moisture sensitive [(TPP)Sb(Me)(Br)]$^+$Br$^-$ (**3-Br**) [34] with oxalyl bromide. **3-Br** was treated in situ with anhydrous *t*-butyl hydroperoxide in nonane [35] to give [(TPP)Sb(Me)(OO*t*-Bu)]$^+$PF$_6^-$ (**4-PF$_6$**) in 88% yield after counteranion exchange (Scheme 2).

4-PF$_6$ was relatively stable toward atmospheric moisture, but it was gradually decomposed during neutral alumina column chromatography. **4-PF$_6$** was identified by elemental analysis and X-ray crystallographic analysis (vide infra). The ^{1}H NMR spectrum of **4-PF$_6$** showed a characteristic *t*-butyl signal at a very high field (δ − 1.79) due to the large ring current effect of the porphyrin nucleus [36]. The reactions of **4-OH** with some nucleophiles, such as triphenylphosphine, *p*-bromothioanisole, and styrene, were examined at room temperature. The oxidation of triphenylphosphine with **4-OH** gave triphenylphosphine oxide, **1-OH**, and $(Me)_2C=CH_2$ quantitatively, which were characterized by their ^{1}H NMR spectra. *p*-Bromothioanisole and styrene did not react with **4-OH**.

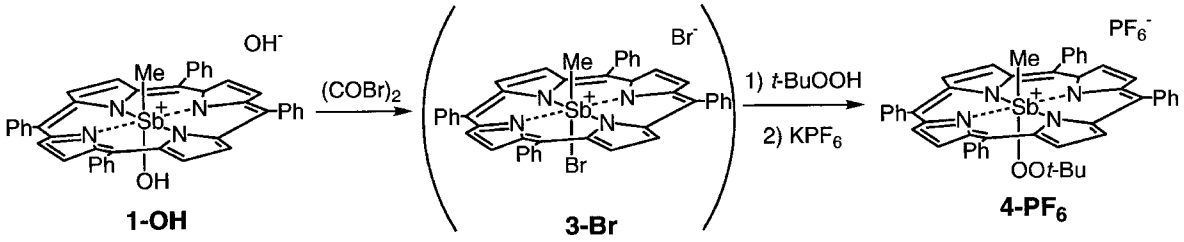
*X-Ray Structure of [(TPP)Sb(Me)(OOt-Bu)]$^+PF_6^-$ (**4-PF$_6$**)*

Crystals of [(TPP)Sb(Me)(OO*t*-Bu)]$^+$PF$_6^-$ (**4-PF$_6$**) suitable for X-ray analysis were obtained by recrystallization from dichloromethane/hexane (1:1). The unit cell of **4-PF$_6$** contains three independent molecules with slightly different orientations. The selected bond lengths and angles for three molecules are presented in Table 1, and Figure 1 shows the ORTEP drawing of one of these molecules.

The geometry about antimony is a distorted octahedron, and the average Sb–N bond length is calculated to be 2.09(3) Å, which is almost identical with that of [(TPP)Sb(Me)(OC(O)*m*-ClC$_6$H$_4$)]$^+$PF$_6^-$ (**5-PF$_6$**) (2.09(1) Å) [34] and [(TPP)Sb(Me)(F)]$^+$PF$_6^-$ (**7-PF$_6$**) (2.086(4) Å) [33]. The average Sb–O bond length (1.98(2) Å) in **4-PF$_6$** is slightly shorter than the reported Sb–O bond length in Ph$_4$Sb(OO*t*-Bu) (2.111 Å) [37] and Ph$_3$Sb(OO*t*-Bu)$_2$ (2.057 Å and 2.065 Å) [38], probably due to the cationic nature of the antimony atom in **4-PF$_6$**. It is interesting to note that the antimony atom lies ca. 0.13 Å (1st molecule: 0.16 Å, 2nd molecule: 0.11 Å, 3rd molecule: 0.12 Å) out-



SCHEME 1



SCHEME 2

TABLE 1 Selected Bond Lengths and Angles for $[(TPP)Sb(Me)(OOt\text{-}Bu)]^+PF_6^-$ (**4-PF$_6$**)

1st Molecule	Bond Lengths (Å)		
Sb(1)–C(101)	2.18(3)	Sb(1)–O(101)	2.00(2)
Sb(1)–N(101)	2.09(3)	Sb(1)–N(102)	2.08(2)
Sb(1)–N(103)	2.13(3)	Sb(1)–N(104)	2.11(3)
O(101)–O(102)	1.48(3)	O(102)–C(146)	1.44(4)
	Bond Angles (°)		
C(101)–Sb(1)–O(101)	176.3(10)	C(101)–Sb(1)–N(101)	95(1)
C(101)–Sb(1)–N(102)	93(1)	C(101)–Sb(1)–N(103)	93(1)
C(101)–Sb(1)–N(104)	95(1)	O(101)–Sb(1)–N(101)	84.5(9)
O(101)–Sb(1)–N(102)	82.9(8)	O(101)–Sb(1)–N(103)	87.2(9)
O(101)–Sb(1)–N(104)	88.5(9)	Sb(1)–O(101)–O(102)	110(1)
O(101)–O(102)–C(146)	106(2)		
2nd Molecule	Bond Lengths (Å)		
Sb(2)–C(201)	2.15(3)	Sb(2)–O(201)	1.95(2)
Sb(2)–N(201)	2.08(2)	Sb(2)–N(202)	2.08(2)
Sb(2)–N(203)	2.11(2)	Sb(2)–N(204)	2.07(2)
O(201)–O(202)	1.48(3)	O(202)–C(246)	1.42(6)
	Bond Angles (°)		
C(201)–Sb(2)–O(201)	177.2(10)	C(201)–Sb(2)–N(201)	93.6(10)
C(201)–Sb(2)–N(202)	92(1)	C(201)–Sb(2)–N(203)	92.7(10)
C(201)–Sb(2)–N(204)	92(1)	O(201)–Sb(2)–N(201)	88.3(9)
O(201)–Sb(2)–N(202)	84.9(10)	O(201)–Sb(2)–N(203)	85.4(9)
O(201)–Sb(2)–N(204)	89.2(10)	Sb(2)–O(201)–O(202)	119(2)
O(201)–O(202)–C(246)	106(3)		
3rd Molecule	Bond Lengths (Å)		
Sb(3)–C(301)	2.12(3)	Sb(3)–O(301)	1.99(3)
Sb(3)–N(301)	2.09(3)	Sb(3)–N(302)	2.12(3)
Sb(3)–N(303)	2.10(2)	Sb(3)–N(304)	2.05(3)
O(301)–O(302)	1.39(4)	O(302)–C(346)	1.52(6)
	Bond Angles (°)		
C(301)–Sb(3)–O(301)	173(1)	C(301)–Sb(3)–N(301)	95(1)
C(301)–Sb(3)–N(302)	90(1)	C(301)–Sb(3)–N(303)	90(1)
C(301)–Sb(3)–N(304)	95(1)	O(301)–Sb(3)–N(301)	88(1)
O(301)–Sb(3)–N(302)	84(1)	O(301)–Sb(3)–N(303)	85(1)
O(301)–Sb(3)–N(304)	89(1)	Sb(3)–O(301)–O(302)	114(2)
O(301)–O(302)–C(346)	95(3)		

of-plane of the four nitrogens toward the carbon atom in **4-PF$_6$**, and the distance is less than that of **5-PF$_6$** (0.182 Å) and **7-PF$_6$** (0.201 Å). Since an -OO*t*-Bu group can be considered as a less electronegative group than -OC(O)Ar and -F groups, the smaller deviation from the plane in **4-PF$_6$** is consistent with the conclusion that the deviation becomes larger as the difference of electronegativity between two axial groups becomes larger [39].

*Preparation of [(TPP)Sb(Me)(OOC(O)m-ClC$_6$H$_4$)]$^+$ClO$_4^-$ (**6-ClO$_4$**)*

In order to obtain the *m*-chloroperbenzoic acid (*m*-CPBA) adduct, $[(TPP)Sb(Me)(OOC(O)m\text{-}ClC_6H_4)]^+X^-$ (**6-X**), the reaction of **3-X** (X = Br, ClO_4 and PF_6) with *m*-CPBA in acetonitrile was carried out. However, formation of **6-X** was found to be largely dependent on the kind of counteranion. By use of the bromide as a counteranion, the reaction of **3-Br** with *m*-CPBA gave $[(TPP)Sb(Me)(OC(O)m\text{-}ClC_6H_4)]^+Br^-$ (**5-Br**) as a major product, and **5-PF$_6$** was characterized by the ^{1}H NMR spectrum and the X-ray crystallographic analysis (Scheme 3) [34].

