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Review

The chemistry of Group 15 element porphyrins bearing element–carbon bonds: synthesis and properties

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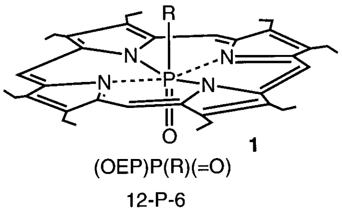
Abstract

A variety of Group 15 element porphyrins bearing element–carbon bond(s) were synthesized mainly by use of R_3Al as an alkylating reagent. The synthetic methods, X-ray crystallographic structures, some spectral data (^{1}H-NMR), and some reactions of the porphyrins were surveyed. One of the most important properties of these compounds is the formation of the element–oxygen double bond in the phosphorus and arsenic porphyrins. The bond formation was confirmed by X-ray crystallographic analysis of (OEP)P(Et)(=O). The P–O bond length of $[(OEP)P(Et)(OH)]^+Cl^-$ and (OEP)P(Et)(=O) was 1.636(4) and 1.484(9) Å, respectively (cf. P–O bond length of $Ph_3P=O$ is 1.483 Å). Since (OEP)P(Et)(=O) was stabilized by the formation of the P=O bond, the OH proton of $[(OEP)PEt(OH)]^+Cl^-$ was acidic (pK_a ca. 7–8). Although the similar formation of the double bond was not observed in the corresponding antimony compounds, the corresponding As=O formation was observed in newly synthesized (OEP)As(R)(=O). The relatively high acidity of the OH protons in $[(OEP)M(R)(OH)]^+X^-$ (M = P, As) {and the stability of the (OEP)M(R)(=O)} would be the main reason for the relatively high reactivity of phosphorus and arsenic porphyrins, $[(OEP)M(R)(OH)]^+X^-$, toward (OEP)Al(Me) to give μ-oxobridged dinuclear porphyrins and the high reactivity of phosphorus and arsenic porphyrins bearing a OOH group toward triphenylphosphine. In addition, X-ray analysis of a variety of phosphorus(V), arsenic(V), antimony(V) octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) derivatives showed the effect of the axial ligand(s) on the distortion of the porphyrin core from the plane. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Porphyrin; Phosphorus; Arsenic; Antimony; Hexacoordinate; Hypervalent; X-ray analysis; Ruffling

1. Introduction

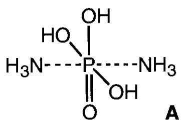
We have been interested in hypervalent compounds [1,2] especially compounds of Group 15 elements [3]. For example, hexafluorocumyl alcohol ligand, so called Martin ligand [4], has been used to stabilize the hexacoordinate antimony anion [5], and the tridentate ligand, so called van Koten ligand, was used to stabilize the edge inversion transition state [6]. The inversion at the central trivalent antimony was accelerated by the intramolecular coordination and was confirmed to proceed via edge inversion, which was proposed by Arduengo and Dixon [7]. Recently we became interested in porphyrins because the ligand system could be regarded as a relatively rigid tetradentate ligand. Among the Group 15 elements, phosphorus porphyrins are interesting because in general phosphorus atom has been known to form a double bond with an oxygen atom and it may lead the quite unique hypervalent compounds (**1**) such as the stabilized intermediate (**A**) in the nucleophile-associated edge inversion. The bonding around the phosphorus atom is hypervalent and the compound can be designated as a 12-P-6 compound according to the accepted formalism [8].



1

(OEP)P(R)(=O)

12-P-6



A

calculated intermediate
for nucleophile-associated
edge inversion

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In addition, phosphorus has been the smallest atom which can occupy the center of a porphyrin ring and based on some recent reports the porphyrin core is severely ruffled in order to accommodate the small phosphorus(V) cation [9]. Ruffled porphyrin core has sometimes been observed in biological systems and the effect of the porphyrin ring distortion on properties such as spin state, redox potentials has been the subject of recent interest [10]. However, systematic study on the electronic or steric effect of the axial ligands on the degree of ruffling of the porphyrin core has not been carried out.

Moreover, when we started the project of porphyrins, Group 15 element porphyrins having element–carbon bond(s) had never been reported although the porphyrins with metal–carbon bond(s) had been drawing intensive interest in relation to porphyrins with Fe–C bonds which are intermediates in metabolism of cytochrome P450 complexes [11], and the corresponding Group 13 porphyrins or Group 14 porphyrins (Al [12], Ga [13], In [14], Tl [15], Si [16], Ge [17], Sn [18]) containing σ-bonded element–carbon bond(s) had been reported. Therefore, first of all we tried to synthesize the Group 15 porphyrins having element–carbon bond(s).

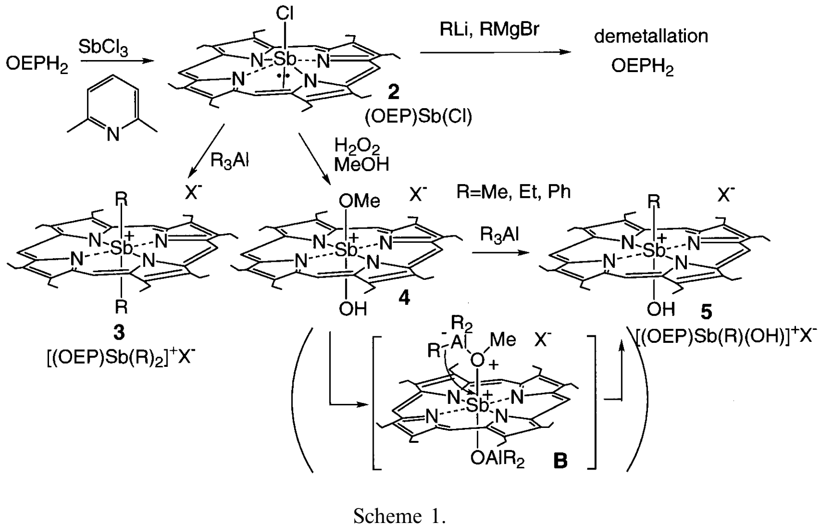
2. Synthesis of antimony porphyrins bearing Sb–C bond(s)

