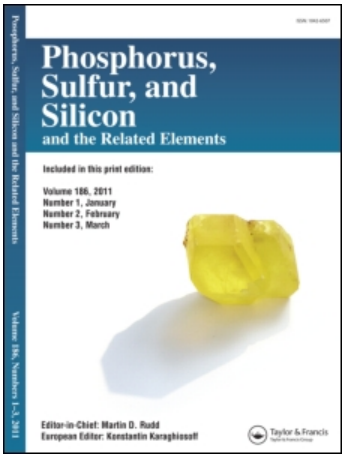


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# SYNTHESIS AND MOLECULAR STRUCTURES OF FLUOROPHOSPHORANES, $R_3PF_2$, ISOELECTRONIC WITH ANIONIC FLUOROSILICATES

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# SYNTHESIS AND MOLECULAR STRUCTURES OF FLUOROPHOSPHORANES, $R_3PF_2$, ISOELECTRONIC WITH ANIONIC FLUOROSILICATES[1,2]

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

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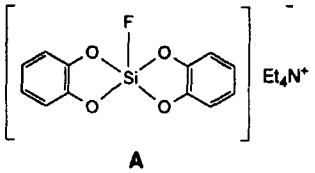
The new difluorophosphoranes Ph(*o*-Tol)$_2$PF$_2$ (**1**), Mes$_3$PF$_2$ (**2**), Ph(*1*-Np)$_2$PF$_2$ (**3**), (*o*-Tol)$_3$PF$_2$, (*p*-Tol)$_3$PF$_2$, Ph(*t*-Bu)$_2$PF$_2$, and (Ph$_2$PF$_2$)$_2$CH$_2$ containing bulky substituents were prepared by the fluorination reaction of precursor organophosphines with dimethylaminosulfur trifluoride. They were characterized by $^1$H, $^{31}$P, and $^{19}$F NMR spectra. The molecular structures of **1–3** revealed trigonal bipyramidal geometries. Comparison of the structural data with that of isoelectronic anionic fluorosilicates along with the NMR data suggests the operation of a steric effect that increases bond lengths in the difluorophosphoranes **1–3** and in related anionic silicates. The data are discussed relative to enhanced reactivity observed for anionic silicates. **1** crystallizes in the monoclinic space group C2/c with a = 11.819(3) Å, b = 10.163(2) Å, c = 13.992(3) Å, $\beta$ = 99.14(2)°, and Z = 4. **2** crystallizes in the monoclinic space group C2/c with a = 10.531(2) Å, b = 12.667(2) Å, c = 18.110(4) Å, $\beta$ = 104.21(2)°, and Z = 4. **3** crystallizes in the monoclinic space group P2$_1$/c with a = 15.868(2) Å, b = 7.434(1) Å, c = 18.213(4) Å, $\beta$ = 112.34(2)°, and Z = 4. The final conventional unweighted residuals are 0.063 (**1**), 0.060 (**2**), and 0.040 (**3**).

*Key words:* Difluorophosphoranes, anionic fluorosilicates, x-ray structures, NMR spectra



## INTRODUCTION

The synthesis and X-ray structural study of a series of cyclic[3–5] and acyclic[6–12] anionic five-coordinated fluorosilicates varying in electronic and steric requirements have been reported recently. The geometries exist as trigonal bipyramids (TBP) except for **A** which represents the first square pyramidal geometry for silicon.[3a]




**A**

It is of interest to compare bond parameters with related fluorophosphoranes,[13–21] particularly in view of the proposed existence of the pentacoordinated state as an intermediate in nucleophilic displacement reactions.[22–24] Such a comparison would also benefit judgements on the enhanced reactivity ascribed to the pentacoordinate silicon state.[9,23–35]

To make this comparison more meaningful, we report the synthesis and molecular structures of Ph(*o*-Tol)$_2$PF$_2$ (**1**), Mes$_3$PF$_2$ (**2**), and Ph(*1*-Np)$_2$PF$_2$ (**3**) (Tol = tolyl,

Mes = mesityl, Np = naphthyl). The availability of the structures of these fluorophosphoranes having appreciable steric requirements provides a comparison with anionic fluorosilicates with related steric features, *e.g.*, $[Ph_2(1\text{-Np})SiF_2][(Me_2N)_3S]$.[8] Also reported are the syntheses of $(o\text{-Tol})_3PF_2$, $(p\text{-Tol})_3PF_2$, $Ph(t\text{-Bu})_2PF_2$, and $(Ph_2PF_2)_2CH_2$. $^1H$, $^{31}P$, and $^{19}F$ NMR spectra are obtained on all of the organodifluorophosphoranes.