On the other hand, the reaction of **3-PF$_6$** with *m*-CPBA yielded $[(TPP)Sb(Me)(F)]^+PF_6^-$ (**7-PF$_6$**) as a major product.

The desired product **6-X** (X = Br, PF_6) was characterized as a minor product based on the ^{1}H NMR spectra in both cases. However, **6-X** was gradually

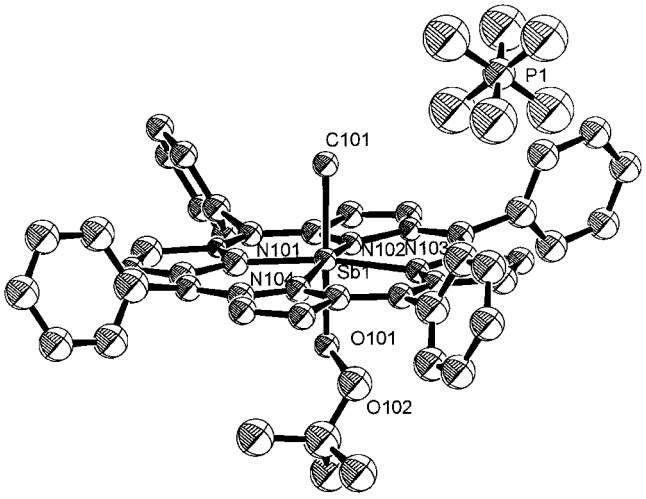


FIGURE 1 Crystal structure (30% thermal ellipsoids) of $[(TPP)Sb(Me)(OOt\text{-}Bu)]^+PF_6^-$ (**4-PF$_6$**) (one of the three independent molecules is shown). Hydrogen atoms are omitted for clarity.

decomposed by chromatographic treatment to give a mixture of **6-X** and **1-X**.

The reaction of **3-ClO$_4$** with *m*-CPBA gave **6-ClO$_4$** almost exclusively. After removal of an excess of *m*-CPBA by cooled neutral alumina column chromatography using acetonitrile (ca. 0°C) as an eluent, **6-ClO$_4$** was obtained in 97% yield.

6-ClO$_4$ gradually decomposed at room temperature to give **1-ClO$_4$** in air but was relatively stable under Ar. The benzene protons of **6-ClO$_4$** appeared at lower fields than the corresponding protons of **5-Br**, [**6-ClO$_4$**: δ 5.68 (2-H, s), 5.88 (6-H, d), 6.93 (5-H, t), 7.28 (4-H, d)] and [**5-Br**: 4.00, 4.60, 6.23, 6.65], probably because the benzene protons in **6-ClO$_4$** are further away from the porphyrin plane by one oxygen atom, and the ring current effect of the porphyrin core becomes less effective in **6-ClO$_4$**.

The reaction of **6-ClO$_4$** with triphenylphosphine gave the triphenylphosphine oxide quantitatively, but *p*-bromothioanisole and styrene did not react with **6-ClO$_4$**. After the reaction with triphenylphosphine, **6-ClO$_4$** was converted to **1-ClO$_4$** and *m*-chlorobenzoic acid.

*Preparation of $[(TPP)Sb(Me)(OOH)]^+ClO_4^-$ (**8-ClO$_4$**)*

Next we tried to prepare the target hydroperoxy derivative. However, the reaction of **3-ClO$_4$** with 35% aqueous hydrogen peroxide at room temperature for 6 hours gave only **1-ClO$_4$**. After several trials the reaction of **3-ClO$_4$** with relatively anhydrous hydrogen peroxide in acetonitrile at room temperature for 1 day afforded the desired $[(TPP)Sb(Me)(OOH)]^+ClO_4^-$ (**8-ClO$_4$**) in 92% purity based on its ^{1}H NMR spectrum (Scheme 4). Relatively anhydrous hydrogen peroxide was obtained by removal of water from 35% aqueous H_2O_2 using a vacuum pump at room temperature for several hours.

8-ClO$_4$ was unstable to atmospheric moisture and gradually decomposed to **1-ClO$_4$** at room temperature. **8-ClO$_4$** was less stable than **6-ClO$_4$** and **4-PF$_6$**. However, the molecular ion peak of **8-ClO$_4$** could be observed by fast atom bombardment (FAB) mass spectrometry (matrix; nitrobenzyl alcohol).

Then, we found the activation of the axial hydroxy group in **1-ClO$_4$** by conversion to the triflate was quite effective to form **8-ClO$_4$** without contamination. The reaction of **1-ClO$_4$** with trifluoromethanesulfonic anhydride (Tf_2O) at room temperature for 0.5 hour gave $[(TPP)Sb(Me)(OTf)]^+ClO_4^-$ (**9-ClO$_4$**), which was treated with relatively anhydrous hydrogen peroxide at room temperature for 1 day in situ to give **8-ClO$_4$** quantitatively.

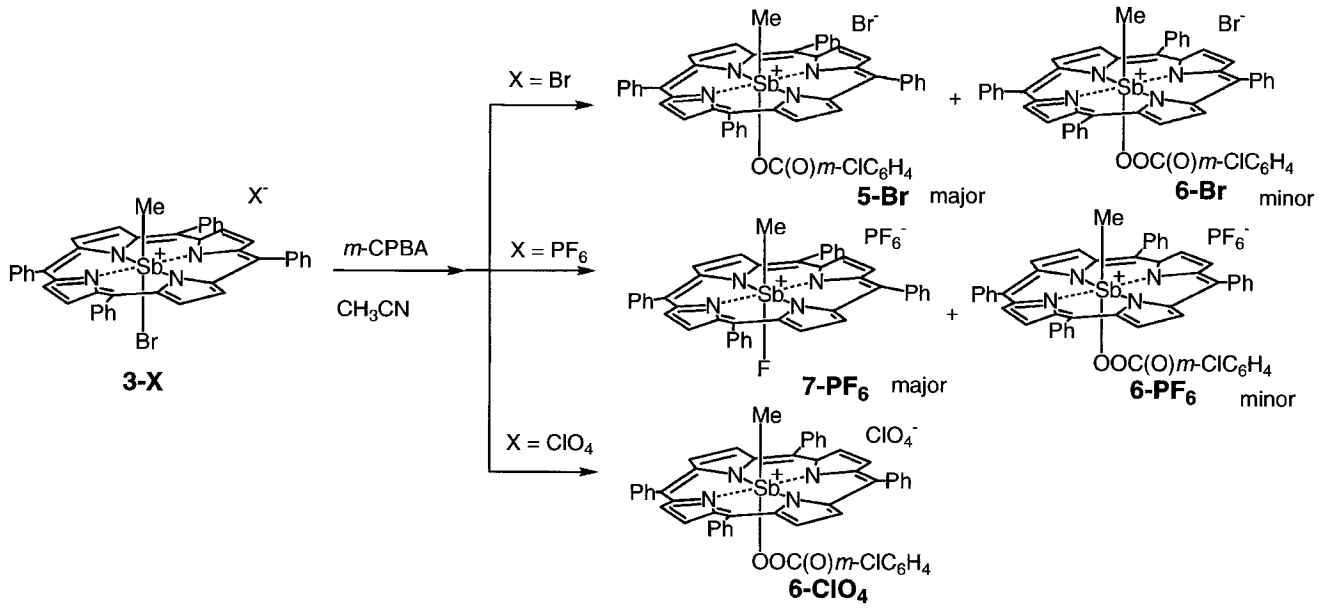
The ^{1}H NMR spectrum of **8-ClO$_4$** was superimposable on that of **8-ClO$_4$**, which was prepared from **3-ClO$_4$**. The FAB mass spectrum also showed the molecular ion peak. **8-ClO$_4$** reacted with triphenylphosphine and *p*-bromothioanisole at room temperature within 0.5 hour to give the corresponding oxides, but, even after several days at room temperature, the reaction of **8-ClO$_4$** with olefins such as styrene and stilbene did not take place, and **8-ClO$_4$** remained intact under Ar.

