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Synthesis of Unsymmetrically Substituted Antimony(V) Tetraphenylporphyrins

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The following nine unsymmetrically axially substituted antimony(V) tetraphenylporphyrins with an antimony–carbon bond or an antimony–fluorine bond were synthesized: $[(TPP)Sb(Me)(OEt)]^+ClO_4^-$ (**1-ClO$_4$**), $[(TPP)Sb(Me)(OC_6H_4CH_3$-*p*$)]^+ClO_4^-$ (**2-ClO$_4$**), $[(TPP)Sb(Me)(SC_6H_4CH_3$-*p*$)]^+ClO_4^-$ (**3-ClO$_4$**), $[(TPP)Sb(Me)(NHC_6H_4CH_3$-*p*$)]^+ClO_4^-$ (**4-ClO$_4$**), $[(TPP)Sb(Me)(NHCH_2C_6H_5)]^+ClO_4^-$ (**5-ClO$_4$**), $[(TPP)Sb(Me)(OC(=O)C_6H_4Cl$-*m*$)]^+PF_6^-$ (**6-PF$_6$**), $[(TPP)Sb(Me)(Et)]^+PF_6^-$ (**7-PF$_6$**), $[(TPP)Sb(Me)(CH_2CHMe_2)]^+PF_6^-$ (**8-PF$_6$**), and $[(TPP)Sb(F)(OH)]^+ClO_4^-$ (**9-ClO$_4$**). All nine compounds were stable towards atmospheric moisture. X-Ray crystallographic analysis of **6-PF$_6$** revealed that the antimony atom lies at 0.182 Å out-of-plane of the four nitrogens (Δ4N) toward the carbon atom; **6-PF$_6$**: space group $P2_1/n$, a = 25.49(2), b = 11.27(1), c = 16.58(1) Å, β = 96.74(5)°, R = 0.064.

Porphyrins with a group 15 element as a central atom have attracted recent interest,[1—4] but until recently only a few unsymmetrically axially substituted compounds have been reported.[2a,2l,2q] The lack of this type of compounds is due to the difficulty in the substitution reaction from the readily available $[(Por)M(Cl)_2]^+Y^-$ in a stepwise manner. Shimidzu et al. reported the use of silver ion in the substitution reaction from $[(TPP)P(Cl)_2]^+Y^-$ to give $[(TPP)P(OR)(OH)]^+Y^-$ as a major product.[2q] In a recent paper we reported the synthesis of $[(TPP)Sb(R)(OH)]^+Y^-$ (R = Me, or Et) and the antimony–oxygen bond could be converted to the corresponding chloride $[(TPP)Sb(R)(Cl)]^+Y^-$ with the antimony–carbon bond intact.[3a] A couple of unsymmetrically substituted compounds such as $[(TPP)Sb(R)(OMe)]^+Y^-$ could be prepared from the chloride, but the reactivity was not enough to yield substituted products with EtOH. Here we report on the synthesis and the use of $[(TPP)Sb(Me)(Br)]^+Y^-$ for the reactions with several nucleophiles including EtOH, *p*-cresol, *p*-toluenethiol, *p*-toluidine, benzylamine, sodium *m*-chlorobenzoate, triethylaluminum, and triisobutylaluminum. It turned out that the bromide was reactive enough to afford the corresponding substituted products in high yields. The effect of the axial substituent on the ^{1}H NMR chemical shifts of the axial methyl group was examined and the chemical shift was shifted to downfield as the electronegativity of the other axial substituent increased. In addition, unsymmetrically substituted fluoride $[(TPP)Sb(F)(OH)]^+Y^-$ could be prepared from the oxidation of (TPP)SbBr with an equimolar amount of *t*-BuOOH, followed by treatment with $AgBF_4$. The X-ray structural characterization of $[(TPP)Sb(Me)(OC(=O)C_6H_4Cl$-*m*$)]^+PF_6^-$ was carried out. The direction and the degree of the deviation of the central antimony atom from the mean plane of the four nitrogen atoms (Δ4N) was found to be dependent on the electronegativity difference of the two axial substituents.