## EXPERIMENTAL

### *Reagents and Procedures*

Chemicals were obtained from Aldrich, Eastman Kodak, Fisher Scientific, and Alfa and used without further purification. Solvents used were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[36] All reactions were carried out in a dry nitrogen atmosphere using Schlenk-type glassware. $^1H$, $^{19}F$, and $^{31}P$ NMR spectra were recorded on a Varian XL 300 FT/NMR spectrometer equipped with a multinuclear broad-band probe and operated at 300, 282.2, and 121.4 MHz, respectively. Resonances are referenced versus tetramethylsilane ($^1H$), $CFCl_3$ used as an internal standard ($^{19}F$), and 85% orthophosphoric acid (external standard, $^{31}P$). All NMR spectra were recorded at 23°C. Chemical shifts are in ppm with negative shifts upfield.

### *Syntheses*

*Phenyl Di-o-Tolyldifluorophosphorane, $Ph(o\text{-}Tol)_2PF_2$* (**1**). Phenyl di-*o*-tolylphosphine ($\delta$ $^{31}P$ = −21.9) (0.73 g, 2.52 mmol) was dissolved in diethyl ether (20 mL) and dimethylaminosulfur trifluoride (0.25 mL, 0.34 g, 2.56 mmol) was added to the solution with a syringe. Reaction time was 8 h. Crystals were obtained by slow evaporation of solvent at 20°C; m.p. 120°C (yield 0.50 g, 60%). $^1H$ NMR ($CDCl_3$): 2.41 (s, 9 H, *o*-$CH_3$), 6.90–8.00 (m, 13 H, $H_{Ar}$). $^{31}P$ NMR ($CDCl_3$): −41.2 (t, $^1J$(P—F) = 630 Hz); +40 (s, PhP(*o*-Tol)$_2$(O), minor). $^{19}F$ NMR ($CDCl_3$): −30.1 (d, $J$(P—F) = 628 Hz). Anal. Calcd for $C_{20}H_{19}F_2P$: C, 73.20; H, 5.80. Found: C, 73.38; H, 6.07.

*Trimesityldifluorophosphorane, $Mes_3PF_2$* (**2**). Trimesitylphosphine[37] ($\delta$ $^{31}P$ = −36.2) (0.20 g, 0.51 mmol) was dissolved in dry diethyl ether (20 mL) and dimethylaminosulfur trifluoride (0.050 mL, 0.068 g, 0.51 mmol) was added to the solution via a syringe under a nitrogen atmosphere. The reaction mixture was stirred for 24 h and the volume of solution reduced to *ca.* 10 mL. Slow evaporation of the solvent gave plate-like crystals of **2**; m.p. 268–272°C (yield 0.15 g, 68%). $^1H$ NMR ($CDCl_3$): 2.20 (s, 18 H, *o*-$CH_3$), 2.25 (s, 9 H, *p*-$CH_3$), 6.80 [d, 9 H, $H_{Ar}$, $^4J$(P—H) = 5.3 Hz]. $^{31}P$ NMR ($CDCl_3$): −40.4 (t, $J$(P—F) = 654 Hz). $^{19}F$ NMR ($CDCl_3$): −25.8 (d, $^1J$(P—F) = 647 Hz. Anal. Calcd for $C_{27}H_{33}F_2P$: C, 76.05; H, 7.70. Found: C, 75.40; H, 8.24.

*Phenyl-Di-1-Naphthylphosphine, $Ph(1\text{-}Np)_2P$.* *n*-Butyllithium (2.5 M solution in *n*-hexane) (3.20 g, 50.0 mmol) was syringed into a three-necked flask under a stream of dry purified argon. Freshly distilled diethyl ether was added (20 mL). *1*-Bromonaphthalene (10.34 g, 49.9 mmol) dissolved in diethyl ether (30 mL) was slowly added over a period of 10 min to the butyllithium solution. Initially, there was formation of a precipitate. A turbid milky solution resulted after the addition of bromonaphthalene was complete. After allowing the reaction mixture to stir for 5 min at room temperature, phenyldichlorophosphine (4.47 g, 25.0 mmol) dissolved in diethyl ether (50 mL) was added dropwise to the *1*-naphthyl lithium formed *in situ*. The reaction mixture was heated under reflux for 3 h, allowed to come to room temperature, and treated with 50 mL of 10% aqueous sodium hydroxide. The organic layer was separated, washed with water (2 × 50 mL). The aqueous solution was extracted with benzene (3 × 50 mL). The organic layers were combined and dried ($Na_2SO_4$). Removal of solvent yielded an oil which upon addition of *n*-hexane yielded a pale yellow solid. Recrystallization from *n*-butanol yielded the title compound; m.p. 212°C (lit m.p. 210–212°C[38]) (yield 4.2 g, 46.4%).