Evidence of the Presence of an OOH Bond by Chemical Transformation

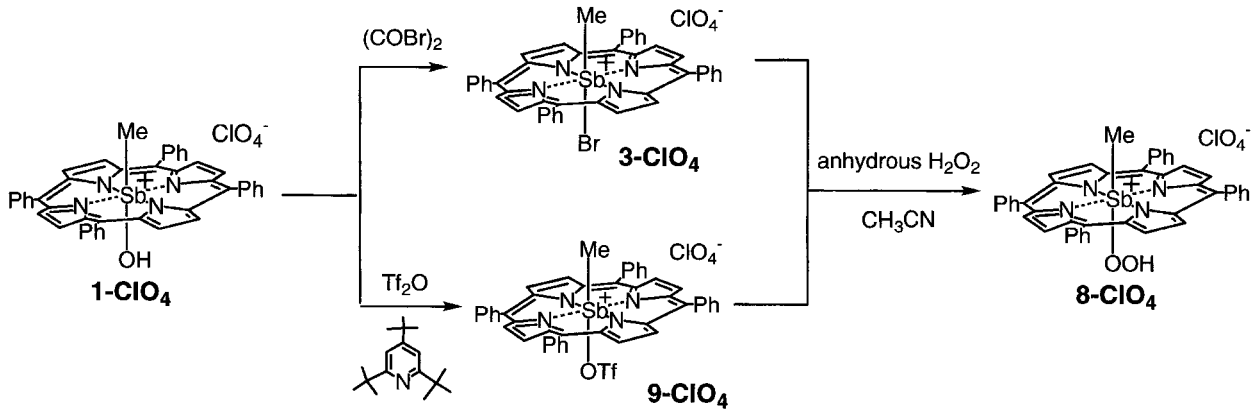
In order to characterize the OOH bond of **8-ClO$_4$** by transformation to other more stable peroxides, **8-ClO$_4$** was converted to $[(TPP)Sb(Me)(OOC(O)m\text{-}ClC_6H_4)]^+ClO_4^-$ (**6-ClO$_4$**) and $[(TPP)Sb(Me)(OOSiMe_3)]^+ClO_4^-$ (**10-ClO$_4$**). The reaction of **8-ClO$_4$** with *m*-chlorobenzoyl bromide [38] in the presence of 2,4,6-tri-*t*-butylpyridine as an acid scavenger at room temperature for 1 day gave **6-ClO$_4$** in 76% yield, based on the ^{1}H NMR spectrum. **6-ClO$_4$**, which was formed by this transformation, was identical with **6-ClO$_4$**, which was prepared by the reaction of **3-ClO$_4$** with *m*-CPBA.

In addition, treatment of **8-ClO$_4$** with trimethylsilyl bromide in the presence of 2,4,6-tri-*t*-butylpyridine at room temperature for 1 hour yielded **10-ClO$_4$** in 91% yield, based on the ^{1}H NMR spectrum (Scheme 5). **10-ClO$_4$** was identified by their high-resolution mass spectrometry (HRMS) (FAB[+]) spectra.

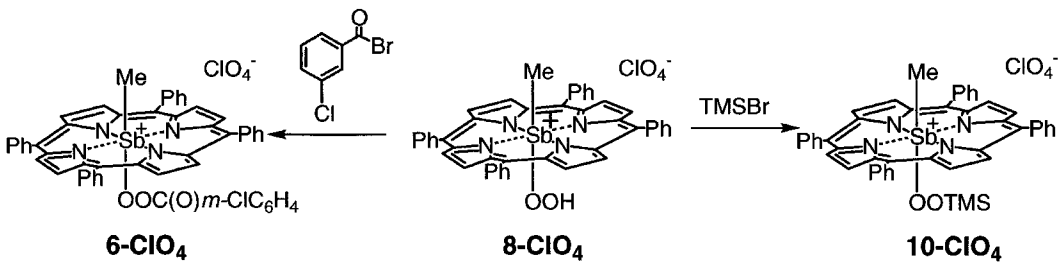
The characteristic trimethylsilyl proton signal in



SCHEME 3



SCHEME 4



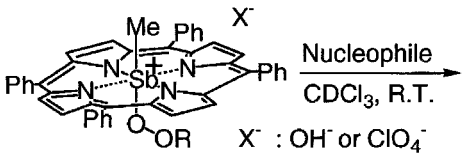
SCHEME 5

10-ClO_4 (δ −4.97) appeared at lower field in comparison with that of [(TPP)Sb(Me)($OSiMe_3$)]$^+ClO_4^-$ (**11-ClO_4**) (δ −5.11) since these protons in **10-ClO_4** are further away from the porphyrin ring. **11-ClO_4** as the reference compound was prepared by reaction of **1-OH** with trimethylsilyl bromide in excellent yield. **10-ClO_4** gradually decomposed to **11-ClO_4** at room temperature. It can be concluded that the formation of **8-ClO_4** bearing an OOH group was fully established by the previous transformations.

Reactivity of Antimony Porphyrin Peroxides

A comparison of reactivity among antimony tetraphenylporphyrin peroxides is summarized in Table 2. The reactions of **4-OH, 6-ClO_4**, and **8-ClO_4** with nucleophiles, such as triphenylphosphine, *p*-bromothioanisole, and styrene, were carried out at room temperature for several days and monitored by ^{1}H NMR spectroscopy. The oxidizing ability of these peroxides increased in the order of -OO*t*-Bu, *m*-CPBA, and -OOH derivatives. Only **8-ClO_4** reacted with *p*-bromothioanisole to give the corresponding sulfoxide.

TABLE 2 Reactivity of Antimony Tetraphenylporphyrin Peroxides towards Nucleophiles



OOR	OO*t*-Bu **4-OH**	OOC(O)*m*-ClC_6H_4 **6-ClO_4**	OOH **8-ClO_4**
Ph_3P	50 h	24 h	10 minutes
Br-⟨⟩-SMe	no reaction	no reaction	30 minutes
Ph⟨	no reaction	no reaction	no reaction

*Preparation of [(OEP)Sb(R)(OOH)]$^+ClO_4^-$ (***16-ClO_4, 17-ClO_4***)*

In order to investigate electronic effects of the porphyrin skeleton, antimony octaethylporphyrin peroxides were prepared. The reaction of [(OEP)Sb(Me)(OH)]$^+ClO_4^-$ (**12-ClO_4**) with Tf_2O at room temperature for 1 hour gave [(OEP)Sb(Me)(OTf)]$^+ClO_4^-$ (**14-ClO_4**), which was reacted in situ with relatively anhydrous hydrogen peroxide at room temperature for 1 hour to give [(OEP)Sb(Me)(OOH)]$^+ClO_4^-$ (**16-ClO_4**) quantitatively. **16-ClO_4** was stable to moisture but gradually decomposed during chromatographic treatment. [(OEP)Sb(Et)(OOH)]$^+ClO_4^-$ (**17-ClO_4**) was also prepared from [(OEP)Sb(Et)(OH)]$^+ClO_4^-$ (**13-ClO_4**) by similar procedures (Scheme 6). **17-ClO_4** was also stable to moisture. **16-ClO_4** and **17-ClO_4** were characterized by their HRMS (FAB[+]) spectra.

We tried to prepare the corresponding OO*t*-Bu and *m*-CPBA adducts from [(OEP)Sb(R)(OTf)]$^+ClO_4^-$ (R = Me, **14-ClO_4**; R = Et, **15-ClO_4**) under similar conditions, but the corresponding peroxides [(OEP)Sb(R)(OO*t*-Bu)]$^+ClO_4^-$ (**18-ClO_4**) and [(OEP)Sb(R)(OOC(O)*m*-ClC_6H_4)]$^+ClO_4^-$ (**19-ClO_4**) were not obtained.

*Preparation of [(OEP)P(R)(OOH)]$^+OTf^-$ (***26-OTf, 27-OTf, 28-OTf***)*

The reaction of [(OEP)P(Me)(OH)]$^+X^-$ (**20-X**) [38] (X = Cl, ClO_4, and PF_6) with Tf_2O at room temperature for 1 hour gave [(OEP)P(Me)(OTf)]$^+X^-$ (**23-X**), respectively. The reaction of **23-X** with relatively anhydrous hydrogen peroxide at room temperature for 1 day gave the desired [(OEP)P(Me)(OOH)]$^+OTf^-$ (**26-OTf**) only in the case of the chloride (**20-Cl**). The use of other counteranions resulted in decomposition to insoluble products in acetonitrile. [(OEP)P(Et)(OH)]$^+Cl^-$ (**21-Cl**) and [(OEP)P(Ph)(OH)]$^+Cl^-$ (**22-Cl**) gave [(OEP)P(Et)(OOH)]$^+OTf^-$ (**27-OTf**) and [(OEP)P(Ph)(OOH)]$^+OTf^-$ (**28-OTf**), respectively, by similar procedures. In both cases, the desired hydroperoxides (**27-OTf** and **28-OTf**) were obtained only when chloride was used as a counteranion (Scheme 7).