Initially, the synthesis of antimony porphyrins bearing element–carbon bonds was attempted by the following methods: (i) reaction of $OEPH_2$ with p-$CH_3C_6H_4SbCl_2$ [19] under pyridine reflux; (ii) reactions of (OEP)Sb(Cl) (**2**) [20] with C_6H_5MgBr, C_6F_5Li, or n-BuMgBr. However, the former reaction (i) gave (OEP)Sb(Cl) and the latter reactions (ii) resulted in a mixture of $OEPH_2$ and unidentified tarry substance.

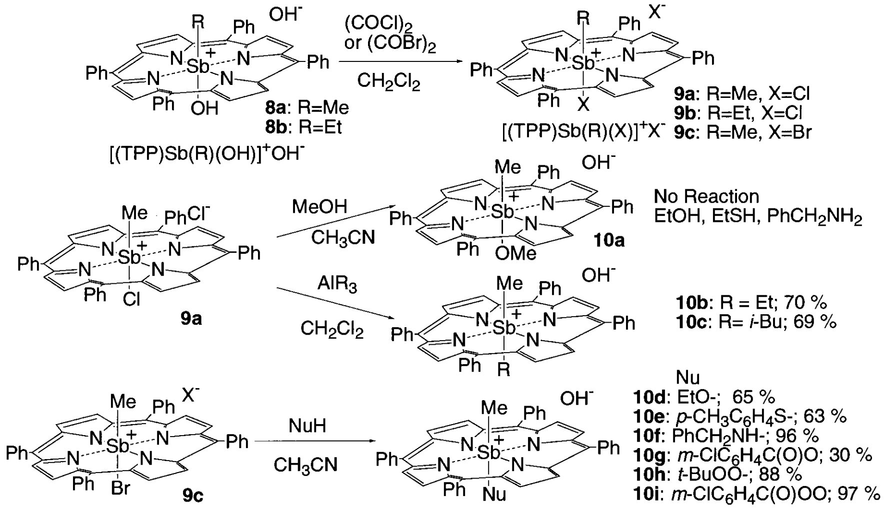
Eventually, the desired antimony porphyrin with antimony–carbon bonds could be obtained by the reaction of **2** with excess Me_3Al in CH_2Cl_2 after 4 days of stirring at room temperature. Surprisingly, the compound isolated turned out to be a dimethyl compound with a higher oxidation state Sb(V), $[(OEP)Sb(Me)_2]^+$ PF_6^- (**3a-PF$_6$**), which was obtained in 70% yield by column chromatography (neutral alumina: benzene–methanol = 75:1) followed by counteranion exchange with ammonium hexafluorophosphate [21]. The compound was remarkably stable in comparison with corresponding Group 13 and 14 analogues [12–18].

Unsymmetrically substituted compounds, $[(OEP)Sb(R)(OH)]^+X^-$ (**5a**: R = Me, **5b**: R = Et), were prepared from the reaction of R_3Al with $[(OEP)Sb(OMe)(OH)]^+$ Cl^- (**4-Cl**), which was prepared from **2** with aqueous hydrogen peroxide (30%) in MeOH (Scheme 1). We believe the formation of an active aluminumate complex intermediate (**B**) triggers the reaction as shown in Scheme 1 [21].

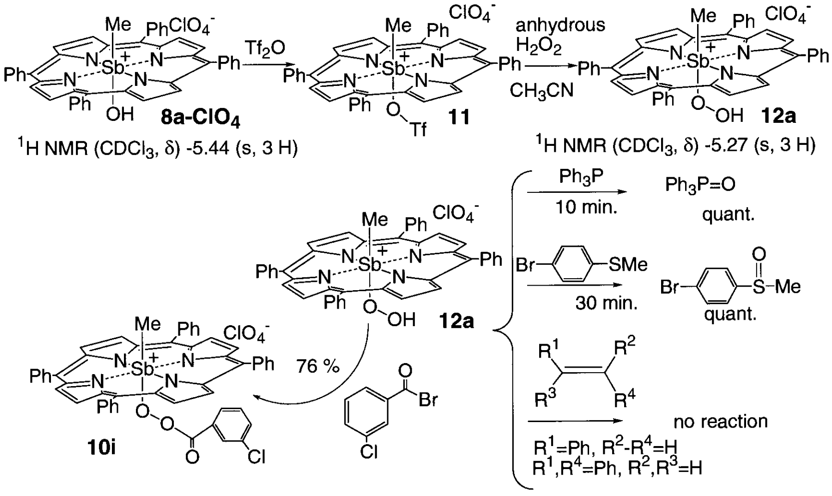
Similar procedures could be applied for teteraphenylporphyrin (TPP) derivatives. For the introduction of the antimony atom toward the tetraphenylporphyrin ligand ($TPPH_2$), 2,6-lutidine was found to be a base of choice instead of pyridine, giving (TPP)Sb(Br) (**6**) in high yield (95%). $[(TPP)Sb(R)(OH)]^+Y^-$ (**8a**: R = Me, **8b**: R = Et) were obtained based on the trialkylaluminum method from $[(TPP)Sb(OMe)(OH)]^+Y^-$ (**7**), which was prepared from **6** with aqueous hydrogen peroxide (30%) in MeOH. The antimony–oxygen bond in **8** was converted to the corresponding chloride $[(TPP)Sb(R)(Cl)]^+Y^-$ (**9a**: R = Me, **9b**: R = Et) with the antimony–carbon bond intact [22]. A couple of unsymmetrically substituted compounds such as $[(TPP)Sb(Me)(OMe)]^+Y^-$ (**10a**) could be prepared from the chloride but the reactivity was not enough to yield substituted products with EtOH. However, it turned out that the corresponding bromide



Scheme 1.