Experimental

Materials and Measurements. All solvents were dried and distilled prior to use. All reactions were carried out under an argon atmosphere, and subsequent isolation and purification procedures were carried out in the air. Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H NMR (400 MHz) spectra were recorded on a JEOL EX-400 spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane. Column chromatography was carried out on Merck alumina neutral 1077. HRMS spectra were measured by a JEOL SX 102A spectrometer. $[(TPP)Sb(Me)(OH)]^+ClO_4^-$ was prepared according to the reported procedures.[3a]

Preparation of $[(TPP)Sb(Me)(OEt)]^+ClO_4^-$ (1-ClO$_4$). To a solution of $[(TPP)Sb(Me)(OH)]^+ClO_4^-$ (85 mg, 0.10 mmol) in dry dichloromethane (10 mL) was added 0.2 mL (1.41 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (10 mL). Dry ethanol (1.0 mL) was added to the solution and the mixture was heated under reflux for 5.5 d under Ar. After the solvent was evaporated, the residue was treated with dichloromethane (15 mL)/water (15 mL). The organic layer was extracted with dichloromethane (50 mL×2), and washed with water (30 mL), and dried (Na_2SO_4). After removal of the solvent in vacuo, the residue was subjected to neutral alumina column chromatography with benzene–methanol (15 : 1) as an eluent. Counteranion exchange with sodium perchlorate gave $[(TPP)Sb(Me)(OEt)]^+ClO_4^-$ (57 mg, 65%): ^{1}H NMR ($CDCl_3$), δ = −5.36 (s, 3 H), −2.81 (q, 2 H, J = 6.3 Hz), −2.45 (t, 3 H, J = 6.3 Hz), 7.85—8.00 (m, 12 H), 8.18—8.43 (m, 8 H), 9.50 (s, 8 H); UV (CH_2Cl_2) λ (log ε) 333 (4.31), 409 (4.54), 429 (5.60), 566 (4.16), 607 (4.20); HRMS (EI) Calcd for $C_{44}H_{28}N_4Sb^+$ (^{121}Sb): M, 733.1352. Found: *m/z* 733.1376. Calcd for (^{123}Sb) M, 735.1365. Found: *m/z* 735.1342. Anal. Calcd for $C_{47}H_{36}ClN_4O_5Sb$: C, 63.13; H, 4.06; N, 6.27%. Found: C, 62.80; H, 3.93; N, 6.10%.

Preparation of [(TPP)Sb(Me)(OC$_6$H$_4$CH$_3$-*p*)]$^+$ClO$_4^-$ (2-ClO$_4$). To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (72 mg, 0.083 mmol) in dry dichloromethane (3 mL) was added 0.15 mL (1.04 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (3 mL). *p*-Cresol (0.2 mL, 1.91 mmol) was added to the solution and the mixture was heated under reflux for 4 d under Ar. After the solvent was evaporated, the residue was washed with hexane to remove most of the unreacted *p*-cresol. The residue was extracted with dichloromethane (15 mL×2). The organic layer was washed with water (20 mL) and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–methanol (30 : 1) as an eluent. Counteranion exchange with sodium perchlorate gave [(TPP)Sb(Me)(OC$_6$H$_4$CH$_3$-*p*)]$^+$ClO$_4^-$ (46 mg, 58%): ^{1}H NMR (CDCl$_3$) δ = −5.02 (s, 3 H), 1.14 (d, 2 H, J = 8.1 Hz), 1.56 (s, 3 H), 5.32 (d, 2 H, J = 6.3 Hz), 7.84—8.00 (m, 12 H), 8.22—8.45 (m, 8 H), 9.33 (s, 8 H). HRMS (EI) Calcd for C$_{44}$H$_{28}$N$_4$Sb$^+$ (^{121}Sb) : M, 733.1352. Found : *m/z* 733.1370. Calcd for (^{123}Sb) : M, 735.1365. Found : *m/z* 735.1366.