The attempted transformations of **26-OTf, 27-OTf,** and **28-OTf** with *m*-chlorobenzoyl bromide or trimethylsilyl bromide to the corresponding *m*-CPBA and TMS derivatives were unsuccessful. Under the similar conditions used for antimony tetraphenylporphyrin peroxides, only **20-Cl, 21-Cl,** and **22-Cl** were recovered instead of the expected TMS and *m*-CPBA derivatives.

Moreover, the reaction of **23-Cl** with anhydrous *t*-butyl hydroperoxide and *m*-CPBA at room temperature for 5 days did not occur, probably because **23-Cl** was too bulky for *t*-BuOOH and *m*-CPBA reagents. Neither **23-Cl** nor **24-Cl** was able to afford the corresponding peroxides.

*Preparation of [(OEP)As(Me)(OOH)]$^+OTf^-$ (***33-OTf***)*

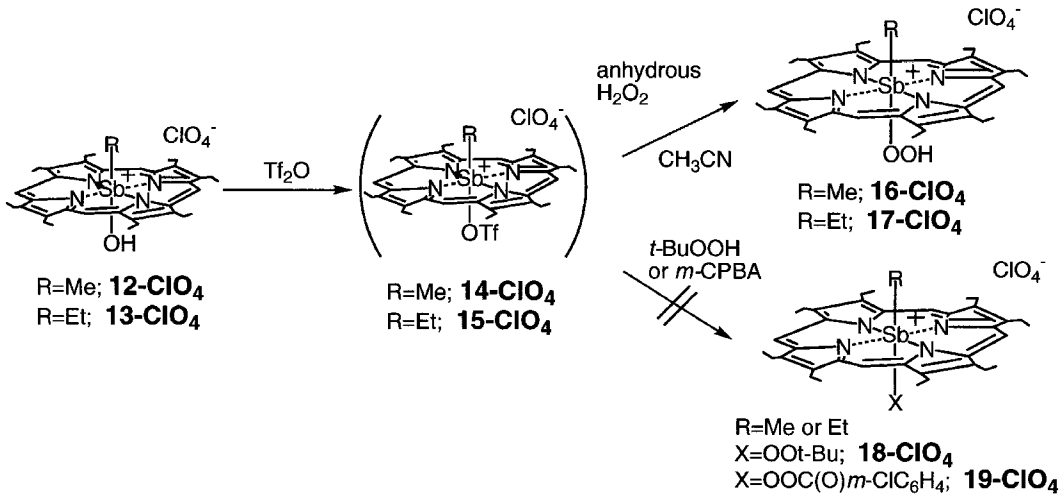
Arsenic porphyrin peroxide [(OEP)As(Me)(OOH)]$^+OTf^-$ (**33-OTf**) was prepared from [(OEP)As(Me)(OH)]$^+Cl^-$ (**31-Cl**) [39,40] by the similar method for

phosphorus porphyrin peroxides (Scheme 8). Only chloride **31-Cl** was effective for the formation of **33-OTf**. **33-OTf** could be prepared quantitatively, but it was less stable than the corresponding antimony porphyrin hydroperoxides (**16-ClO$_4$** and **17-ClO$_4$**). The reactions of **33-OTf** with *m*-chlorobenzoyl bromide and trimethylsilyl bromide under similar conditions gave only **31-OTf**.

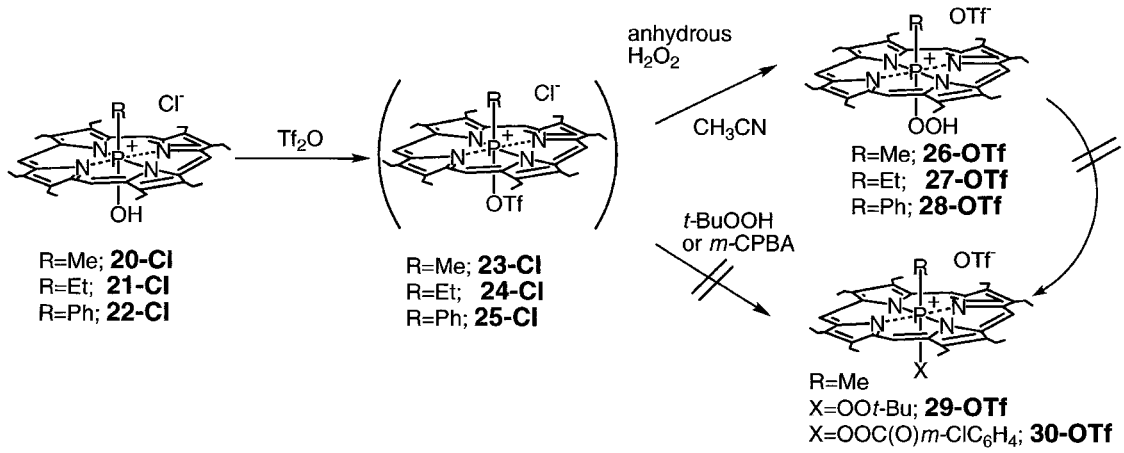
The reactions of **26-OTf, 27-OTf, 28-OTf**, and **33-OTf** with nucleophiles, such as triphenylphosphine and *p*-bromothioanisole, proceeded smoothly at room temperature during 0.5 hour, but the reaction with styrene did not take place even after a week.

Reactivity of Phosphorus, Arsenic, and Antimony Porphyrin Peroxides

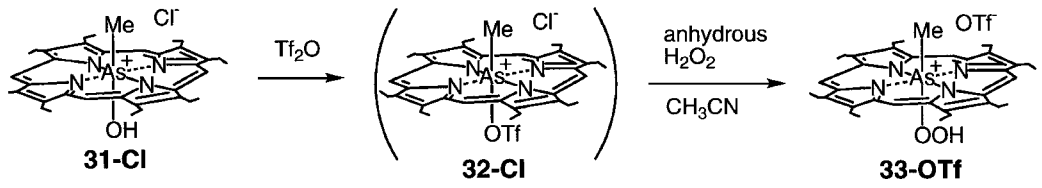
With nine kinds of group 15 element porphyrin peroxides bearing an OOR group in hand, the reactivity



SCHEME 6



SCHEME 7



SCHEME 8

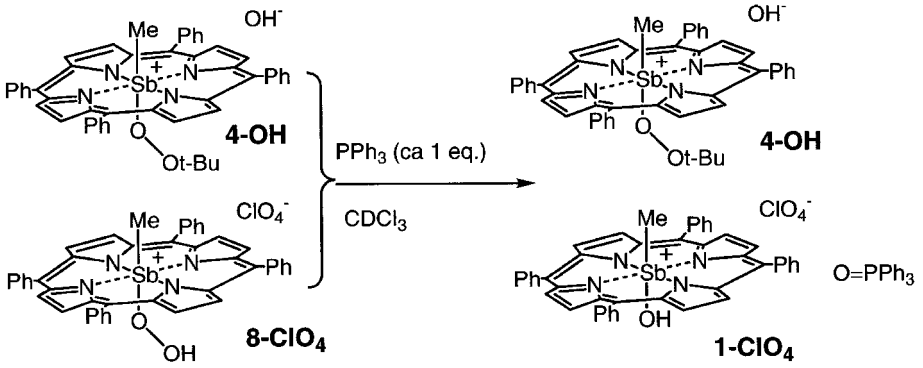
of these peroxides was examined in the light of the difference among central elements, electronic effects from porphyrin skeletons, and axial alkyl groups.

In order to compare the reactivities of [(TPP)Sb(Me)(OOt-Bu)]$^+$OH$^-$ (**4-OH**) [(TPP)Sb(Me)(OOC(O)*m*-ClC_6H_4)]$^+ClO_4^-$ (**6-ClO_4**), and [(TPP)Sb-(Me)(OOH)]$^+ClO_4^-$ (**8-ClO_4**), triphenylphosphine (less than 1 equivalent) was added portionwise to a mixture of an equimolar amount of **4-OH** and **8-ClO_4** at room temperature in deuteriochloroform, and the reaction was monitored by ^{1}H NMR spectroscopy. The experiment clearly indicated that **8-ClO_4** reacted with triphenylphosphine to give **1-ClO_4** and O=PPh_3, whereas **4-OH** remained intact during 0.5 hour. A similar experiment was carried out with an equimolar mixture of **6-ClO_4** and **8-ClO_4**, and it was found that **8-ClO_4** was much more reactive than **6-ClO_4** (Schemes 9 and 10).

