Synthesis of Antimony(V) Octaethylporphyrins That Contain a σ-Bonded Element–Carbon Bond[1]

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Antimony(V) octaethylporphyrins with σ-bonded antimony–carbon bonds were synthesized: $[(OEP)SbR(OH)]^+PF_6^-$ (**1a**-PF_6, R = Me; **1b**-PF_6, R = Et) and $[(OEP)SbMe_2]^+PF_6^-$ (**2a**-PF_6). Compounds **1a** and **1b** were prepared by the reaction of $[(OEP)Sb(OMe)(OH)]^+Cl^-$ (**6**) with an excess amount of R_3Al, and **2a** was obtained from (OEP)SbCl (**3**) and an excess amount of Me_3Al. The compounds **1a**-PF_6, **1b**-PF_6, and **2a**-PF_6 were remarkably stable toward air and moisture in comparison with corresponding group 13 and 14 analogues. The ^1H NMR of these compounds showed characteristic axial alkyl signals at very high field (δ −6.10 in **1a**-PF_6, −5.87 and −4.33 in **1b**-PF_6, and −6.73 in **2a**-PF_6) because of the ring current effect of the porphyrin nucleus. X-ray crystallographic analysis of **2a**-PF_6 is presented; space group $P2_1/m$, a = 11.777(3) Å, b = 18.183(4) Å, c = 9.712(2) Å, β = 100.75(2)°, R = 0.051.

Introduction

Porphyrins with metal–carbon bonds have been drawing intensive interest, especially in relation to porphyrins with Fe–C bonds which are intermediates in the metabolism of cytochrome P450 complexes.[2,3] Recently, the interest has expanded from transition metals to main group elements in order to examine the specific role of the porphyrin ligand and the central metals.[4,5] In fact, intensive efforts have been carried out recently for group 13 and group 14 elements, that is, synthesis, electrochemistry, and reactions of porphyrins with group 13 and group 14 elements (Al,[6] Ga,[7] In,[8] Tl,[9] Si,[10] Ge,[11] Sn[12]) that contain σ-bonded element–carbon bonds. However, porphyrins with group 15 elements bearing element–carbon bonds have never been reported because synthetic methods have not been available for these compounds. In order to extend our recent interest on hypervalent pentacoordinate and hexacoordinate antimony compounds,[13] antimony–alkyl(aryl) σ-bonded porphyrins were chosen as target molecules because the bonding around the antimony atom is hypervalent and these can be designated as 12-Sb-6 compounds according to the accepted formalism,[14] if they are prepared. Here we report the first synthesis of porphyrins with antimony–carbon bonds.

Results and Discussion

Preparation of $[(OEP)SbMe_2]^+PF_6^-$ (2a-PF_6) and $[(OEP)SbEt(OH)]^+PF_6^-$ (1b-PF_6) from (OEP)SbCl (3). Initially, the synthesis of antimony porphyrins bearing element–carbon bonds was attempted by the following methods: (i) reaction of $OEPH_2$ with p-$CH_3C_6H_4SbCl_2$[15] under pyridine reflux; (ii) reactions of (OEP)SbCl (**3**)[16] with C_6H_5MgBr, C_6F_5Li, or n-BuMgBr. However, the former reaction (i) gave (OEP)SbCl and the latter reactions (ii) resulted in a mixture of $OEPH_2$ and an unidentified tarry substance.

Eventually, the desired antimony porphyrin with antimony–carbon bonds could be obtained by the reaction of **3** 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), $[(OEP)SbMe_2]^+PF_6^-$ (**2a**-PF_6), which was obtained in 70% yield by column chromatography (neutral alumina: benzene/methanol = 75/1) followed by counteranion exchange with ammonium hexafluorophosphate. The compound was remarkably stable in comparison with corresponding group 13 and 14 analogues[6-12] and was characterized by HRMS, elemental analysis, X-ray analysis (*vide infra*), and ^1H NMR, which showed a characteristic methyl signal of six hydrogens at