Preparation of [(TPP)Sb(Me)(SC$_6$H$_4$CH$_3$-*p*)]$^+$ClO$_4^-$ (3-ClO$_4$). To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (43 mg, 0.050 mmol) in dry dichloromethane (2 mL) was added 0.10 mL (0.71 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (1 mL) and transferred into a mixture of *p*-toluenethiol (0.2 g, 1.61 mmol) and MS 3A (0.54 g) in dry acetonitrile (2 mL). The mixture was heated under reflux for 15.5 h under Ar. After filtration through Celite, the solvent was evaporated. The residue was extracted with dichloromethane (20 mL×2). The organic layer was washed with water (20 mL) and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–methanol (15 : 1) as an eluent. Counteranion exchange with sodium perchlorate gave [(TPP)Sb(Me)(SC$_6$H$_4$CH$_3$-*p*)]ClO$_4$ (30 mg, 63%): ^{1}H NMR (CDCl$_3$) δ = −5.41 (s, 3 H), 2.06 (s, 3 H), 3.00 (d, 2 H, J = 8.1 Hz), 5.98 (d, 2 H, J = 8.1 Hz), 7.87—7.98 (m, 12 H), 8.15—8.40 (m, 8 H), 9.35 (s, 8 H). HRMS (EI) Calcd for C$_{44}$H$_{28}$N$_4$Sb$^+$ (^{121}Sb) : M, 733.1352. Found : *m/z* 733.1377. Calcd for (^{123}Sb) : M, 735.1365. Found : *m/z* 735.1343.

Preparation of [(TPP)Sb(Me)(NHC$_6$H$_4$CH$_3$-*p*)]$^+$ClO$_4^-$ (4-ClO$_4$). To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (180 mg, 0.021 mmol) in dry dichloromethane (5 mL) was added 0.35 mL (2.47 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (6 mL) and transferred into a mixture of *p*-toluidine (0.83 mL, 7.75 mmol) and MS 3A (3 g) in dry acetonitrile (4 mL). The mixture was heated under reflux for 1.5 d under Ar. After filtration through Celite, the solvent was evaporated. The residue was extracted with dichloromethane (20 mL×2). The organic layer was washed with water (30 mL) and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–methanol (30 : 1) as an eluent. Counteranion exchange with sodium perchlorate gave [(TPP)Sb(Me)(NHC$_6$H$_4$CH$_3$-*p*)]$^+$ClO$_4^-$ (109 mg, 55%): ^{1}H NMR (CDCl$_3$) δ = −5.60 (s, 3 H), 1.63 (d, 2 H, J = 7.9 Hz), 1.76 (s, 3 H), 5.54 (d, 2 H, J = 7.9 Hz), 7.83—7.99 (m, 12 H), 8.07—8.40 (m, 8 H), 9.35 (s, 8 H). HRMS (EI) Calcd for C$_{44}$H$_{28}$N$_4$Sb$^+$ (^{121}Sb): M, 733.1352. Found : *m/z* 733.1378. Calcd for (^{123}Sb) : M, 735.1365. Found : *m/z* 735.1339.

Preparation of [(TPP)Sb(Me)(NHCH$_2$C$_6$H$_5$)]$^+$ClO$_4^-$ (5-ClO$_4$). To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (51 mg, 0.059 mmol) in dry dichloromethane (3 mL) was added 0.10 mL (0.71 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (1 mL) and transferred into a mixture of benzylamine (0.1 mL, 0.92 mmol) and MS 3A (1.0 g) in dry acetonitrile (2 mL). The mixture was stirred for 1.5 d at room temperature under Ar. After filtration through Celite, the solvent was evaporated. The residue was extracted with dichloromethane (25 mL×2). The organic layer was washed with water (30 mL) and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–methanol (15 : 1) as an eluent. Counteranion exchange with sodium perchlorate gave [(TPP)Sb(Me)(NHCH$_2$C$_6$H$_5$)]$^+$ClO$_4^-$ (54 mg, 96%): ^{1}H NMR (CDCl$_3$) δ = −5.73 (s, 3 H), −2.02 (s, 2 H), 4.09 (d, 2 H, J = 7.6 Hz), 6.35 (t, 2 H, J = 7.6 Hz), 6.59 (t, 1 H, J = 7.6 Hz), 7.90—7.95 (m, 12 H), 8.23—8.33 (m, 8 H), 9.35 (s, 8 H). HRMS (EI) Calcd for C$_{44}$H$_{28}$N$_4$Sb$^+$ (^{121}Sb) : M, 733.1352. Found : *m/z* 733.1360. Calcd for (^{123}Sb) : M, 735.1365. Found : *m/z* 735.1346.