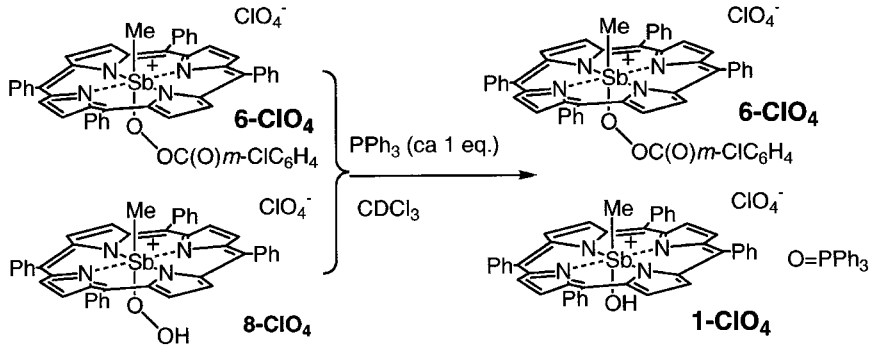
The experiment between antimony porphyrin hydroperoxide (**16-ClO_4**) and the corresponding phosphorus porphyrin hydroperoxide (**26-OTf**) under similar conditions clearly indicated that **26-OTf** was much more reactive to triphenylphosphine than **16-ClO_4**. **26-OTf** was converted to **20-OTf** but **16-ClO_4** still remained intact. The reaction between **16-ClO_4** and the corresponding arsenic porphyrin hydroperoxide (**33-OTf**) gave similar results, showing that **33-OTf** was much more reactive than **16-ClO_4** (Scheme 11).

Recently, we reported that (OEP)MR(=O) (M=P, As, R=Me, Et, Ph) were found to be almost planar and very stable in the case of the phosphorus [40] and arsenic porphyrins [41,42], but the corresponding antimony compound could not be isolated [33,34]. Therefore, we concluded that the higher reactivity of phosphorus and arsenic hydroperoxides could be due to the stability of the M=O bonding system itself and also due to the stability that might be gained by the change of the shape of the molecules from ruffled [(OEP)P(R)(OH)]$^+$ to planar (OEP)PR(=O), as shown in Scheme 12. That is, in the reaction of **26-OTf** with triphenylphosphine, the stable, neutral species (OEP)P(Me)(=O) should be the intermediate of the reaction (step A in Scheme 12). In contrast, the reaction of **16-ClO_4** with triphenylphosphine (step B in Scheme 12) gave planar **12-ClO_4** through relatively less stabilized **35**. This was exemplified by the weaker acidity of **12-ClO_4** compared with the corresponding phosphorus and arsenic porphyrin hydroxides (**20-OTf** and **31-OTf**) [40,41,42].

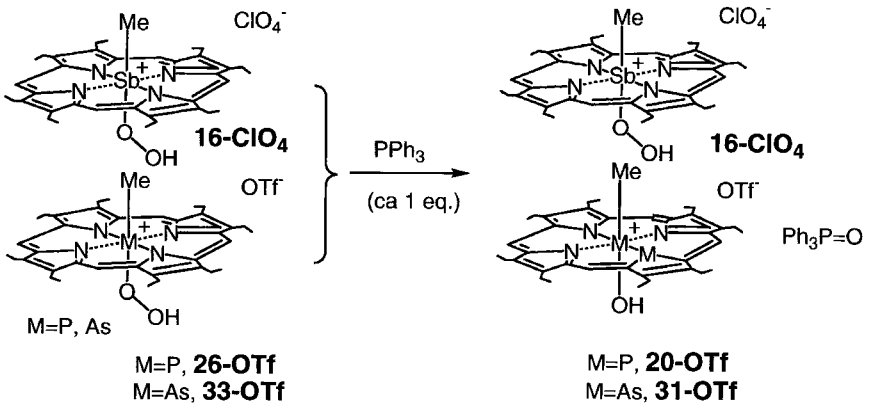
Let us consider electronic effect of axial groups



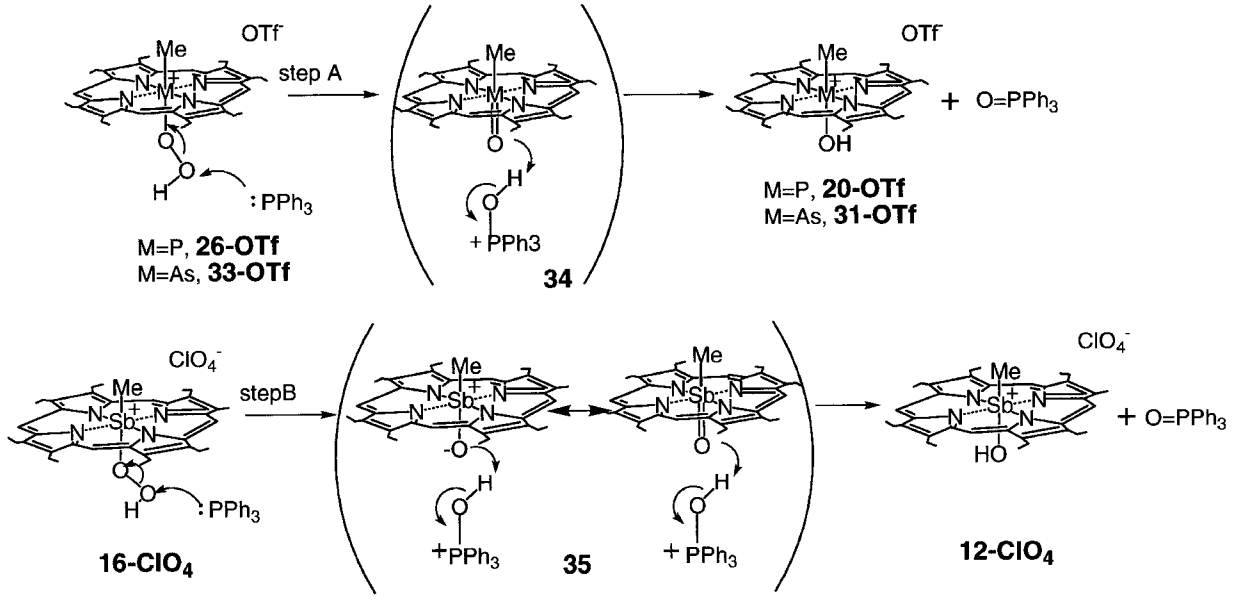
SCHEME 9



SCHEME 10



SCHEME 11



SCHEME 12

of the phosphorus porphyrin peroxides. Similar experiments were carried out between **26-OTf** and **28-OTf** and between **27-OTf** and **28-OTf** for comparison. The reaction of **28-OTf** with triphenylphosphine proceeded almost at the same rate as that with **26-OTf** (ratio ca. 1:1). The reaction between **28-OTf** and **27-OTf** with triphenylphosphine gave similar results. That is, the reactivity of **26-OTf, 27-OTf**, and **28-OTf** to triphenylphosphine is almost the same. The results indicated that the stability of the neutral species (OEP)P(R)(=O) was not noticeably different in these compounds (Scheme 13).

On the other hand, the reactivities of the antimony porphyrin hydroperoxides **16-ClO_4** and **17-ClO_4** were largely dependent on the electronic effect of the axial alkyl group. **16-ClO_4** reacted with triphenylphosphine at room temperature for 1 hour in $CDCl_3$, whereas **17-ClO_4** was inert to the same reagent at room temperature for even 5 days in $CDCl_3$. These results indicate that the electron-donating effect of the axial alkyl groups influences the stability of the starting hydroperoxides. That is, the degree of stabilization by the ethyl group is greater for the hydroperoxide than that for the intermediate.

In order to examine the electronic effects of porphyrin skeletons, a competition experiment between **8-ClO_4** with electron-poor tetraphenylporphyrin skeleton and **16-ClO_4** with electron-rich octaethylporphyrin skeleton was performed. The reaction of **8-ClO_4** with triphenylphosphine under similar conditions was faster than that of **16-ClO_4**. After the reaction with triphenylphosphine, the ratio of **8-ClO_4**

to **16-ClO$_4$** was about 1:3, indicating that electron-poor tetraphenylporphyrin was more reactive toward nucleophiles (Scheme 14). The electron-donating effect of the octaethylporphyrin core may be effective to stabilize the starting hydroperoxide in the antimony(V) porphyrins.