Scheme 2.



Scheme 3.

$[(TPP)Sb(Me)(Br)]^+Y^-$ (**9c**) was reactive enough with several nucleophiles including EtOH, *p*-cresol, *p*-toluenethiol, *p*-toluidine, benzylamine, sodium *m*-chlorobenzoate, *t*-butyl hydroperoxide, sodium *m*-chloroperbenzoate, triethylaluminum, and tri-*i*-butylaluminum to afford the corresponding substituted products in high yields [23] (Scheme 2). X-ray structural analysis was carried out for stable $[(TPP)Sb(Me)(OO\text{-}t\text{-}Bu)]^+PF_6^-$ [24].

The hydroperoxide compounds were obtained from $[(TPP)Sb(Me)(OTf)]^+Y^-$ (**11**) [24] and correspond to a peroxide compound in catalytic oxidation cycle of cytochrome P450 [25]. After several trials, the reaction of **11** with relatively anhydrous hydrogen peroxide in acetonitrile at room temperature for 1 day afforded the desired $[(TPP)Sb(Me)(OOH)]^+ClO_4^-$ (**12a**) in 92% purity based on the ^{1}H-NMR spectrum (Scheme 3). **12a** was unstable to atmospheric moisture and gradually decomposed to **8a-ClO$_4$** at room temperature. However, the molecular ion peak of **12a** could be observed by FAB mass spectrum (matrix; nitrobenzyl alcohol), **12a** could be converted to **10i** by the reaction with *m*-chlorobenzoyl bromide.

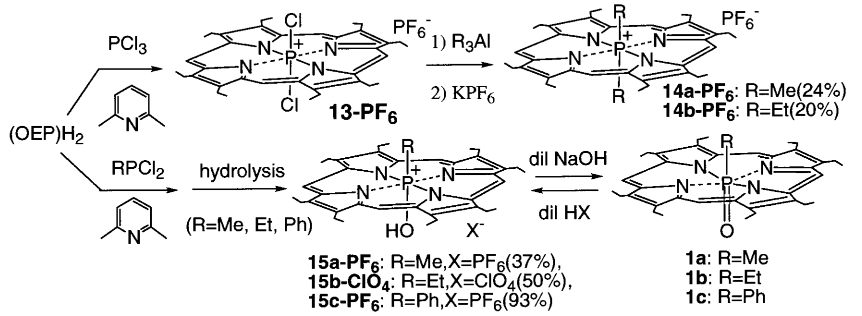
The reaction of **12a** with triphenylphosphine at room temperature for 10 min afforded the corresponding triphenylphosphine oxide. Moreover the reaction of **12a** with *p*-bromothioanisole at room temperature for 30 min also gave the corresponding oxide. However, even after several days at room temperature the reaction of **12a** with olefins did not take place and **12a** remained intact under Ar.

3. Synthesis and structures of phosphorus porphyrins bearing P–C bond(s)

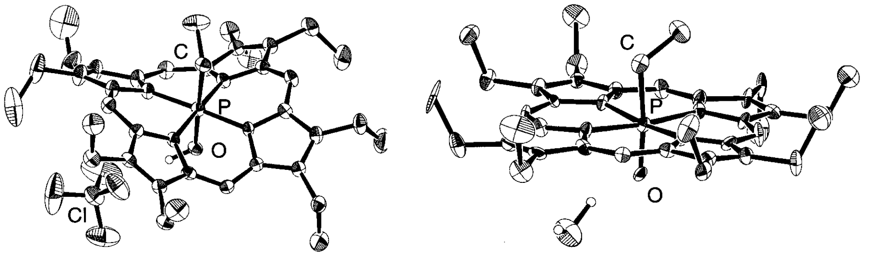
The insertion of phosphorus into octaethylporphyrin was accomplished by reaction of $OEPH_2$ with PCl_3 in the presence of 2,6-lutidine. The main product was found to be $[(OEP)P(Cl)_2]^+Cl^-$ (**13-Cl**) probably due to the air oxidation during the reaction. The dichloride was converted to the dialkylated compounds, $[(OEP)P(R)_2]^+Y^-$ (**14a**: R = Me, **14b**: R = Et), by treatment with R_3Al. Monoalkylated compounds, $[(OEP)P(R)(OH)]^+Y^-$ (**15a**: R = Me, **15b**: R = Et, **15c**: R = Ph), could be prepared by the simple reaction of $OEPH_2$ with alkylphosphorus dichloride ($RPCl_2$). The OH proton of **15** was acidic enough to generate (OEP)P(R)(=O) (**1a**: R = Me, **1b**: R = Et, **1c**: R = Ph) after treatment of a solution of **15** with aq NaOH or DBU. These compounds, **1** and **15**, showed different UV spectra, and the acidity of the OH proton of **15b** could be determined by use of the spectral difference to be ca. 7–8. By adjusting the pH in the medium, **15** and **1** could be isolated separately (Scheme 4).