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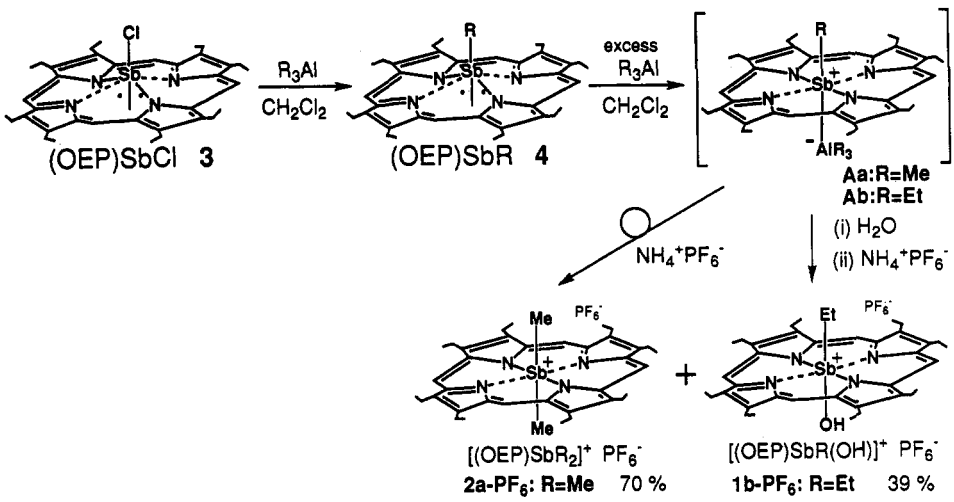
Scheme 1



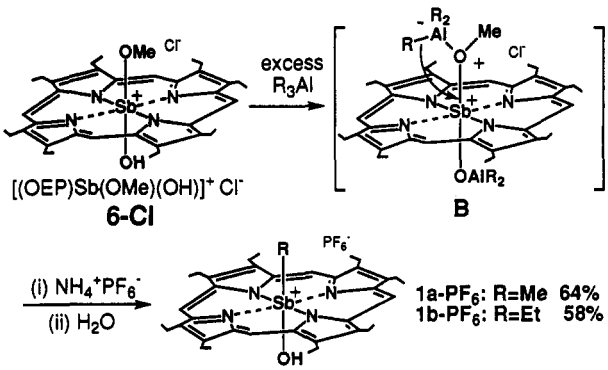
a very high field (δ −6.73) because of the ring current effect of the porphyrin nucleus.[6-12]

A similar reaction of **3** with Et_3Al in CH_2Cl_2 also gave a compound bearing an antimony–carbon bond, but the compound isolated was a monoethyl compound with Sb(V), $[(OEP)SbEt(OH)]^+PF_6^-$ (**1b**-PF_6) (Scheme 1). The ^1H NMR spectrum of this compound also showed a characteristic ethyl signal (Sb–*Et*) at a very high field (δ −5.87 (q, 2H) and −4.33 (t, 3H)), but the integration showed the presence of only one ethyl group. In addition, the methylene protons of the ethyl group of the OEP ring were diastereotopic, suggesting the unsymmetrical nature around the antimony atom.[17] Final characterization was carried out by use of elemental analysis and HRMS.

In order to gain detailed insight for the reaction path, the reaction of **3** with Me_3Al was monitored by ^1H NMR ($CDCl_3$). The ^1H NMR showed that a singlet of the methyl group appeared at a higher field (δ −7.95 (s, 3H)) than that of **2a**, suggesting the formation of (OEP)SbMe (**4a**) within 20 min. The peaks assigned to **4a** gradually disappeared to afford those of **2a** during 24 h through some intermediate (**Aa**). In the reaction of Et_3Al with **3**, the initial sets of protons could be observed at a higher field for the ethyl group [δ −7.10 (q, 2H, J = 8 Hz), −4.10 (t, 3H, J = 8 Hz)] of (OEP)SbEt (**4b**), which shifted downfield to give a certain stable intermediate (**Ab**) showing peaks very close to those of **1b** $[(OEP)SbEt(OH)]^+$. These results show that the initially formed alkylantimony(III) **4** is a highly reactive species, which reacts with the second molecule of R_3Al to form an intermediate **A**. The intermediate **Aa** rearranges in the presence of another Me_3Al to give **2a** when R is methyl, but **Ab** does not rearrange to **2b** and remains there probably because of considerable steric hindrance.[18]