In conclusion, the reactivity of the peroxides described in this article can be explained primarily on the basis of the stability of the M=O bonding system. The electron-donating properties of porphyrin skeletons and axial groups play important roles in the reactivities of antimony porphyrins in which the Sb=O bonding system is not stable.

EXPERIMENTAL

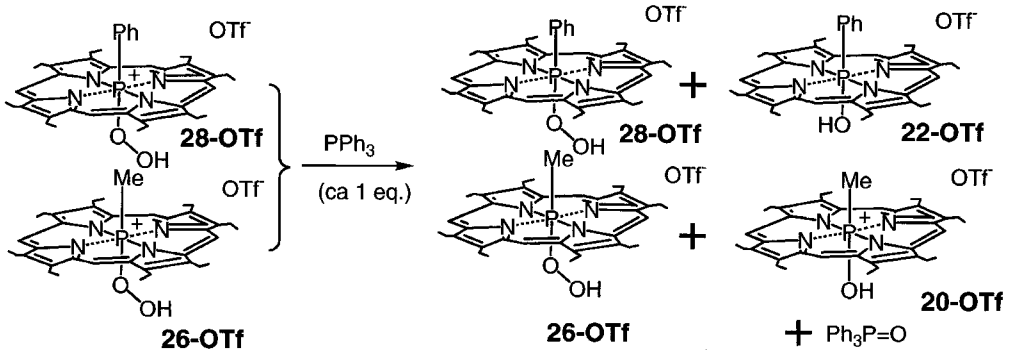
All solvents were dried and distilled prior to use. All reactions were carried out under Ar, and subsequent isolation and purification procedures were carried out in air. Melting points were measured with a Yanagimoto micromelting point apparatus and were uncorrected. ^{1}H NMR (400MHz) spectra were recorded on a JEOL EX-400 spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane. Elemental analyses were performed by a Perkin Elmer 2400 CHN elemental analyzer. Column chromatography was carried out on Merck alumina neutral 1077. The HRMS spectra were measured by a JEOL SX 102A spectrometer.

*Preparation of [(TPP)Sb(Me)(OOt-Bu)]$^+$PF$_6^-$ (**4-PF$_6$**)*

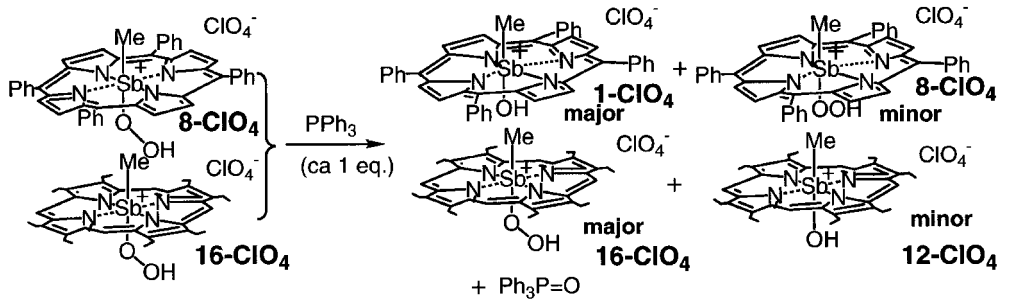
To a solution of [(TPP)Sb(Me)(OH)]$^+$OH$^-$ [33] (153 mg, 0.20 mmol) in dry dichloromethane (3 mL) was added oxalyl bromide (0.3 mL, 2.12 mmol) at room temperature. The mixture was stirred at room temperature for 1 hour under Ar. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (3.5 mL) under Ar. To the solution was added *t*-BuOOH in nonane (0.25 mL, 2.49 mmol) at 0°C. The mixture was stirred at room temperature for 3.5 days under Ar. After removal of the solvent in vacuo, extraction with dichloromethane (10 mL × 2) and removal of the solvent yielded a purple solid [(TPP)Sb(Me)(OO*t*-Bu)]$^+$OH$^-$ (147 mg, 88%). Counteranion exchange of the resulting hydroxide with potassium hexafluorophosphate in dichloromethane/acetonitrile (1:1) gave [(TPP)Sb(Me)(OO*t*-Bu)]$^+$PF$_6^-$ (**4-PF$_6$**) quantitatively. **4-PF$_6$**: m.p. 180–188°C (dec); ^{1}H NMR ($CDCl_3$) −5.20 (s, 3 H), −1.79 (s, 9 H), 7.84–7.95 (m, 12 H), 8.16–8.45 (m, 8 H), 9.41 (s, 8 H); Anal. Calcd for $C_{49}H_{40}F_6N_4O_2PSb$: C, 59.84; H, 4.10; N, 5.70. Found: C, 59.88; H, 3.99; N, 5.71.

*Preparation of [(TPP)Sb(Me)(OOC(O)m-ClC$_6$H$_4$)]$^+$ClO$_4^-$ (**6-ClO$_4$**)*

To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (76 mg, 0.088 mmol) in dry dichloromethane (2 mL) was



SCHEME 13



SCHEME 14

added 0.13 mL (0.92 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 hour at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (7 mL). *m*-CPBA (65 mg, 0.38 mmol) in acetonitrile (1 mL) was transferred to the solution at 0°C under Ar. The mixture was stirred for 24 hours at room temperature. After removal of the solvent in vacuo, the residue was chromatographed on neutral alumina (acetonitrile, 0°C) to remove excess *m*-CPBA. Evaporation of the solvent gave [(TPP)Sb(Me)(OOC(O)*m*-ClC_6H_4)]$^+ClO_4^-$ (**6-ClO_4**, 78 mg, 97%). **6-ClO_4**: m.p. 162–164°C (dec). ^{1}H NMR ($CDCl_3$) −4.81 (s, 3 H), 5.68 (s, 1 H), 5.88 (d, 1 H, J = 8 Hz), 6.93 (t, 1 H, J = 8 Hz), 7.28 (d, 1 H, J = 8 Hz), 7.79–7.93 (m, 12 H), 8.04–8.50 (m, 8 H), 9.44 (s, 8 H); HRMS [FAB(+)] calcd for $C_{52}H_{35}N_4O_3ClSb^+$(^{121}Sb, ^{35}Cl), 919.1436; found, 919.1392; calcd for (^{121}Sb, ^{37}Cl) and (^{123}Sb, ^{35}Cl), 921.1406 and 921.1440, respectively; found, 921.1433; calcd for (^{123}Sb, ^{37}Cl), 923.1410; found, 923.1445.

*Preparation of [(TPP)Sb(Me)(OOH)]$^+ClO_4^-$ (**8-ClO_4**) from [(TPP)Sb(Me)(Br)]$^+ClO_4^-$ (**3-ClO_4**)*

To a solution of [(TPP)Sb(Me)(OH)]$^+ClO_4^-$ (20 mg, 0.023 mmol) in dry dichloromethane (1 mL) was added 0.04 mL (0.28 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 hour at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (0.75 mL). Relatively anhydrous H_2O_2 (10 equivalents), which was obtained by removal of water from 35% aqueous H_2O_2 using a vacuum pump at room temperature for several hours in dry acetonitrile (0.5 mL), was added to the solution under Ar. The mixture was stirred for 1 day at room temperature. After the solvent was evaporated, [(TPP)Sb(Me)(OOH)]$^+ClO_4^-$ (quant. yield based on ^{1}H NMR spectroscopy, but the compound was contaminated with Br_2) was obtained.

*Preparation of Pure [(TPP)Sb(Me)(OOH)]$^+ClO_4^-$ (**8-ClO_4**) from [(TPP)Sb(Me)(OTf)]$^+ClO_4^-$ (**9-ClO_4**)*

To a solution of [(TPP)SbMe(OH)]$^+ClO_4^-$ (20 mg, 0.023 mmol) in dry dichloromethane (0.75 mL) was added a solution of 2,4,6-tri-*t*-butylpyridine (15 mg, 0.06 mmol) and trifluoromethanesulfonic anhydride (Tf_2O, 0.01 mL, 0.06 mmol) in dry dichloromethane (1 mL) under Ar. The mixture was stirred for 1 hour at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (1 mL). Relatively anhydrous H_2O_2 (10 equivalents) prepared as before in dry acetonitrile (0.5 mL) was added to the solution. The mixture was stirred for 1 day at room temperature under Ar. After the solvent was evaporated, [(TPP)Sb(Me)(OOH)]$^+ClO_4^-$ (quant. yield based on the ^{1}H NMR) was obtained. ^{1}H NMR ($CDCl_3$) −5.24 (s, 3 H), 7.83–7.91 (m, 12 H), 8.28–8.38 (m, 8 H), 9.40 (s, 8 H).