Crystals of **1b** and **15b-ClO$_4$** suitable for X-ray analysis were obtained by recrystallization from dichloromethane for **1b** and from ethyl acetate for **15b-ClO$_4$** [26]. Fig. 1 shows the crystal structure of **1b** with a water molecule found incorporated in the crystal lattice, and **15b-ClO$_4$** with the perchlorate anion, respectively. Each of the geometries about the phosphorus atom is a distorted octahedron, of which the bond length of the P–O bond (1.484(9) Å) in **1b** is very short in contrast to the usual single bond length (1.636(4) Å) in **15b-ClO$_4$**. The P–O bond in **1b** should be regarded as a double bond [26,27] since the P–O bond length is almost identical with the reported distance (1.483 Å) of that of triphenylphosphine oxide [28]. The bonding around the phosphorus atom in **1b** is quite unique, the first example of a hypervalent 12-P-6 compound bearing a P=O double bond. The only examples of compounds of this class bearing a P=O double bond are theoretically proposed species, i.e. $F_3P(=O)\cdot 2NH_3$ and $(HO)_3P(=O)\cdot 2NH_3$, concerning the mechanism of associated edge inversion in which two molecules of ammonia are coordinated with the phosphoryl group [29].

Interestingly, the porphyrin core of **1b** is almost planar in contrast to **15b-ClO$_4$** which is severely ruffled. Although there have been several reports on ruffled structures on phosphorus(V) tetraphenylporphyrin derivatives [30] but no systematic study about the electronic effect of the axial ligands on the degree of ruffling of the porphyrin core has been carried out. In order to examine the relationship between ruffling of the porphyrin core and the nature of the axial ligands, a variety of phosphorus(V) octaethylporphyrin derivatives of the type $[(OEP)P(X)(Y)]^+Z^-$ (OEP: octaethylporphyrine) (X = Me, Et, Ph, F; Y = Me, Et, OH, OMe, OEt, O-*n*-Pr, O-*i*-Pr, O-*sec*-Bu, NHBu, NEt_2, Cl, F, O^-; Z = ClO_4, PF_6) were prepared and X-ray crystallographic analysis of ten compounds (shown in Table 1) were carried out [27]. The deviation in meso positions from planarity in the porphyrin core is clearly observed in all compounds except **1b**, therefore, the type of distortion should be regarded as ruffled [31]. In order to elucidate the relationship between the degree of ruffling of the porphyrin core and the nature of the



Scheme 4.



15b-ClO$_4$
$[(OEP)P(Et)(OH)]^+ClO_4^-$

1b
$(OEP)P(Et)(=O)\ H_2O$

Fig. 1. ORTEP diagram (30% probability ellipsoids) for **1b** and **15b-ClO$_4$**.

Table 1
Average P–N bond distances and the degree of ruffling of phosphorus(V) porphyrins, $[(OEP)P(X)(Y)]^+Z^-$

X	F	Cl	O-*n*Pr	F	OH	OH	NEt_2	Et	Me	=O
Y	OH	Cl	Ph	Me	Ph	Et	Et	Et	Me	Et
Z	ClO_4	PF_6	ClO_4	PF_6	PF_6	ClO_4	ClO_4	PF_6	PF_6	
Average P–N bond distance (Å)	1.848(5)	1.840(8)	1.869(7)	1.85(1)	1.877(5)	1.892(5)	1.92(1)	1.947(3)	1.990(8)	2.01 (1)
Deviation from the mean plane of the core porphyrin (Å) (Δr) [a]	0.539	0.518	0.505	0.499	0.485	0.462	0.381	0.266	0.128	0.073

[a] (Δr): Root mean squares of displacements for entire 24 atom core.

axial ligands, average P–N bond lengths and the degree of ruffling of the core (Δr), which was calculated by the root mean square of the deviation of the 24 atoms [31a], are summarized in Table 1. The table lists the compounds in order of the degree of ruffling based on Δr. **15d-ClO$_4$** (axial ligands: F, OH) is most ruffled and is placed at the left end of the table. The order is as follows: **15d-ClO$_4$** (axial ligands: F, OH. Δr: 0.539) > **13-PF$_6$** (Cl, Cl. 0.518) > **16-ClO$_4$** (Ph, O-*n*-Pr. 0.505) > **17a-PF$_6$** (Me, F. 0.499) > **15c-PF$_6$** (Ph, OH. 0.485) > **15b-ClO$_4$** (Et, OH. 0.462) > **18-ClO$_4$** (Et, $N(Et)_2$. 0.381) > **14b-PF$_6$** (Et, Et. 0.266) > **14a-PF$_6$** (Me, Me. 0.128) > **1b** (Et, O^-. 0.073). Generally speaking, as the axial ligands become more electronegative the degree of ruffling becomes greater and the averaged P–N bond distance becomes shorter. Therefore, the electronic effects of the axial substituents play a major role in determining the degree of ruffling and the averaged P–N bond distance. The steric effects of the substituents play some roles since the degree of ruffling is greater in **14b-PF$_6$** than that in **14a-PF$_6$**. Among the series **1b** is placed at the right end of the table (the degree of ruffling is the smallest and the averaged P–N bond distance is the longest), the oxygen atom in **1b** should be more electrondonating than carbon substituents.

Our interest in the distortion from planarity in the porphyrin core has extended to the synthesis of octaalkyltetraphenylporphyrins, in which deformation (saddle type deformation) from planarity is induced by crowding of substituents at the periphery of the macrocycle [32]. Since octaalkyltetraphenylporphyrins bearing a main group element as a central atom have not been reported, phosphorus octaethyltetraphenylporphyrins, $[(OETPP)P(Me)(X)]^+Y^-$ (**19**: X = OH, **20**: X = Me, **21**: X = F), were synthesized and the X-ray structures showed strong effects of the axial ligands on the conformations, that is, the saddle conformation was observed in $[(OETPP)P(Me)_2]^+PF_6^-$ (**20-PF$_6$**) but ruffled ones were observed in $[(OETPP)P(Me)(OH)]^+ClO_4^-$ (**19-ClO$_4$**) and $[(OETPP)P(Me)(F)]^+PF_6^-$ (**21-PF$_6$**) (Fig. 2) [33].

