

Fluoride Ion Abstraction of Phosphonium Cations from Their Counter Anion: A Novel Synthetic Method of Fluorophosphoranes

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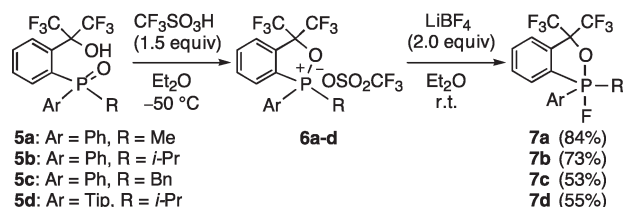
The phosphonium cations bearing the Martin ligand abstracted a fluoride ion from their counter anion, tetrafluoroborate, and the corresponding fluorophosphoranes were obtained in good yields.

Organofluorophosphoranes (R_nPF_{5-n} , $n = 1-4$) have long been known as one of the most thermally stable phosphoranes because of the stabilization effect of high electronegativity of fluorine atoms.¹ Organofluorophosphoranes bearing more than two fluorine atoms (R_nPF_{5-n} , $n = 1-3$) have been synthesized by various methods such as oxidative fluorination of trivalent phosphorus compounds, fluorination of phosphine sulfides, and halogen exchange of chlorophosphoranes, respectively.^{1b} On the other hand, only limited synthetic methods have traditionally been used for the synthesis of monofluorophosphoranes, for example, hydrofluorination of a phosphorus ylide,² substitution reactions of tri- or difluorophosphoranes,^{3,4} and fluorination of monochlorophosphoranes and phosphonium triflates,⁵ respectively. In the last case, the addition of external tetramethylammonium fluoride or tris(diethylamino)difluorophosphorane is essential to fluorination of the phosphorus compounds. In this paper we report a novel synthetic method of monofluorophosphoranes by a fluoride ion abstraction of the corresponding phosphonium cations from their counter anion. The Martin ligand was used for the stabilization of phosphorane structure.⁶

S-Alkylation reaction of cyclic thiophosphinate **1** bearing the Martin ligand with 2.0 equiv of triethyloxonium tetrafluoroborate in CH_2Cl_2 at 50 °C gave the corresponding phosphonium salt **2a** (Scheme 1). In $^{31}P\{^1H\}$ NMR spectra, phosphonium salt **2a** showed a singlet at δ_P 116.4, indicating no interaction between the phosphorus atom and fluorine atoms of its counter anion, tetrafluoroborate, in CH_2Cl_2 . When the solvent was removed and exchanged to ether, the signal of phosphonium salt **2a** completely disappeared with appearance of a new doublet (δ_P -20.9, $^1J_{PF} = 801$ Hz), suggesting quantitative conversion of **2a** to (ethylthio)fluorophosphorane **3**. On the other hand, exchange of the solvent from ether to $CDCl_3$ resulted in the reverse reaction back to the phosphonium tetrafluoroborate. Thus, interconversion between the fluorophosphorane and the phosphonium tetrafluoro-

borate was found to be controlled by the solvent. In order to obtain the fluorophosphorane, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) that is known to form its complex with trifluoroborate was added to the ethereal solution.⁷ Removal of the precipitates by filtration, evaporation of the filtrate, and further separation with HPLC gave (ethylthio)fluorophosphorane **3** as colorless solid in 90% yield. In ^{31}P NMR spectrum ($CDCl_3$) the isolated phosphorane **3** showed a doublet at δ_P -20.9 with $^1J_{PF} = 801$ Hz. Its chemical shift is a typical value of pentacoordinate phosphorus compounds, similarly to that in ether.⁸ The coupling constant of the P-F bond is in the range of those of apical P-F bonds of fluorophosphoranes.^{1b} (Ethylthio)fluorophosphorane **3** is stable at room temperature under argon atmosphere. On exposure in open air for several days, however, it gradually hydrolyzed to give the corresponding cyclic phosphinate **4**.