Preparation of [(TPP)Sb(Me)(OC(O)C$_6$H$_4$Cl-*m*)]$^+$PF$_6^-$ (6-PF$_6$). To a solution of [(TPP)Sb(Me)(OH)]$^+$OH$^-$ (64 mg, 0.082 mmol) in dry dichloromethane (5 mL) was added 0.20 mL (1.41 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry acetonitrile (6 mL). *m*-Chlorobenzoic acid (41 mg, 0.26 mmol) and sodium carbonate (33 mg, 0.31 mmol) were added to the solution. The mixture was refluxed for 4.5 d under Ar. After removal of the solvent in vacuo, the residue was extracted with dichloromethane (20 mL×2). The organic layer was washed with water (15 mL) and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–methanol (15 : 1) as an eluent to give [(TPP)Sb(Me)(OC(O)C$_6$H$_4$Cl-*m*)]$^+$OH$^-$ (26 mg, 30%). Counteranion exchange with potassium hexafluorophosphate gave [(TPP)Sb(Me)(OC(O)C$_6$H$_4$Cl-*m*)]$^+$PF$_6^-$ quantitatively: Mp 221—228 °C; ^{1}H NMR (CDCl$_3$) δ = −4.71 (s, 3 H), 4.00 (s, 1 H), 4.60 (d, 1 H, J = 7.6 Hz), 6.23 (t, 1 H, J = 7.6 Hz), 6.65 (d, 1 H, J = 7.6 Hz), 7.78—8.16 (m, 12 H), 8.35—8.53 (m, 8 H), 9.34 (s, 8 H); UV (CH$_2$Cl$_2$) λ (log ε) 335 (4.37), 409 (4.54), 429 (5.67), 563 (4.25), 605 (4.22). Anal. Calcd for C$_{52}$H$_{35}$ClN$_4$F$_6$O$_2$PSb: C, 59.48; H, 3.36; N, 5.34%. Found: C, 59.67; H, 2.86; N, 5.23%.

Preparation of [(TPP)Sb(Me)(Et)]$^+$PF$_6^-$ (7-PF$_6$). To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (35 mg, 0.040 mmol) in dry dichloromethane (3 mL) was added 0.1 mL (0.71 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry dichloromethane (7 mL). Triethylaluminum (15% solution in hexane, 0.15 mL, 0.135 mmol) was added to the solution. The mixture was refluxed for 2 d under Ar and was poured onto ice. After filtration with Celite, the filtrate was evaporated. The residue was extracted with dichloromethane (15 mL×2) and organic layer was washed with water (15 mL). The solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–dichloromethane–methanol (15 : 12 : 1) as an eluent. Counteranion exchange with potassium hexafluorophosphate gave [(TPP)Sb(Me)(Et)]$^+$PF$_6^-$ (25 mg, 70%): Mp > 300 °C; ^{1}H NMR (CDCl$_3$) δ = −6.06 (s, 3 H),

−5.86 (q, 2 H, J = 7.8 Hz), −4.21 (t, 3 H, J = 7.8 Hz), 7.77—7.95 (m, 12 H), 8.22—8.37 (m, 8 H), 9.36 (s, 8 H); UV (CH_2Cl_2) λ (log ε) 347 (4.39), 420 (4.68), 441 (5.58), 584 (4.05), 627 (4.33). HRMS (EI) Calcd for $C_{44}H_{28}N_4Sb^+$ (^{121}Sb) : M, 733.1352. Found : m/z 733.1364. Calcd for (^{123}Sb) : M, 735.1365. Found : m/z 735.1342. Anal. Calcd for $C_{47}H_{36}N_4F_6PSb$: C, 61.12; H, 3.93; N, 6.07%. Found: C, 60.80; H, 3.83; N, 6.03%.