*Phenyl-Di-1-Naphthyldifluorophosphorane, $Ph(1\text{-}Np)_2PF_2$* (**3**). Phenyl-di-*1*-naphthylphosphine (1.0 g, 2.85 mmol) was dissolved in freshly distilled diethyl ether (50 mL) under an atmosphere of dry argon. Dimethylaminosulfur trifluoride (0.42 g, 3.16 mmol) dissolved in diethyl ether (30 mL) was added dropwise to the phosphine solution at room temperature over a period of 15 min and the reaction mixture was stirred for 2 h. The precipitate formed was filtered (0.30 g). The filtrate was allowed to slowly evaporate under a positive flow of dry Ar at room temperature. After a day, chunky crystals grew. It was found that the initial precipitate and the crystals that grew out of solution were the same

and gave the title compound; m.p. 207–212°C (yield 0.60 g, 54.3%). $^1$H NMR ($C_6D_6$): 6.80–7.20, 7.50–8.50 (m, $H_{Ar}$). $^{31}$P NMR ($C_6D_6$): −41.6 ($^1J$(P—F) = 644 Hz. $^{19}$F NMR ($C_6D_6$): −21.3 ($^1J$(P—F) = 644 Hz). Anal. Calcd for $C_{26}H_{19}PF_2$: C, 78.00; H, 4.78. Found: C, 77.95; H, 4.95.

The following compounds were synthesized using a similar procedure to that described for **1–3**.

*Tri-o-Tolyldifluorophosphorane, (o-Tol)$_3PF_2$.* M.p. 162°C (yield 45% for 2.5 mmol of (*o*-Tol)$_3$P used). $^1$H NMR ($CDCl_3$): 2.52 (s, 9 H, *o*-C$H_3$), 6.76–7.16, 7.69–7.82 (m, 12 H, $H_{Ar}$). $^{31}$P NMR ($CDCl_3$): −34.3 (t, $^1J$(P—F) = 621 Hz), +37.01 (s, (*o*-Tol)$_3$P(O)), minor). $^{19}$F ($CDCl_3$): −26.0 (d, $^1J$(P—F) = 620 Hz). Anal. Calcd for $C_{21}H_{21}F_2P$: C, 73.69; H, 6.14. Found: C, 73.20; H, 6.46. This compound hydrolyses very rapidly in air to (*o*-Tol)$_3$P(O), m.p. 148°C.

*Phenyl Dimesityldifluorophosphorane, PhMes$_2PF_2$: (a) Synthesis of PhMes$_2$P.* The phosphine used, Mes$_2$P(Ph), was prepared by the reaction of dichlorophenylphosphine with two mole equivalents of mesityl magnesium bromide in THF (25% yield for 20 mmol of $PhPCl_2$ used), m.p. 103°C. $^1$H NMR ($CDCl_3$): 2.09 (s, 12 H, *o*-C$H_3$), 2.26 (s, 6 H, *p*-C$H_3$), 6.82 (d, 4 H, $H_{Mes}$, $^4J$(P—H) = 2 Hz), 7.25, 7.35 (m, 5 H, $H_{Ph}$). $^{31}$P NMR ($CDCl_3$): −23.0. Anal. Calcd for $C_{24}H_{27}P$: C, 83.23; H, 7.80. Found: C, 83.39; H, 7.93.

*(b) Synthesis of PhMes$_2PF_2$.* M.p. 172°C (80% yield for 1.3 mmol of PhMes$_2$P used). $^1$H NMR ($CDCl_3$): 2.07 (s, 6 H, *p*-C$H_3$), 2.14 (s, 12 H, *o*-C$H_3$), 6.76–7.16, 7.69–7.82 (m, 9 H, $H_{Ar}$). $^{31}$P NMR ($CDCl_3$): −44.2 (t, $^1J$(P—F) = 636 Hz), 29.9 (s) (*ca.* 3%, Mes$_2$PPh(O)). $^{19}$F NMR ($CDCl_3$): −31.4 (d, $^1J$(P—F) = 635 Hz). Anal. Calcd for $C_{24}H_{27}F_2P$: C, 75.00, H, 7.03. Found: C, 74.85; H, 7.14.