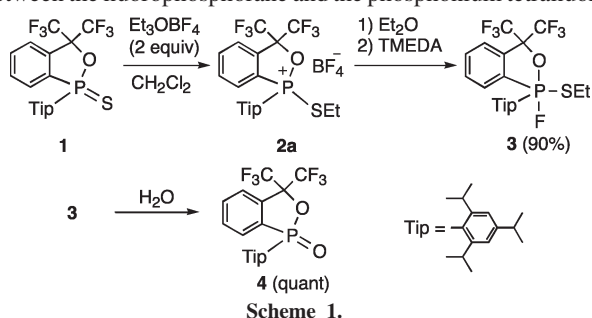
Alkylfluorophosphoranes can also be synthesized by a similar method (Scheme 2). The reactions of the corresponding phosphine oxides **5a-d** with trifluoromethanesulfonic acid gave the phosphonium triflates **6a-d**, respectively. Replacement of the counter anion of **5a-d** by tetrafluoroborate immediately afforded the corresponding fluorophosphoranes **7a-d** in good yields (53–84%), respectively. In contrast to the ethylthio derivative **3**, the alkyl derivatives **7a-d** are stable in open air.



Scheme 2.

The crystal structure of (ethylthio)fluorophosphorane **3** was determined by X-ray crystallographic analysis (Figure 1).⁹ This is the first example of the monofluorophosphorane with a P-S bond. Compound **3** has a pentacoordinate structure with an oxygen and a fluorine atoms at the apical positions and two carbon and a sulfur atoms at the equatorial positions, respectively. The bond angle between two apical bonds ($179.2(1)^\circ$) and the sum of three angles between each two equatorial bonds (359.5°) are very close to those of the ideal TBP structure ($\%TBP \rightarrow SP = 17.0$).¹⁰ The P-F bond length ($1.647(3)$ Å) is the almost same value as that ($1.659(1)$ Å) of a monofluorophosphorane bearing the Martin ligand and benzyl group and that ($1.643(2)$ Å) of 2-fluoro-2,2'-diphenyl-1,3,2-naphthodioxo- λ^5 -phosphole.¹¹ The P-S bond length ($2.092(2)$ Å) is almost same as those ($2.098(2)$ Å,^{12a} $2.0834(8)$ Å^{12b}) of two phosphoranes bearing a sulfur atom at the equatorial position.

Formation of fluorophosphoranes in these reactions clearly shows that phosphonium cations abstracted a fluoride ion from its



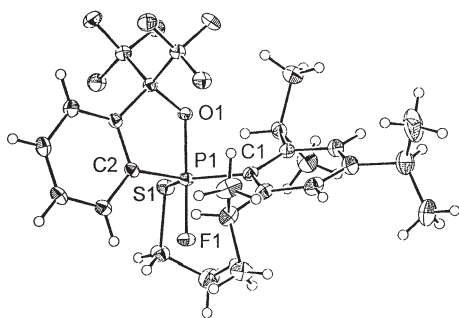
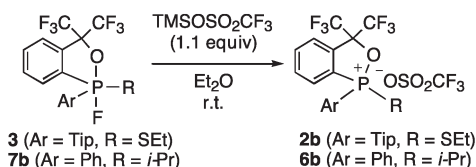


Figure 1. ORTEP drawing of **3** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and bond angles (deg): P(1)–F(1) 1.647(3), P(1)–O(1) 1.767(3), P(1)–C(1) 1.835(5), P(1)–C(2) 1.815(5), P(1)–S(1) 2.092(2), O(1)–P(1)–F(1) 179.2(1), O(1)–P(1)–C(1) 89.3(2), O(1)–P(1)–C(2) 87.4(2), O(1)–P(1)–S(1) 86.0(1), C(1)–P(1)–S(1) 124.12(2), S(1)–P(1)–C(2) 109.8(1), C(1)–P(1)–C(2) 125.6(2).

counter anion, tetrafluoroborate ion.¹³ There has been no report on preparation of a fluorophosphorane by such a fluoride ion abstraction of a phosphonium salt, although the reverse reaction, that is, the conversion of a fluorophosphorane to a phosphonium salt by trifluoroborane etherate has already been reported.^{14,15} The present reaction is formally similar to that of arylum ion in Schiemann reaction, which affords a fluoroarene from an aryldiazonium salt with tetrafluoroborate ion.¹⁶ Both Lewis acidity of the phosphonium cation enhanced by strong electron-withdrawing effect of the Martin ligand and coordination of ether to trifluoroborane seem to have played an important role in abstraction of a fluoride ion.

Fluorophosphoranes thus formed are easily defluorinated. Treatment of **3** or **7b** with 1.1 equiv of trimethylsilyl triflate instead of trifluoroborane etherate in ether at room temperature quantitatively gave the corresponding phosphonium triflate, respectively (Scheme 3). Irreversibility of this reaction causes the formation of fluorotrimethylsilane whose Si–F bond is very strong and hard to dissociate.



Scheme 3.