The results can be explained based on the above conclusions on $[(OEP)P(X)(Y)]^+Z^-$. That is, the introduction of the electronegative axial substituents [X = OH (**19**) and X = F (**21**) in (OETPP)P(Me)(X)] reduce the size of the central phosphorus atom and the average P–N bond distances become shorter [1.94(1) Å in **20-PF$_6$** (X = Me), 1.849(4) Å in **19-ClO$_4$** (X = OH), and 1.810(8) Å in **21-PF$_6$** (X = F)], then ruffled conformations become preferable in **19-ClO$_4$** and **21-PF$_6$** in order to accommodate the small phosphorus atom. Although metal size dependence of the degree of deformation of saddle conformations was already investigated for transition metals [34], such large electronic effects of the

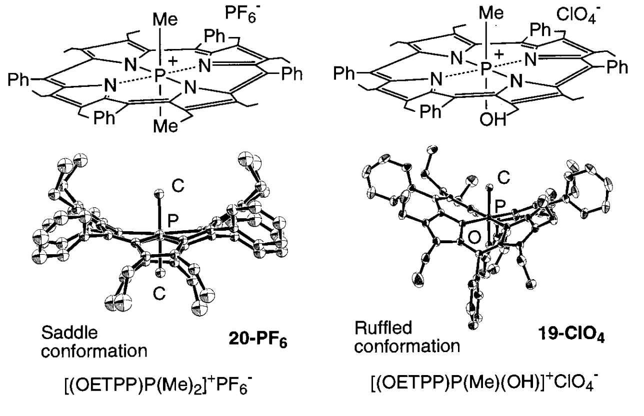


Fig. 2. ORTEP diagram (30% probability ellipsoids) for **19b-ClO$_4$** and **20-PF$_6$**.

axial ligands to change the fundamental conformations have never been observed. In fact, these structures of **19-ClO$_4$** and **21-PF$_6$** are the first examples for metallooctaalkyltetraphenyl-porphyrins bearing ruffled conformation.

It is also interesting to note that the Q(0, 0) band of the ruffled **19** (627 nm) and **21** (622 nm) are significantly blue shifted in the UV–vis absorption in comparison with those of **20** (667 nm) and free base octaethyltetraphenylporphyrin (686 nm) with saddle conformation. Since such a large shift has not been observed in $[(OEP)P(Me)(Y)]^{+}Z^{-}$ series, the shift can be ascribed to the difference of core conformations.

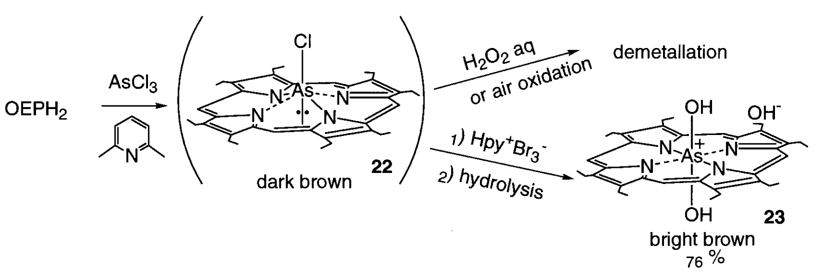
4. Synthesis and structures of arsenic porphyrins bearing As–C bonds

As described above, (OEP)P(Et)(=O) (**1b**) was prepared by treating $[(OEP)P(Et)(OH)]^{+}Cl^{-}$ (**15b-ClO$_4$**) with DBU and the chemical shifts in the ^{1}H-NMR and the wave length of the absorption maxima in the UV–vis spectra changed by the addition of DBU. But similar change of the spectra was not observed in the corresponding antimony compounds. Therefore, it was of interest to examine the ability of the corresponding arsenic porphyrins to form stable arsenic–oxygen double bonds by monitoring the change in chemical shift upon addition of bases.

As for arsenic porphyrins, only a few papers had been published to claim the synthesis of arsenic porphyrins [35] and there had been no reliable result on the preparation of arsenic porphyrins until our first successful synthesis and X-ray structural characterization of arsenic porphyrins such as $[(OEP)As(Me)(OH)]^{+}ClO_4^{-}$ (**24-ClO$_4$**) [36].

Our first attempt to insert an arsenic atom to the porphyrin ligand by the reaction of OEPH$_2$ with AsCl$_3$ in dichloromethane in the presence of 2,6-lutidine indicated that (OEP)As(Cl) (**22**) was clearly formed based on the characteristic UV–vis spectrum [35a]. However, the arsenic(III) porphyrin was very unstable toward hydrolysis/oxidation in air and treatment with aqueous hydrogen peroxide. Only a trace amount of $[(OEP)As(OH)_2]^{+}Cl^{-}$ (**23-Cl**) was obtained in both cases and almost all **22** was demetallated to afford OEPH$_2$ in the reaction with air oxidation and with hydrogen peroxide. We thought that **22** was reluctant to be oxidized by air and the strong nucleophilicity of hydrogen peroxide should be the reason for the demetallation. Our new synthetic approach for the preparation of arsenic porphyrins is based on oxidative conversion of unstable arsenic(III) porphyrins into arsenic(V) complexes by use of less-nucleophilic halogenating reagents such as pyridinium tribromide ($Hpy^{+}Br_3^{-}$). The reaction of **22** with $Hpy^{+}Br_3^{-}$ gave $[(OEP)As(OH)_2]^{+}Cl^{-}$ (**23-Cl**) in 76% yield after hydrolytic treatment (Scheme 5). $[(OEP)As(Me)(OH)]^{+}ClO_4^{-}$ (**24-ClO$_4$**) was obtained from **23-Cl** by conversion to the corresponding dibromide followed by treatment with R$_3$Al.