*Conversion of **8-ClO_4** to [(TPP)Sb(Me)(OOTMS)]$^+ClO_4^-$ (**10-ClO_4**)*

To a solution of **8-ClO_4** (10 mg, 0.011 mmol) in dry dichloromethane (0.75 mL) was added 2,4,6-tri-*t*-butylpyridine (19 mg, 0.076 mmol) and trimethylsilyl bromide (0.01 mL, 0.076 mmol) at room temperature under Ar. The mixture was stirred for 1 hour at room temperature. After removal of the solvent in vacuo, the residue was redissolved in dry deuteriochloroform (0.75 mL). Based on the ^{1}H NMR spectrum, **8-ClO_4** was converted to [(TPP)Sb(Me)(OOTMS)]$^+ClO_4^-$ in 91% yield and [(TPP)Sb(Me)(OTMS)]$^+ClO_4^-$ was obtained in 9% yield. ^{1}H NMR ($CDCl_3$) −4.97 (s, 3 H), −2.11 (s, 9 H), 7.98–8.16 (m, 12 H), 8.36–8.47 (m, 8 H), 9.59 (s, 8 H). HRMS (FAB(+)) calcd for $C_{48}H_{40}N_4O_2SiSb^+$(^{121}Sb), 853.1959; found, 853.1951.

*Conversion of **8-ClO_4** to [(TPP)Sb(Me)(OOC(O)m-ClC_6H_4)]$^+ClO_4^-$ (**6-ClO_4**)*

To a solution of **8-ClO_4** (10 mg, 0.011 mmol) in dry dichloromethane (0.75 mL) was added 2,4,6-tri-*t*-butylpyridine (18 mg, 0.076 mmol) and *m*-chlorobenzoyl bromide (0.01 mL, 0.075 mmol) at room temperature under Ar. The mixture was stirred for 1 day. After removal of the solvent in vacuo, the residue was redissolved in dry deuteriochloroform (0.75 mL). Based on the ^{1}H NMR spectrum, **8-ClO_4** was converted to [(TPP)Sb(Me)(OOC(O)*m*-ClC_6H_4)]$^+ClO_4^-$ (**6-ClO_4**) in 76% yield, and the rest was [(TPP)Sb(Me)(OH)]$^+ClO_4^-$.

Preparation of [(OEP)M(R)(OOH)]$^+ClO_4$

To a solution of [(OEP)M(R)(OH)]$^+ClO_4^-$ [34] (0.013 mmol) in dry dichloromethane (0.75 mL) was added a solution of 2,4,6-tri-*t*-butylpyridine (15 mg, 0.06 mmol) and Tf_2O (0.01 mL, 0.06 mmol) in dry dichloromethane (1 mL) under Ar. The mixture was stirred for 1 hour. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (1 mL). Relatively anhydrous H_2O_2 (10 equivalents) prepared as before in dry acetonitrile (0.5 mL) was added to the solution under Ar. The mixture was

stirred for 1 day under Ar. After the solvent was evaporated, $[(OEP)M(R)(OOH)]^+ClO_4^-$ (almost quant. based on the ^1H NMR) was obtained. Some of the products were chromatographed on neutral alumina (acetonitrile 0°C) to remove excess 2,4,6-tri-*t*-butylpyridine. Evaporation of the solvent gave pure product almost quantitatively. Products were characterized by ^1H NMR and HRMS.

$[(OEP)Sb(Me)(OOH)]^+ClO_4^-$ (**16-ClO$_4$**): ^1H NMR ($CDCl_3$) −5.89 (s, 3 H), 2.09 (t, 24 H, J = 7 Hz), 4.33 (q, 16 H, J = 7 Hz), 10.81 (s, 4 H); HRMS (FAB[+]) calcd for $C_{37}H_{48}N_4O_2Sb^+$ (^{121}Sb), 701.2816; found, 701.2817.

$[(OEP)Sb(Et)(OOH)]^+ClO_4^-$ (**17-ClO$_4$**, quant.). ^1H NMR ($CDCl_3$) −5.59 (q, 2 H, J = 7 Hz), −4.18 (t, 3 H, J = 7 Hz), 2.07 (t, 24 H, J = 7 Hz), 4.37 (q, 16 H, J = 7 Hz), 10.91 (s, 4 H); HRMS (FAB[+]) calcd for $C_{38}H_{50}N_4O_2Sb^+$ (^{121}Sb), 715.2972; found, 715.3014.

$[(OEP)P(Me)(OOH)]^+OTf^-$ (**26-OTf**, 96%): ^1H NMR ($CDCl_3$) −5.53 (s, 3 H), 1.88 (t, 24 H, J = 7 Hz), 3.98 (q, 16 H, J = 7 Hz), 9.59 (s, 4 H); HRMS (FAB[+]) calcd for $C_{37}H_{48}N_4O_2P^+$, 611.3515; found, 611.3560.

$[(OEP)P(Et)(OOH)]^+OTf^-$ (**27-OTf**, 91%): ^1H NMR ($CDCl_3$) −5.41 (dq, 2 H, J = 7 Hz, J = 7 Hz), −4.30 (dt, 3 H, J = 7 Hz, J = 7 Hz), 1.90 (t, 24 H, J = 7 Hz), 4.03 (q, 16 H, J = 7 Hz), 9.64 (s, 4 H); HRMS (FAB[+]) calcd for $C_{38}H_{50}N_4O_2P^+$, 625.3671; found, 625.3658.

$[(OEP)P(Ph)(OOH)]^+OTf^-$ (**28-OTf**, 85%): ^1H NMR ($CDCl_3$) 0.52 (dd, 2 H, J = 7 Hz, J = 7 Hz), 1.80 (t, 24 H, J = 7 Hz), 3.91 (bq, 16 H, J = 7 Hz), 4.86 (bm, 2 H), 5.53 (dt, 1 H, J = 7 Hz, J = 4 Hz), 9.41 (bs, 4 H); HRMS (FAB[+]) calcd for $C_{42}H_{50}N_4O_2P^+$, 673.3671; found, 673.3690.

$[(OEP)As(Me)(OOH)]^+OTf^-$ (**33-OTf**, quant): ^1H NMR ($CDCl_3$) −5.52 (s, 3 H), 2.06 (t, 24 H, J = 7 Hz), 4.25 (q, 16 H, J = 7 Hz), 10.56 (s, 4 H); HRMS (FAB[+]) calcd for $C_{37}H_{48}N_4O_2As^+$, 655.2993; found, 655.2979.

*Reactions of a Mixture of [(TPP)Sb(Me)(OOt-Bu)]$^+$OH$^-$ (**4-OH**) and [(TPP)Sb(Me)(OOH)]$^+$ClO$_4^-$ (**8-ClO$_4$**) with Triphenylphosphine*

A mixture of **4-OH** (9.4 mg, 0.011 mmol) and **8-ClO$_4$** (10 mg, 0.011 mmol) was dissolved in dry deuteriochloroform (0.75 mL). After portionwise addition of a small amount of triphenylphosphine (up to 1 equivalent) to the solution, the reaction mixture was monitored by ^1H NMR spectroscopy. Only **8-ClO$_4$** was converted to $[(TPP)Sb(Me)(OH)]^+ClO_4^-$, whereas **4-OH** still remained intact.

*[(TPP)Sb(Me)(OOC(O)m-ClC$_6$H$_4$)]$^+$ClO$_4^-$ (**6-ClO$_4$**) and [(TPP)Sb(Me)(OOH)]$^+$ClO$_4^-$ (**8-ClO$_4$**) with Triphenylphosphine*

The same procedure as in previous paragraph. Only **8-ClO$_4$** was converted to $[(TPP)Sb(Me)(OH)]ClO_4$, whereas **6-ClO$_4$** still remained intact.

*[(TPP)Sb(Me)(OOH)]$^+$ClO$_4^-$ (**8-ClO$_4$**) and [(OEP)Sb(Me)(OOH)]$^+$ClO$_4^-$ (**16-ClO$_4$**) with Triphenylphosphine*

The same procedure as previously described. The reaction of **8-ClO$_4$** with triphenylphosphine was faster than that of the corresponding **16-ClO$_4$** (ratio of 1:3 based on the integral ratio of the ^1H NMR spectrum).