In summary, we developed the novel synthetic method of fluorophosphoranes. The key in this method seems to be the cooperative action of high Lewis acidity of the phosphorus atom with coordination of ether to trifluoroborane. And we demonstrated that the phosphonium triflates are readily obtained from the fluorophosphoranes.

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Dedicated to Prof. Teruaki Mukaiyama on the occasion of his 75th birthday.

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- 3**: colorless crystals, mp 129.6–132.0 °C (dec.); ¹H NMR (500 MHz, CDCl₃) δ 0.59 (d, ³J_{HH} = 6.7 Hz, 3H, *o*-(CH₃)(C'H₃)CH of Tip), 1.21–1.28 (m, 12H, *p*-(CH₃)₂CH of Tip, CH₃CH₂S, *o*-(CH₃)(C'H₃)CH of Tip), 1.30 (d, ³J_{HH} = 6.7 Hz, 3H, *o*'-(CH₃)(C'H₃)CH of Tip), 1.39 (d, ³J_{HH} = 6.7 Hz, 3H, *o*'-(CH₃)(C'H₃)CH of Tip), 2.79–2.95 (m, 3H, CH₃CH₂S, *p*-(CH₃)(C'H₃)CH of Tip), 3.39–3.50 (m, 1H, *o*-(CH₃)(C'H₃)CH of Tip), 4.91 (sept, ³J_{HH} = 6.7 Hz, 1H, *o*'-(CH₃)(C'H₃)CH of Tip), 6.93 (d, ⁴J_{PH} = 7.5 Hz, 1H, *m*-H of Tip), 7.11 (d, ⁴J_{PH} = 5.3 Hz, 1H, *m*'-H of Tip), 7.65–7.76 (m, 3H), 8.31 (dd, ³J_{PH} = 11.5 Hz, ³J_{HH} = 7.8 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 15.6 (d, ³J_{PC} = 9 Hz), 23.6 (s), 23.7 (s), 23.8 (s), 24.5 (s), 25.7 (s), 27.6 (dd, ²J_{PC} = 18 Hz, ³J_{FC} = 6 Hz), 30.2 (d, ³J_{PC} = 5 Hz), 31.2 (dd, ³J_{PC} = 5 Hz, ⁴J_{FC} = 8 Hz), 33.9 (s), 82.4 (sept, ²J_{FC} = 31 Hz), 122.1 (q, ¹J_{FC} = 289 Hz), 122.3 (d, ³J_{PC} = 17 Hz), 122.4 (q, ¹J_{FC} = 288 Hz), 123.7 (d, ³J_{PC} = 17 Hz), 125.2 (d, ³J_{PC} = 16 Hz), 131.4 (d, ³J_{PC} = 15 Hz), 132.7 (dd, ¹J_{PC} = 181 Hz, ²J_{FC} = 28 Hz), 133.0 (d, ⁴J_{PC} = 3 Hz), 133.7 (dd, ²J_{PC} = 8 Hz, ³J_{FC} = 12 Hz), 135.5 (dd, ²J_{PC} = 21 Hz, ³J_{FC} = 4 Hz), 136.4 (dd, ¹J_{PC} = 157 Hz, ²J_{FC} = 30 Hz), 148.8 (d, ²J_{PC} = 16 Hz), 150.0 (d, ⁴J_{PC} = 4 Hz), 151.6 (dd, ²J_{PC} = 15 Hz, ³J_{FC} = 7 Hz); ¹⁹F NMR (254 MHz, CDCl₃) δ –25.4 (d, ¹J_{PF} = 801.0 Hz, 1F), –74.8 (q, ⁴J_{FF} = 9.1 Hz, 3F), –75.4 (q, ⁴J_{FF} = 9.1 Hz, 3F); ³¹P{¹H} NMR (109 MHz, CDCl₃) δ –20.9 (d, ¹J_{PF} = 801.0 Hz). Anal. Calcd for C₂₆H₃₂F₇OPS: C, 56.11; H, 5.86%. Found: C, 56.25; H, 5.60%.
- Crystallographic data for **3**: C₂₆H₃₂F₇OPS, FW = 556.56, T = 173 K, monoclinic, P2₁/n, a = 8.640(4), b = 18.800(1), c = 16.724(7) Å, β = 90.730(3)°, V = 2713.1(2) Å³, Z = 4, D_{calc} = 1.362 g cm^{–3}. The final cycle of full-matrix least squares refinement was based on 4069 observed reflections (I > 3.00σ(I)) and 325 variable parameters and converged at R(Rw) = 0.054 (0.058). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-176386. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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