When **24-ClO$_4$** in CDCl$_3$ was treated with DBU, the characteristic methyl signal shifted upfield from δ − 5.62 to − 6.13. The change was found to be reversible when the basic solution was treated with dilute HCl (pH 4). These results indicated that (OEP)As(Me)(=O) (**25**) were formed by treatment with DBU and could be converted to **24-Cl** by addition of HCl. The ^{1}H-NMR chemical shifts of corresponding phosphorus compounds are shown in Table 2, and it is clear that the degree of the ^{1}H-NMR chemical shift differences ($\Delta\delta$) of axial groups between (OEP)M(R)(=O) and $[(OEP)M(R)(OH)]^{+}X^{-}$ is larger in the phosphorus compounds than that in the corresponding arsenic por-



Scheme 5.

phyrins ($\Delta\delta$: R = Me; 0.63 in P, 0.51 in As; R = Et (CH_3); 0.69 in P, 0.52 in As; R = Et (CH_2); 0.56 in P, 0.28 in As; R = Ph (ortho); 0.55 in P, 0.23 in As; R = Ph (meta); 0.24 in P, 0.12 in As; R = Ph (para); 0.29 in P, 0.10 in As). In the phosphorus compounds, X-ray structural results showed that the porphyrin core of (OEP)P(Et)(=O) was almost planar in contrast $[(OEP)P(Et)(OH)]^+ClO_4^-$ was severely ruffled. Therefore, the ring current effects of the porphyrin core should be different between [(OEP)P(R)(=O)] and $[(OEP)P(R)(OH)]^+X^-$. Since the X-ray structural analysis of $[(OEP)As(Me)(OH)]^+ClO_4^-$ (**24-ClO$_4$**) shows that the porphyrin core is almost planar (which is not shown as an ORTEP drawing but the structure is similar to that of $[(OEP)As(F)_2]^+PF_6^-$ (**27-PF$_6$**) in Fig. 3), the chemical shift differences in the arsenic porphyrins are considered to be originated from the pure electronic effects of the axial ligands. In fact, downfield shifts were observed for the meso protons from $[(OEP)P(R)(OH)]^+X^-$ to (OEP)P(R)(=O) indicating that the ring current effect of the core was larger in the planar (OEP)P(R)(=O) than that of the ruffled $[(OEP)P(R)(OH)]^+X^-$. In contrast, the corresponding arsenic analogue showed upfield shifts of the meso protons from $[(OEP)As(R)(OH)]^+X^-$ to (OEP)As(R)(=O) probably due to the electron donation from the axial oxide without considerable change of ruffling.

Arsenic tetraphenylporphyrin derivatives were also prepared and the X-ray crystallographic analyses of $[(TPP)As(Me)_2]^+PF_6^-$ (**25-PF$_6$**) and $[(TPP)As(F)_2]^+PF_6^-$ (**26-PF$_6$**) were carried out. The X-ray structure of $[(OEP)As(F)_2]^+PF_6^-$ (**27-PF$_6$**) was cited for comparison [37]. Interestingly, the porphyrin core of **25-PF$_6$** and **27-PF$_6$** is almost planar in contrast to **26-PF$_6$** which adapts S_4 ruffled conformation. The ORTEP drawings of **25-PF$_6$**, **26-PF$_6$**, and **27-PF$_6$** are shown in Fig. 3. The averaged As–N bond distance is much shorter in $[(TPP)As(F)_2]^+PF_6^-$ (**26-PF$_6$**: 1.927(2) Å) than that in $[(TPP)As(Me)_2]^+PF_6^-$ (**25-PF$_6$**: 2.062(2) Å). The degree of ruffling of the core (Δr: Å) in **26-PF$_6$** is calculated by root mean square of the deviation of the 24 atoms to be 0.427 and that of **25-PF$_6$** as 0.035. These results are consistent with the discussion about phosphorus octaethylporphyrins $[(OEP)P(X)(Y)]^+Z^-$. That is, as the axial ligands (X and Y) became more electronegative the average As–N bond distance became shorter. In the corresponding phosphorus porphyrins, we observed the presence of clear threshold distance (ca. 1.95 Å) of the P–N bond between the extensively ruffled porphyrin core ($[(OEP)P(Et)(NEt_2)]^+ClO_4^-$ (**18-ClO$_4$**): av. P–N

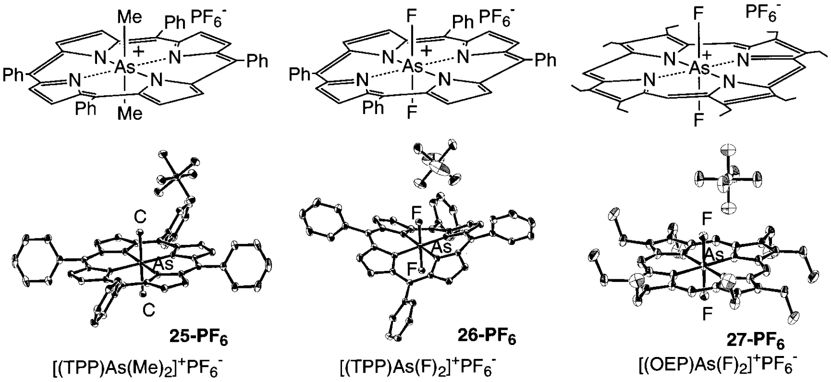


Fig. 3. ORTEP diagram (30% probability ellipsoids) for **25-PF$_6$**, **26-PF$_6$**, and **27-PF$_6$**.