*[(OEP)Sb(Me)(OOH)]$^+$ClO$_4^-$ (**16-ClO$_4$**) and [(OEP)P(Me)(OOH)]$^+$OTf$^-$ (**26-OTf**) with Triphenylphosphine*

The same procedure as previously described. Only **26-OTf** was converted to $[(OEP)P(Me)(OH)]^+OTf^-$, whereas **16-ClO$_4$** still remained intact.

*[(OEP)Sb(Me)(OOH)]$^+$ClO$_4^-$ (**16-ClO$_4$**) and [(OEP)As(Me)(OOH)]$^+$OTf$^-$ (**33-OTf**) with Triphenylphosphine*

The same procedure as previously described. Only **33-OTf** was converted to $[(OEP)As(Me)(OH)]^+OTf^-$, whereas **16-ClO$_4$** still remained intact.

*[(OEP)P(Me)(OOH)]$^+$OTf$^-$ (**26-OTf**) and [(OEP)P(Ph)(OOH)]$^+$OTf$^-$ (**28-OTf**) with Triphenylphosphine*

The same procedure as previously described. The reaction of **26-OTf** with triphenylphosphine was almost as fast as that of the corresponding **28-OTf** (ratio ca. 1:1 based on the integral ratio of the ^1H NMR spectrum).

*[(OEP)P(Et)(OOH)]$^+$OTf$^-$ (**27-OTf**) and [(OEP)P(Ph)(OOH)]$^+$OTf$^-$ (**28-OTf**) with Triphenylphosphine*

The same procedure as previously described. The reaction of **27-OTf** with triphenylphosphine was almost as fast as that of the corresponding **28-OTf** (ratio ca. 1:1 based on the integral ratio of the ^1H NMR spectrum).

*X-Ray Structure Determination of [(TPP)Sb(Me)(OOt-Bu)]$^+$PF$_6^-$ (**4-PF$_6$**)*

A crystal of $[(TPP)Sb(Me)(OO$*t*$-Bu)]^+PF_6^-$ suitable for X-ray structure determination was mounted on

a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for data collection. Lattice parameters were determined by least-squares fitting of 31 reflections with $21° < 2\theta < 30°$. Data were collected by use of the $2\theta/\omega$ scan mode. The structures were solved using the SIR-92 program in the teXsan (Rigaku) package [43] and refined by full-matrix least-squares treatment. No absorption correction was made. Refinement on *F* was carried out by full-matrix least-squares treatment. Hydrogen atoms were included in the refinement on calculated positions (C–H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. All computations were carried out on an SGI O_2 computer using the teXsan program [43].

SUPPLEMENTARY MATERIAL AVAILABLE

A complete description of the X-ray crystallographic structure determination on **4-PF$_6$** have been deposited at the Cambridge Crystallographic Data Centre.

REFERENCES

[1] Ortiz de Montellano, P. R., Ed. Cytochrome P450, 2nd. ed.; Plenum: New York, 1995, p 1.
[2] Sheldon, R. A., Ed. Metalloporphyrins in Catalytic Oxidations; Marcel Dekker, Inc.: New York, 1994; p 1.
[3] Dugas, H. In Bioorganic Chemistry, 3rd ed.; Springer: New York, 1996; p 407.
[4] Cowan, J. A., Ed. Inorganic Chemistry; Wiley-VCH: New York, 1997; p 1.
[5] Baldwin, J. E.; Perlmutter, P. Top Current Chem 1984, 121, 181.
[6] Collman, J. P.; Zhang, X. in Comprehensive Supramolecular Chemistry Vol. 5, Atwood, J. L., Ed.; Pergamon: Oxford, 1986, p 1.
[7] Almog, J.; Baldwin, J. E.; Dyer, R. L.; Peters, M. J Am Chem Soc 1975, 97, 226.
[8] Almog, J.; Baldwin, J. E.; Huff, J. J Am Chem Soc 1975, 97, 227.
[9] Chang, C. K.; Traylor, T. G. Proc Nat Acad Sci USA 1973, 70, 2647.
[10] Chang, C. K.; Traylor, T. G. J Am Chem Soc 1973, 95, 5810.
[11] Chang, C. K.; Traylor, T. G. J Am Chem Soc 1973, 95, 8475.
[12] Chang, C. K.; Traylor, T. G. J Am Chem Soc 1973, 95, 8477.
[13] Traylor, T. G.; Campbell, D.; Tsuchiya, S. J Am Chem Soc 1979, 101, 4748.
[14] Collman, J. P. Acc Chem Res 1977, 10, 265.
[15] Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. Proc Nat Acad Sci USA 1978, 75, 1052.
[16] Collman, J. P.; Gagne, R. R.; Reed, C. A.; Robinson, W. T.; Rodley, G. A. Proc Nat Acad Sci USA 1974, 71, 1326.
[17] Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. J Am Chem Soc 1980, 102, 3224.
[18] Jameson, G. B.; Rodley, G. A.; Robinson, W. T.; Gagne, R. R.; Reed, C. A.; Collman, J. P. Inorg Chem 1978, 17, 850.
[19] Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. J Am Chem Soc 1978, 100, 6769.
[20] Phillips, S. E. V. J Mol Biol 1980, 142, 531.
[21] Phillips, S. E. V. Nature (London) 1978, 273, 247.
[22] Scheidt, W. R.; Lee, Y. J. Struct Bonding (Berlin) 1987, 64, 10.
[23] Guengerich, F. P.; MacDonald, T. L. Acc Chem Res 1984, 17, 9.
[24] Tajima, K. Inorg Chim Acta 1989, 163, 115.
[25] Tajima, K.; Shigematsu, M.; Jinno, J.; Ishizu, K.; Ohya-Nishiguchi, H. J Chem Soc Chem Commun 1990, 144.
[26] Ozawa, S.; Watanabe, Y.; Morishima, I. Inorg Chem 1994, 33, 306.
[27] Burstyn, J. N.; Roe, J. A.; Miksztal, A. R.; Shaevitz, B. A.; Lang, G.; Valentine, J. S. J Am Chem Soc 1988, 110, 1382.
[28] McCandlish, E.; Miksztal, A. R.; Nappa, M.; Sprenger, A. Q.; Valentine, J. S.; Stong, J. D.; Spiro, T. G. J Am Chem Soc 1980, 102, 4268.
[29] Groves, J. T.; Watanabe, Y. J Am Chem Soc 1988, 110, 8443.
[30] Cloutour, C.; Lafargue, D.; Richards, J. A.; Pommier, J.-C. J Organomet Chem 1977, 137, 157.
[31] Cloutour, C.; Lafargue, D.; Pommier, J. C. J Organomet Chem 1980, 190, 35.
[32] Balch, A. L.; Cornman, C. R.; Olmstead, M. M. J Am Chem Soc 1990, 112, 2963.
[33] Kadish, K. M.; Autret, M.; Ou, Z.; Akiba, K.-y.; Masumoto, S.; Wada, R.; Yamamoto, Y. Inorg Chem 1996, 35, 5564.
[34] Satoh, W.; Masumoto, S.; Shimizu, M.; Yamamoto, Y.; Akiba, K.-y. Bull Chem Soc Jpn 1999, 72, 459.
[35] Schmidt, A. H.; Russ, M.; Grosse, D. Synthesis 1981, 216.
[36] Akiba, K.-y.; Onzuka, Y.; Itagaki, M.; Hirota, H.; Yamamoto, Y. Organometallics 1994, 13, 2800.
[37] Shklover, V. E.; Struchkov, Yu. T.; Dodonov, V. A.; Zinoveva, T. I.; Antonovskii, V. L. Metalloorg Khim 1988, 1, 1140.
[38] Starikova, Z. A.; Shchegoleva, T. M.; Trunov, V. K.; Pokrovskaya, I. E.; Kanunnikova, E. N. Kristallografiya 1979, 24, 1211.
[39] Akiba, K.-y.; Nadano, R.; Satoh, W.; Yamamoto, Y.; Nagase, S.; Ou, Z.; Tan, X.; Kadish, K. M. Unpublished results, 2001.
[40] Yamamoto, Y.; Nadano, R.; Itagaki, M.; Akiba, K.-y. J Am Chem Soc 1995, 117, 8287.
[41] Satoh, W.; Nadano, R.; Yamamoto, Y.; Akiba, K.-y. Chem Commun 1996, 2451.
[42] Satoh, W.; Nadano, R.; Yamamoto, G.; Yamamoto, Y.; Akiba, K.-y. Organometallics 1997, 16, 3664.
[43] teXsan, version 1.09; The program is available from Rigaku Co, Japan.