Preparation of [(TPP)Sb(Me)(*i*-Bu)]$^+$PF$_6^-$ (8-PF$_6$). To a solution of [(TPP)Sb(Me)(OH)]$^+$ClO$_4^-$ (50 mg, 0.058 mmol) in dry dichloromethane (4 mL) was added 0.12 mL (0.85 mmol) of oxalyl bromide at room temperature under Ar. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dry dichloromethane (10 mL). Triisobutylaluminum (15% solution in hexane, 0.25 mL, 0.13 mmol) was added to the solution. The mixture was refluxed for 2 d under Ar and was poured onto ice. After filtration with Celite, the filtrate was evaporated. The residue was extracted with dichloromethane (20 mL×2) and the combined organic layer was washed with water (30 mL). The solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–dichloromethane–methanol (15 : 9 : 1) as an eluent. Counteranion exchange with potassium hexafluorophosphate gave [(TPP)Sb(Me)(*i*-Bu)]$^+$PF$_6^-$ (36 mg, 69%): Mp 217—225 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = −6.14 (s, 3 H), −6.03 (d, 2 H, J = 5.6 Hz), −4.89——4.57 (m, 1 H), −2.34 (d, 6 H, J = 6.6 Hz), 7.72—7.97 (m, 12 H), 8.22—8.40 (m, 8 H), 9.38 (s, 8 H); UV (CH_2Cl_2) λ (log ε) 347 (4.35), 421 (4.80), 441 (5.49), 584 (3.99), 627 (4.26). HRMS (EI) Calcd for $C_{44}H_{28}N_4Sb^+$ (^{121}Sb) : M, 733.1352. Found : m/z 733.1376. Calcd for (^{123}Sb) : M, 735.1365. Found : m/z 735.1365.

Preparation of [(TPP)Sb(F)(OH)]$^+$ClO$_4^-$ (9-ClO$_4$). To a solution of (TPP)SbBr (119 mg, 0.15 mmol) in dry dichloromethane (5 mL) was added *t*-butyl hydroperoxide (0.052 M dichloromethane solution (1 M = 1 mol dm^{-3}, 2.9 mL, 0.15 mmol) at −10 °C under Ar. Silver tetrafluoroborate (246 mg, 1.26 mmol) was added to the solution. The mixture was stirred for 10 h at room temperature. After filtration through Celite, the filtrate was evaporated. The residue was extracted with dichloromethane (30 mL×2). The organic layer was washed with water (20 mL) and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was subjected to neutral alumina column chromatography with benzene–methanol (15 : 1) as the eluent. Counteranion exchange with sodium perchlorate gave [(TPP)Sb(F)(OH)]$^+$ClO$_4^-$ (46 mg, 36%): Mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ = 7.86—7.92 (m, 12 H), 8.28—8.33 (m, 8 H), 9.50 (s, 8 H); UV (CH_2Cl_2) λ (log ε) 313 (4.18), 420 (5.53), 552 (4.22), 593 (3.95). Anal. Calcd for $C_{44}H_{29}ClFN_4O_5Sb$: C, 60.75; H, 3.36; N, 6.44%. Found: C, 60.50; H, 3.43; N, 6.30%.

X-Ray Structure Determination of [(TPP)Sb(Me)(OC(O)-C$_6$H$_4$Cl-*m*)]$^+$PF$_6^-$ (6-PF$_6$). Crystals suitable for X-ray structure determination were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) for data collection (Table 1). Lattice parameters were determined by least-squares fitting of 24 reflections with $23° < 2\theta < 30°$. Data were collected with the $2\theta/\omega$ scan mode. All data were not corrected for absorption. The structures were solved by a direct method with program Crystan-GM. Refinement of F was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. 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 the computations were carried out on an Indigo 2 computer. Positional and thermal parameters and interatomic distances and angles for **6-PF$_6$** are deposited as Document No. 72003 at the Office of the Editor of Bull. Chem. Soc. Jpn.