Table 2
^{1}H-NMR of arsenic and phosphorus porphyrins

	[(OEP)AsMe(OH)]	(OEP)AsMe(=O)	[(OEP)AsEt(OH)]	(OEP)AsEt(=O)	[(OEP)AsPh(OH)]	(OEP)AsPh(=O)
Axial protons	−5.62(s, 3H)	−6.13(s, 3H)	−5.68(q, 2H) −4.63(t, 3H)	−6.20(q, 2H) −4.91(t, 3H)	−0.03(d, 2H) 4.87(t, 2H) 5.48(t, 1H)	−0.26(d, 2H) 4.75(t, 2H) 5.38(t,1H)
Meso protons	10.60(s, 4H)	10.45(s, 4H)	10.59(s, 4H)	10.37(s, 4H)	10.41(s, 4H)	10.42(s, 4H)
	[(OEP)PMe(OH)]	(OEP)PMe(=O)	[(OEP)PEt(OH)	(OEP)PEt(=O)	[(OEP)PPh(OH)l	(OEP)PPh(=O)
Axial protons	−5.74(d, 3H)	−6.37(d, 3H)	−5.70(q, 2H) −4.52(t, 3H)	−6.39(dq, 2H) −5.08(dt, 3H)	0.53(d, 2H) 4.78(t, 2H) 5.47(t, 1H)	−0.02(dd, 2H) 4.54(dt, 2H) 5.18 (dt, 1H)
Meso protons	9.68(s, 4H)	9.95(s, 4H)	9.72(s, 4H)	10.20(s, 4H)	9.43(s, 4H)	9.60(s, 4H)

bond, 1.92(1) Å; $\Delta r = 0.381$ Å) and the planar one ($[(OEP)P(Me)_2]^+PF_6^-$ (**14a-PF$_6$**): av. P–N bond, 1.990(8) Å; $\Delta r = 0.128$ Å). This is also the case for arsenic tetraphenylporphyrins, i.e. **26-PF$_6$** is ruffled and **25-PF$_6$** is planar.

It is interesting to mention that the structure of the corresponding arsenic octaethylporphyrin, $[(OEP)As(F)_2]^+PF_6^-$ (**27-PF$_6$**, $\Delta r = 0.024$ Å) was found to be planar and the average As–N bond distance (1.966(1) Å) was longer than the threshold value (1.95 Å). Although the slightly shorter M–N bond distances in metallotetraphenylporphyrins than that of the corresponding octaethylporphyrins have been reported for some metalloporphyrins [38], such large electronic effects of the porphyrin core to change the fundamental conformations have never been observed.

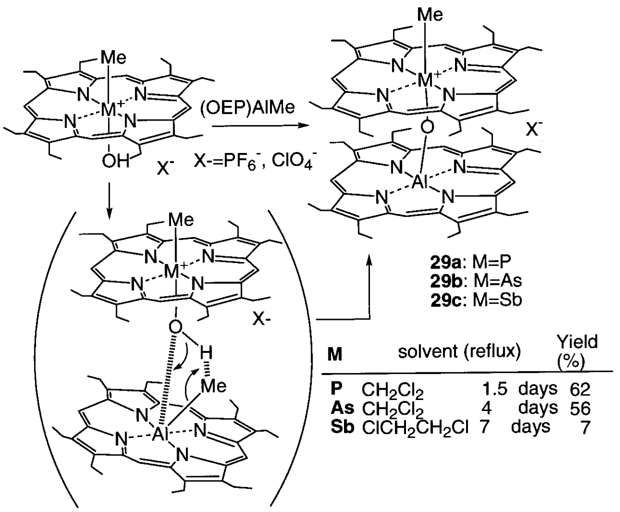
5. Synthesis of μ-oxobridged heterodinuclear porphyrins

μ-Oxobridged dinuclear porphyrins bearing a transition metal such as Fe, Ru, Mn, V, and Ti have been investigated extensively because of the relation to biological interests [39]. Recently, the μ-oxobridged dinuclear porphyrin skeleton having boronic acids has been reported to be useful for molecular recognition of saccharides [40]. However, only a few synthetic methods are available for the synthesis of μ-oxobridged dinuclear transition metal porphyrins, and μ-oxobridged dinuclear porphyrins bearing main group elements have not been reported.

Since aluminum porphyrins bearing an alkyl group such as (OEP)Al(Me) was known to be reactive toward alcohols and phenols bearing acidic protons [41], it was of interest to examine whether the acidic hydroxy groups in $[(OEP)(R)M(OH)]^+X^-$ (M = P, As) were reactive toward (OEP)Al(Me) in spite of the anticipated steric hindrance.