Another possibility to give **1b** is to assume the presence of an intermediate $[(OEP)SbEt(Cl)]^+Y^-$ by the reaction of **4** with Et_2AlCl generated in situ. This cannot be the case, however, because we have found that $[(TPP)SbMe(Cl)]^+Cl^-$ reacts with R_3Al (R: Me, Et, *i*-Bu) very rapidly to afford $[(TPP)SbMe(R)]^+Cl^-$ compared to the rate of these reactions at room temperature.[19]

Scheme 2



Preparation of $[(OEP)SbMe(OH)]^+PF_6^-$ (1a-PF_6) from $[(OEP)Sb(OMe)OH]^+Cl^-$ (6-Cl). Compound **1a**-PF_6 could be prepared in 37% yield from the reaction of Me_3Al with $[(OEP)Sb(OMe)(OH)]^+Cl^-$ (**6-Cl**) under dichloromethane reflux for 22 h followed by counteranion exchange and was characterized by HRMS, elemental analysis, and ^1H NMR (δ −6.10 for Sb–*Me*). In addition, the reaction of **6-Cl** with Et_3Al also gave **1b**-PF_6 in 58% yield. We believe the formation of an active aluminate complex intermediate (**B**) triggers the reaction, as shown in Scheme 2. Compound **6-Cl** was prepared from **3** with aqueous hydrogen peroxide (35%) in MeOH, and $[(OEP)Sb(OH)_2]^+Cl^-$ (**7-Cl**) was prepared from **3** with aqueous hydrogen peroxide (35%) in acetonitrile. **7-Cl** was confirmed not to give **1a** under conditions similar to those of **6-Cl** (Scheme 3).

X-ray Crystal Structures of 2a-PF_6. Crystals of **2a**-PF_6 suitable for X-ray analysis were obtained by recrystallization from acetonitrile. X-ray structural analysis of the compound has been carried out on the basis of the centrosymmetric $P2_1/m$ group, showing the Sb atom and the axial carbon atoms on a crystallographic mirror plane. Refinement led to the final values of R = 0.051 and R_w = 0.068. In this case the solvent acetonitrile (population 0.5) was found incorporated in the crystal lattice. Figure 1 shows the ORTEP drawing, and the solvent was omitted

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(18) We have the following qualitative evidence for the unusually distinct steric hindrance. (i) The rates of reaction of $[(OEP)SbMe(Cl)]^+Cl^-$ with 1000 equiv of ROH to give $[(OEP)SbMe(OR)]^+Cl^-$ in MeCN were the following order: MeOH (12 h, room temperature, 100%) > EtOH (24 h, reflux, 100%) > *i*-PrOH (96 h, reflux, 50%) > *t*-BuOH (no reaction). (ii) The rate of reaction of $[(TPP)SbMe(Br)]^+Br^-$ with 100 equiv of EtOH in MeCN (3.5 days, reflux, 37%) was much higher than that with CF_3CH_2OH (3.5 days, reflux, 0%).

(19) To be published.

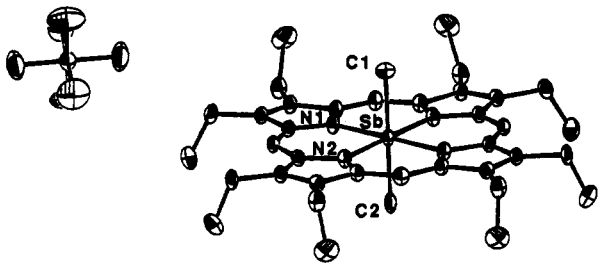

Figure 1. ORTEP diagram (30% probability ellipsoids) for **2a**-PF_6.