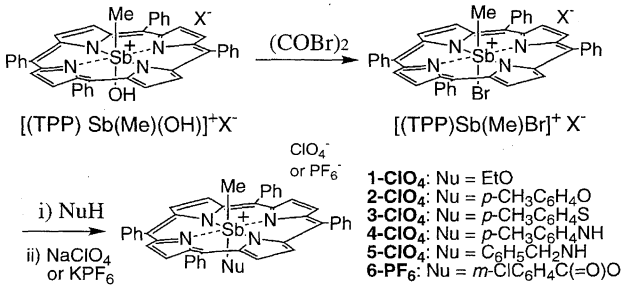
Table 1. Crystallographic Data for [(TPP)Sb(Me)(OC(=O)-C$_6$H$_4$Cl-*m*)]$^+$PF$_6^-$

Formula	$C_{52}H_{35}N_4ClO_2SbPF_6$
Mol wt	1066.10
Cryst. syst.	Monoclinic
Space group	$P2_1/n$
Cryst. dimens./mm	0.30 × 0.30 × 0.10
Color	Violet
Habit	Plate
a/Å	25.49(2)
b/Å	11.27(1)
c/Å	16.58(1)
α/deg	90
β/deg	96.74(5)
γ/deg	90
V/Å^3	4729.45(1)
Z	4
D_{calcd}/g cm^{-3}	1.50
Abs coeff/cm^{-1}	7.448
F (000)	2112
Radiation; λ/Å	Mo Kα, 0.71073
Temp/°C	23 ± 1
$2\theta_{max}$/deg	50
Scan rate/deg min^{-1}	6.0
Linear decay/%	—
Data collected	$\pm h, +k, +l$
Total data collcd, unique, obsd	6876, 4628, 3592 ($I > 5\sigma(I)$)
R_{int}	—
No of params refined	630
R, R_w, S	0.064, 0.072, 5.20
Max shift in final cycle	0.307
Final diff map, max/eÅ^{-3}	1.57

Function minimized was $\sum [w(|F_o|^2 - |F_c|^2)^2]$ which $w = 1.0/[\sigma|F_o|^2 + 0.0003|F_o|^2]$. $R = \sum[(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Results and Discussion

Synthesis. In recent research reported by us,[3a] unsymmetrically substituted [(TPP)Sb(OMe)(OH)]$^+$ClO$_4^-$ was prepared by the reaction of (TPP)SbBr with aqueous hydrogen peroxide in MeOH. The compound was converted to [(TPP)Sb(Me)(Cl)]$^+$PF$_6^-$ with trimethylaluminum and oxalyl chloride and the chloride was substituted with methanol to give [(TPP)Sb(Me)(OMe)]$^+$PF$_6^-$. However, the chloride did not afford substitution products with EtOH, benzenethiol, and benzylamine.[3a] Therefore, we tried to convert the hydroxy group of [(TPP)Sb(Me)(OH)]$^+$X$^-$ to the bromide with a hope for the enhanced reactivity toward nucleophiles. [(TPP)Sb(Me)(OH)]$^+$X$^-$ was treated with oxalyl bromide at room temperature in dichloromethane to give [(TPP)Sb(Me)(Br)]$^+$X$^-$ quantitatively. To our delight the bromide showed enhanced reactivity toward EtOH to give [(TPP)Sb(Me)(OEt)]$^+$PF$_6^-$ (Scheme 1) in 97% yield after counteranion exchange. *p*-Cresol, *p*-toluenethiol, *p*-toluidine, benzylamine, and sodium *m*-chlorobenzoate reacted with [(TPP)Sb(Me)(Br)]$^+$X$^-$ to give the expected substitution products. These proved difficult to purify even after



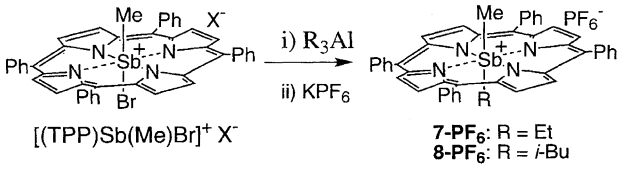
Scheme 1.

repeated chromatography except *m*-chlorobenzoate, which was easily crystallized. Those compounds were characterized on the basis of HRMS and spectroscopic data. The *m*-chlorobenzoate was further characterized by an X-ray crystal structure analysis (vide infra).