To our delight the reaction of $[(OEP)P(Me)(OH)]^+ ClO_4^-$ (**15-ClO$_4$**) with (OEP)Al(Me) (**28**) proceeded smoothly under dichloromethane reflux for 1.5 days and the expected μ-oxobridged P/Al heterodinuclear porphyrin **29a** was isolated in 62% yield [42] (Scheme 6). The compound was stable to atmospheric moisture and chromatographic treatment [neutral Al_2O_3, benzene–CH_2Cl_2–MeOH (15:6:1)], and the characterization was carried out by elemental analysis. The reaction of the corresponding arsenic porphyrin **24-ClO$_4$** with **28** proceeded slowly and **29b** was obtained in 49% yield after 4 days under dichloromethane reflux. The difference of the reactivity between **15** and **24** should be related with the acidity of the hydroxy group in **15** and **24**, in fact **15** was found to be more acidic than **24** since the methyl protons of **15** shifted upfield faster than those of **24** upon portionwise addition of DBU to the mixture of **15** and **24** in $CDCl_3$. As expected, the reaction of the least acidic corresponding antimony porphyrin $[(OEP)Sb(Me)(OH)]^+ClO_4^-$ (**5a-ClO$_4$**) with **28** was very sluggish and only 7% of **29c** was obtained after 2 weeks under 1,2-dichloroethane reflux (Scheme 6). ^{1}H-NMR of the μ-oxobridged heterodinuclear porphyrin $[(OEP)(Me)M–O–Al(OEP)]^+ClO_4^-$ showed characteristic methyl signals at very high fields (δ −7.96 in **29a**, −7.94 in **29b**, −7.92 in **29c**) which were even higher than those of the starting $[(OEP)M(Me)(OH)]^+ClO_4^-$ (δ −5.79 in **15**, −5.63 in **24**, −6.13 in **5a**) probably due to the ring current effect of the aluminum porphyrin nucleus.

Crystals of **29b-ClO$_4$** suitable for X-ray analysis were obtained by recrystallization from dichloromethane-dibutyl ether. X-ray structural analysis of the compound was carried out on the basis of the centrosymmetric *C*2/*c* group, showing the required twofold axis passed through C–As–O–Al bond. Fig. 4 shows the ORTEP drawing of a single molecule of



Scheme 6.

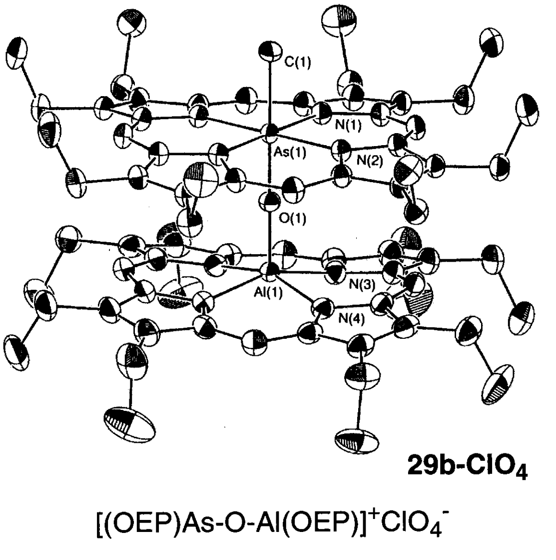
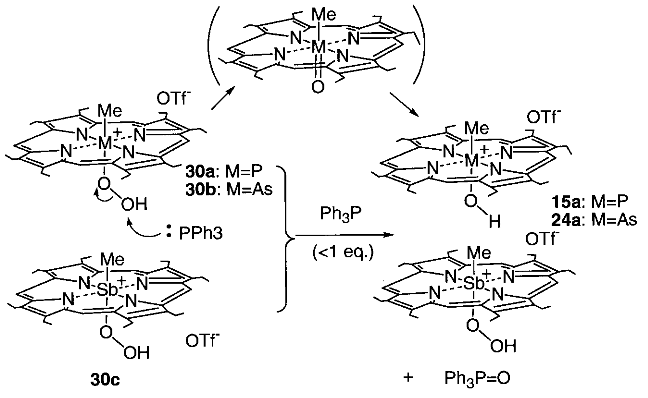


Fig. 4. ORTEP diagram (30% probability ellipsoids) for **29b-ClO$_4$**.



Scheme 7.

29b-ClO$_4$ (solvent dichloromethane was omitted for clarity). Since the As, O, and Al atoms lie on the crystallographic two fold axis the As–O–Al bond is explicitly linear. The averaged torsional angle between N(1)–As–Al–N(3) and N(2)–As–Al–N(4) is 15.3°, the structure of **29b-ClO$_4$** is represented in terms of a near-eclipsed conformation [43]. The interplanar distance between the mean planes of the porphinato cores is 3.71 Å.

Recently, the corresponding μ-oxobridged antimony/aluminum heterodinuclear porphyrins **29c** could be synthesized efficiently by the reaction of **5-ClO$_4$** with **28** with irradiation of light (Xe lamp) [44]. The acceleration would be due to the activation of Al–Me bond in (OEP)Al(Me) as was reported by Inoue [45].

6. Reactivity of phosphorus, arsenic and antimony porphyrin peroxides

In the previous section, synthesis of $[(TPP)Sb(Me)(OOH)]^+ClO_4^-$ (**12a**) was described. In order to examine the reactivity of peroxides among Group 15 element porphyrins, the corresponding octaethylporphyrins $[(OEP)M(Me)(OOH)]^+X^-$ (**30a**: M = P, **30b**: M = As, **30c**: M = Sb) were synthesized. In order to compare the reactivity of **30a** and **30c**, triphenylphosphine (less than one equivalent) was added portionwise to a mixture of an equimolar amount of **30a-OTf** and **30c-OTf** at room temperature in deuteriochloroform and the reaction was monitored by ^{1}H-NMR. The experiment clearly indicated that the phosphorus porphyrin peroxide (**30a-OTf**) was much more reactive to triphenylphosphine than the antimony porphyrin peroxide (**30c-OTf**). **30a-OTf** was converted to **15a-OTf** but **30c-OTf** still remained intact. The reaction between **30b-OTf** and **30c-OTf** gave similar results, showing that the arsenic peroxide (**30b-OTf**) was much more reactive than the antimony peroxide (**30c-OTf**). The higher reactivity of phosphorus and arsenic peroxides toward triphenylphosphine would be due to the stability of (OEP)M(Me)(=O) (M = P, As) in the products of the reaction (Scheme 7) [24].

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