Scheme 3

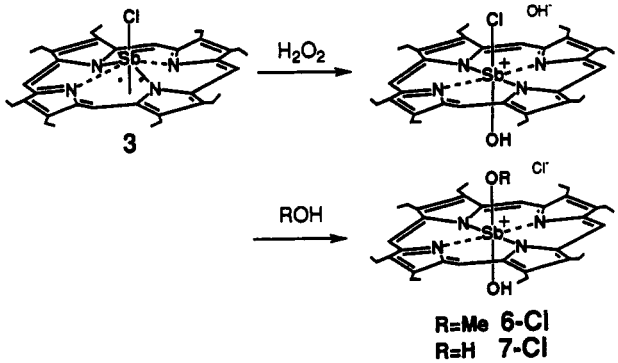

Table 1. Selected Bond Lengths and Angles for 2a-PF_6

	Bond Lengths (Å)		
Sb–C(1)(axial)	2.121(7)	Sb–N(1)	2.108(4)
Sb–C(2)(axial)	2.061(9)	Sb–N(2)	2.104(4)
	Bond Angles (deg)		
C(1)–Sb–C(2)	178.8(3)	C(2)–Sb–N(1)	90.1(2)
C(1)–Sb–N(1)	90.3(2)	C(2)–Sb–N(2)	89.1(2)
C(1)–Sb–N(2)	89.8(2)	N(1)–Sb–N(2)	90.0(1)

to clarify the figure. Selected bond lengths and bond angles for the structure are listed in Table 1. The geometry about antimony was a distorted octahedral, where the lengths of the axial Sb—CH_3 bonds are comparable to the reported lengths for Me_3Sb (2.165 Å)[20] and $Me_3Sb(C{\equiv}CMe)_2$ (2.15 Å).[21] The fairly large difference between the two axial bond lengths (2.121(7) and 2.061(9) Å) is probably because of the packing effect of the crystals.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^1H NMR (400-MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^1H NMR (90-MHz) spectra were also routinely recorded on a Hitachi R-90H spectrometer. ^1H NMR chemical shifts (δ) are given in ppm downfield from internal tetramethylsilane. UV spectra were recorded on a Hitachi 124 spectrophotometer. HRMS spectra were recorded on a JEOL D-300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer. Column chromatography was carried out on Merck alumina neutral 1077.

Preparation of OEPSbCl (3).[16] A mixture of $OEPH_2$ (163 mg, 0.30 mmol) and $SbCl_3$ (1.201 g, 5.27 mmol) in 20 mL of pyridine was heated under reflux for 2 h under Ar. The reaction was quenched with water (10 mL), and hexane (25 mL) and dichloromethane (25 mL) were added. The mixture was filtered through Celite, extracted with dichloromethane (3 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo. Recrystallization of the residue from dichloromethane–ether gave black crystals of **3**. ^1H NMR ($CDCl_3$): 1.95 (t, 24H, J = 8 Hz), 4.23 (dq, 8H, J = 14, 8 Hz), 4.28 (dq, 8H, J = 14, 8 Hz), 10.56 (s, 4H).

Reaction of 3 with Me_3Al. Preparation of [(OEP)Sb-Me_2]$^+PF_6^-$ (2a-PF_6). Trimethylaluminum (1.0 M solution in hexane, 0.38 mL) was added to the solution of **3** (65 mg, 0.094 mmol) in 15 mL of CH_2Cl_2 under nitrogen at room temperature. The mixture was stirred for 4 days at room temperature, and the reaction was quenched with cold water. The mixture was filtered through Celite, extracted with dichloromethane (3 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo. Crude **2a** was subjected to alumina (neutral) column chromatography with benzene–methanol (20:1) as eluent. The residue was dissolved in MeOH, and ammonium hexafluorophosphate (5 equiv) in MeOH was added to the solution. Crude **2a**-PF_6 was recrystallized from dichloromethane–ether to give purple crystals (47 mg, 70%). **2a**-PF_6: mp >300 °C; UV (CH_2Cl_2) λ (log ϵ) 372 (4.81), 402 (4.93 (sch)), 425 (5.30), 488 (3.20 (sch)), 510 (3.40 (sch)), 522 (4.32), 588 (3.85); ^1H NMR ($CDCl_3$) –6.73 (s, 6H), 2.09 (t, 24H, J = 8 Hz), 4.35 (q, 16H, J = 8 Hz), 10.77 (s, 4H); HRMS calcd for $C_{38}H_{50}N_4Sb^+$ (^{121}Sb) 683.3071, found 683.3054; calcd for ^{123}Sb 685.3077, found 685.3052. Anal. Calcd for $C_{38}H_{50}N_4SbPF_6 \cdot 0.5CH_2Cl_2$: C, 53.03; H, 5.89; N, 6.42. Found: C, 52.61; H, 5.64; N, 6.48.