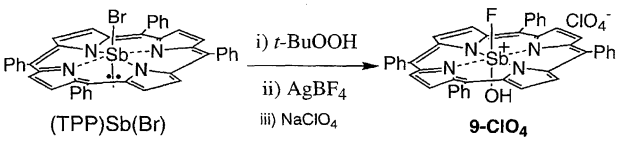
Trialkylaluminum (R = Et, *i*-Bu) also reacted with $[(TPP)Sb(Me)(Br)]^+X^-$ in CH_2Cl_2 to give $[(TPP)Sb(Me)(Et)]^+PF_6^-$ and $[(TPP)Sb(Me)(CH_2CHMe_2)]^+PF_6^-$, respectively, after counteranion exchange. These dialkylated compounds are stable to moisture and could be purified by column chromatography (neutral alumina) (Scheme 2).

Besides the monomethylated compound monofluorinated compound $[(TPP)Sb(F)(OH)]^+ClO_4^-$ could be prepared by treatment of $AgBF_4$ with $[(TPP)Sb(Br)(OH)]^+Y^-$, which was prepared in situ from the oxidation of (TPP)SbBr with an equimolar amount of *t*-BuOOH (Scheme 3).

^{1}H NMR Spectra. Selected ^{1}H NMR data of these compounds are shown in Table 2. Characteristic methyl signals (δ = −4.71——6.41) were observed in $[(TPP)Sb(Me)(X)]^+Y^-$ at very high fields due to large ring current effect of the porphyrin nucleus. The chemical shift was shifted to downfield as the electronegativity of the other axial substituent increased, although a similar trend was not observed in the pyrrole β protons (δ = 9.33—9.45) of these compounds. When the chemical shifts of the methyl signals were plotted against σ_I (Hammett sigma constant for inductive effect of an substituent; Fig. 1), an acceptable straight line was obtained for 14 compounds examined, although that of *m*-chlorobenzoate showed irregular trend. The result indicated that electron density of the porphyrin core was not affected largely by the axial substituents and that of the methyl group was mainly dependent on the inductive effect of the other axial substituent.



Scheme 2.



Scheme 3.

X-Ray Crystal Structure of $[(TPP)Sb(Me)(OC(O)C_6H_4Cl$-*m*$)]^+PF_6^-$. Crystals of $[(TPP)Sb(Me)(OC(O)C_6H_4Cl$-*m*$)]^+PF_6^-$ suitable for X-ray analysis were obtained by recrystallization from dichloromethane/dibutyl ether (1 : 1). X-Ray structural analysis of the compound was carried out on the basis of $P2_1/n$. Refinement led to the final values of R = 0.064 and R_w = 0.072. Figure 2 shows the ORTEP drawing. Selected bond lengths and bond angles are listed in Table 3. The geometry about antimony is a distorted octahedral, where the length of the axial Sb–CH_3 bond (2.13(1) Å) is comparable to the lengths of Sb–CH_3 in $[(TPP)Sb(Me)(F)]^+PF_6^-$ (2.115(6) Å)[3a] and $[(OEP)Sb(Me)_2]^+PF_6^-$ (2.121(7) and 2.061(9) Å).[3d] It is interesting to note that the antimony atom lies at 0.182 Å out-of-plane of the four nitrogens (Δ4N) toward the carbon atom and the degree of the deviation of the central antimony atom from the mean plane of the four nitrogen atoms (Δ4N) becomes

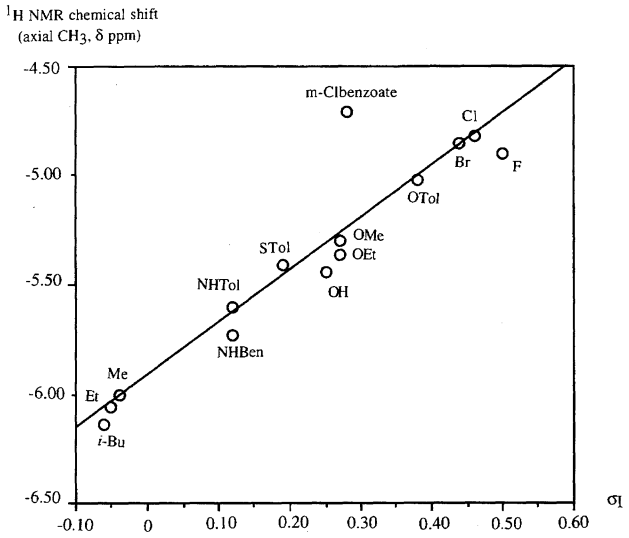


Fig. 1. Plot of the ^{1}H NMR chemical shifts of the methyl signals of $[(TPP)Sb(Me)(X)]^+Y^-$ against σ_I of the axial X group.

Table 2. ^{1}H NMR Chemical Shifts of $[(TPP)Sb(Me)(X)]^+Y^-$

$[(TPP)Sb(Me)X]^+Y^-$														
X	mcb	Br	Cl	F	OTol	OH	OMe	OEt	STol	NHTol	NHBen	Me	Et	*i*-Bu
Axial CH_3	−4.71	−4.85	−4.82	−4.90	−5.02	−5.44	−5.30	−5.36	−5.41	−5.60	−5.73	−6.00	−6.06	−6.14
Pyrrole β	9.34	9.42	9.45	9.47	9.33	9.39	9.42	9.50	9.35	9.35	9.39	9.36	9.36	9.38
σ_I	0.28[a]	0.44	0.46	0.50	0.38[b]	0.25	0.27	0.27[c]	0.19[d]	0.12[e]	0.12[e]	−0.04	−0.05	−0.06[f]

a) for acetyl, b) for OPh, c) for OMe, d) for SMe, e) for NH_2, f) *i*-Pr.

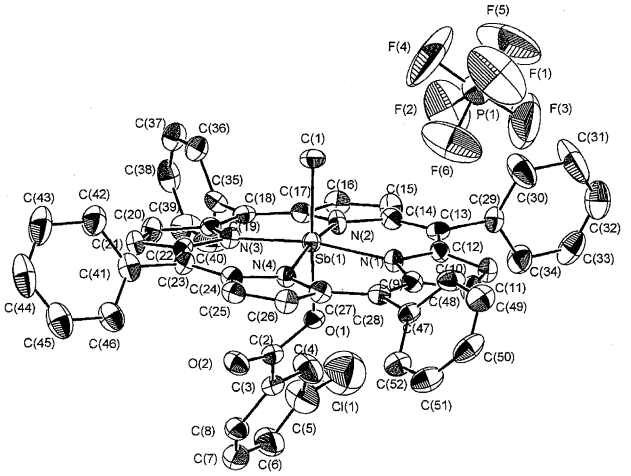


Fig. 2. ORTEP diagram (30% probability ellipsoids) for $[(TPP)Sb(Me)(OC(=O)C_6H_4Cl\text{-}m)]^+PF_6^-$.

Table 3. Selected Bond Lengths and Angles for $[(TPP)Sb(Me)(OC(=O)C_6H_4Cl\text{-}m)]^+PF_6^-$

Bond lengths (Å)			
Sb(1)–C(1)	2.13(1)	Sb(1)–O(1)	2.040(9)
Sb(1)–N(1)	2.08(1)	Sb(1)–N(2)	2.09(1)
Sb(1)–N(3)	2.07(1)	Sb(1)–N(4)	2.13(1)
Bond angles (deg)			
C(1)–Sb(1)–O(1)	173.6(5)	C(1)–Sb(1)–N(1)	96.8(5)
C(1)–Sb(1)–N(2)	94.3(5)	C(1)–Sb(1)–N(3)	93.5(5)
C(1)–Sb(1)–N(4)	96.0(5)	O(1)–Sb(1)–N(1)	82.6(4)
O(1)–Sb(1)–N(2)	79.3(4)	O(1)–Sb(1)–N(3)	87.1(4)
O(1)–Sb(1)–N(4)	90.4(4)		

larger as the axial group X becomes more electronegative, that is, the deviation is larger than that of $[(TPP)Sb(Me)(OOtBu)]^+PF_6^-$ (av. 0.13 Å),[5] but is smaller than that of $[(TPP)Sb(Me)(F)]^+PF_6^-$ (0.201 Å).[3a] A similar relation has been observed for phosphorus octaethylporphyrins and will be discussed in a coming paper.[6]

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6) K.-y. Akiba, R. Nadano, Y. Yamamoto, S. Nagase, K. M. Kadish, will be submitted.