Reaction of 3 with Et_3Al. Preparation of [(OEP)Sb-Et(OH)]$^+PF_6^-$ (1b-PF_6). Triethylaluminum (1.0 M solution in hexane, 0.77 mL) was added to a solution of **3** (53 mg, 0.077 mmol) in 15 mL of CH_2Cl_2 under Ar at room temperature. The mixture was stirred for 5 days at room temperature, and the reaction was quenched with cold water. The mixture was filtered through Celite, extracted with dichloromethane (3 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo. Crude **1b** was subjected to alumina (neutral) column chromatography with benzene–methanol (20:1) as the eluent. The residue was dissolved in MeOH, and ammonium hexafluorophosphate (5 equiv) in MeOH was added to the solution. Crude **1b**-PF_6 was recrystallized from dichloromethane–ether to give red-purple crystals (25 mg, 39%). **1b**-PF_6: mp >300 °C; ^1H NMR ($CDCl_3$) –5.87 (q, 2H, J = 8 Hz), –4.33 (t, 3H, J = 8 Hz), 2.07 (t, 24H, J = 8 Hz), 4.35 (dq, 8H, J = 15, 8 Hz), 4.37 (dq, 8H, J = 15, 8 Hz), 10.85 (s, 4 H); HRMS calcd for $C_{38}H_{50}N_4OSb^+$ (^{121}Sb) 699.3026, found 699.3021; calcd for ^{123}Sb 701.3027, found 701.3047. Anal. Calcd for $C_{38}H_{50}N_4OSbPF_6 \cdot 0.5CH_2Cl_2$: C, 52.07; H, 5.79; N, 6.31. Found: C, 52.30; H, 5.75; N, 5.87.

Preparation of [(OEP)Sb(OMe)(OH)]$^+Cl^-$ (6-Cl). To a solution of **3** (203 mg, 0.294 mmol) in 10 mL of MeOH was added 2 mL of aqueous hydrogen peroxide (35%) at room temperature. The mixture was stirred overnight, and the solvent was evaporated. The mixture was extracted with dichloromethane (3 × 50 mL)–water, dried with $MgSO_4$, and concentrated in vacuo. Crude **6-Cl** was recrystallized from dichloromethane–ether to give purple crystals (180 mg, 83%). **6-Cl**: mp >300 °C; ^1H NMR ($CDCl_3$) –2.74 (s, 3H), 2.07 (t, 24H, J = 8 Hz), 4.34 (q, 16H, J = 8 Hz), 10.85 (s, 4H).

Reaction of 6-Cl with Me_3Al. Preparation of [(OEP)-SbMe(OH)]$^+PF_6^-$ (1a-PF_6). Trimethylaluminum (1.0 M solution in hexane, 1.45 mL) was added to a solution of **6-Cl** (132 mg, 0.182 mmol) in 10 mL of CH_2Cl_2 under Ar at room temperature. The mixture was heated under reflux for 22 h, and the reaction was quenched with cold water. The mixture was extracted with dichloromethane (3 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was subjected to alumina (neutral) column chromatography with benzene–methanol (75:1) as the eluent, crude **1a**-OH from the first eluent was dissolved in MeOH, and ammonium hexafluorophosphate (5 equiv) in MeOH was added to the solution. Crude **1a**-PF_6 was recrystallized from CH_2Cl_2–benzene to give purple needles (48 mg, 37%). **1a**-PF_6: mp >300 °C; ^1H NMR ($CDCl_3$) –6.10 (s, 3H), 2.08 (t, 24H, J = 8 Hz), 4.36 (q, 16H, J = 8 Hz), 10.84 (s, 4H). Anal. Calcd for $C_{37}H_{48}N_4OSbPF_6 \cdot 0.5CH_2Cl_2$: C, 51.53; H, 5.65; N, 6.41. Found: C, 51.76; H, 5.47; N, 6.62.

Reaction of 6-Cl with Et_3Al. Triethylaluminum (1.0 M solution in hexane, 2.1 mL) was added to a solution of **6-Cl** (150

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mg, 0.207 mmol) in 10 mL of CH_2Cl_2 under Ar at room temperature. The mixture was heated under reflux for 24 h, and the reaction was quenched with cold water. The mixture was extracted with dichloromethane (3 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was subjected to alumina (neutral) column chromatography with benzene–methanol (20:1) as the eluent, crude **1b** from the first eluent was dissolved in MeOH, and ammonium hexafluorophosphate (5 equiv) in MeOH was added to the solution. Crude **1b**-PF_6 was recrystallized from CH_2Cl_2–benzene to give purple needles (101 mg, 58%).

Preparation of [(OEP)Sb(OH)$_2$]$^+$Cl$^-$ (7-Cl).[16] A solution of **3** (252 mg, 0.366 mmol) and aqueous hydrogen peroxide (35%, 7 mL) in 15 mL of acetonitrile was stirred for 18 h at room temperature, and the solvent was evaporated. The residue was washed with water and was extracted with dichloromethane (3 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo to give 7-Cl. 7-Cl: mp >300 °C; ^{1}H NMR ($CDCl_3$) 2.08 (t, 24H, J = 8 Hz), 4.34 (q, 16H, J = 8 Hz), 10.85 (s, 4H).

Reaction of 7-Cl with Me$_3$Al. Trimethylaluminum (1.0 M solution in hexane, 1.45 mL) was added to a solution of 7-Cl (24 mg, 0.034 mmol) in 5 mL of CH_2Cl_2 under Ar at room temperature. The mixture was heated under reflux for 22 h, and the reaction was quenched with cold water. ^{1}H NMR of the mixture showed that only a trace amount (<5%) of **1a** was formed.

X-ray Structure Determination of 2a-PF$_6$. Crystal data and numerical details of the structure determinations are given in Table 2. A crystal suitable for X-ray structure determination was mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for data collection. Lattice parameters were determined by least-squares fitting of 31 reflections with 31 ° < 2θ < 35°. Data were collected with the 2θ/ω scan mode. All data were corrected for absorption[22] and extinction.[23] The structures were solved by a direct method with a program, Monte Carlo-Multan.[24] Refinement on F was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters except acetonitrile, whose position was fixed during the refinement. The hydrogen atoms were included in the refinement in calculated positions (C–H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. All the computations were carried out on a Titan-750 computer.

Table 2. Crystal Data for 2a-PF$_6$

formula	$C_{38}H_{50}N_4F_6PSb + 0.5CH_3CN$
mol wt	850.1
cryst syst	monoclinic
space group	$P2_1/m$
cryst dimens, mm	0.90 × 0.40 × 0.25
a, Å	11.777(3)
b, Å	18.183(4)
c, Å	9.712(2)
α, deg	90
β, deg	100.75(2)
γ, deg	90
V, Å^3	2043.1(9)
Z	2
D_{calc}, g cm^{-3}	1.38
abs coeff (ν), cm^{-1}	6.94
F(000)	874
radiation; λ, Å	Mo Kα; 0.710 73
temp, °C	23 ● 1
$2\theta_{max}$, deg	55.0
scan rate, deg/min	6.0
linear decay, %	
data collected	h,−k,±l
total no. of data collcd, unique, obsd	5152, 4839, 3901 ($I > 3\sigma(I)$)
R_{int}	0.03
no of params refined	351
R, R_w, S	0.051, 0.068, 1.69
max shift in final cycle	2.80
final diff map, max, e/Å^3	2.14

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Supplementary Material Available: Lists of the X-ray crystallographic data, intramolecular bond lengths, bond angles, and positional and thermal parameters of **2a**-PF_6 (12 pages). Ordering information is given on any current masthead page.

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