*Tri-p-Tolyldifluorophosphorane, (p-Tol)$_3PF_2$.* M.p. 94–95°C (57% yield, 0.5 g, for 2.5 mmol of (*p*-Tol)$_3$P used). $^1$H NMR ($C_6D_6$): 2.0 (s, 9 H, *p*-C$H_3$), 6.90–7.10, 8.10–8.30 (m, 12 H, $H_{Ar}$). $^{31}$P NMR ($C_6D_6$): −56.1 (t, $^1J$(P—F) = 656 Hz). $^{19}$F ($C_6D_6$): −40.8 (d, $^1J$(P—F) = 654 Hz).

The following represent product formation in NMR tubes.

*Phenyl Di-t-Butyldifluorophosphorane, Ph(t-Bu)$_2PF_2$.* $^1$H NMR ($C_6D_6$): 1.27 (td, 18 H, C$H_3$, $^3J$(P—H) = 18.8 Hz, $^4J$(F—H) = 5.7 Hz), 7.60–7.80, 8.00–8.20 (m, 5 H, $H_{Ar}$). $^{31}$P NMR ($C_6D_6$): −31.2 (t, $^1J$(P—F) = 740.5 Hz). Additional peaks observed at 75.50, 54.56, and 45.79 ppm. $^{19}$F NMR ($C_6D_6$): −60.9 (d, $^1J$(P—F) = 741.0 Hz).

*Methylenebis(diphenyldifluorophopshorane), (Ph$_2PF_2$)$_2CH_2$.* $^1$H NMR ($C_6D_6$): 3.67 [qt, 2 H, $^2J$(P—H) = 19.6 Hz, $^3J$(F—H) = 14.3 Hz], 6.95–7.15, 7.90–8.10 (m, 20 H, $H_{Ar}$). $^{31}$P NMR ($C_6D_6$): −46.9 ($^1J$(P—F) = 640–680 Hz), $^{19}$F NMR ($C_6D_6$): −26.9 ($J$(P—F) ≈ 644 Hz).

## X-RAY EXPERIMENTAL SECTION

All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda$ K$\bar{\alpha}$ = 0.71073 Å) at an ambient temperature of 23 ± 2°C. Details of the experimental procedures have been described previously.[39]

Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data was collected using the $\theta$-2$\theta$ scan mode with $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 50°$. In all cases a quadrant of independent data (+h, +k, ±l) was collected. No corrections were made for absorption. The structures were solved by use of direct methods and were refined by full-matrix least squares.[40]

*X-Ray Study for Ph(o-Tol)$_2PF_2$* (**1**). The crystal used for the study was cut from a larger polyfaceted crystal with frosted surfaces and had dimensions of 0.30 × 0.38 × 0.40 mm.

*Crystal Data:* $C_{20}H_{19}F_2P$, monoclinic space group C2/c (No. 15), a = 11.819(3) Å, b = 10.163(2) Å, c = 13.992(3) Å, $\beta$ = 99.14(2)°, V = 1659.4 Å$^3$, and Z = 4. A total of 1457 independent reflections was measured. The 13 independent non-hydrogen atoms were refined anisotropically. The seven independent aromatic hydrogen atoms were included in the refinement as fixed isotropic scatterers in ideal positions. The three independent methyl hydrogen atoms were omitted from the refinement. The final agreement factors[41] were R = 0.063 and $R_w$ = 0.090 for the 1162 reflections with $I > 2\sigma_I$.

*X-Ray Study for Mes$_3PF_2$* (**2**). The colorless crystal used for the study was cut from a fused mass of chunky crystals and had dimensions of 0.33 × 0.35 × 0.37 mm.

*Crystal Data:* $C_{27}H_{33}F_2P$, monoclinic space group C2/c (No. 15), a = 10.531(2) Å, b = 12.667(2) Å, c = 18.110(4) Å, $\beta$ = 104.21(2)°, V = 2342.0 and Z = 4. A total of 2049 independent reflections was measured. The 17 independent non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were treated as described for **1**. The 12 independent methyl hydrogen atoms which were not disordered with respect to the two-fold axis were located on a difference Fourier and were refined isotropically with fixed isotropic thermal parameters. Hydrogen atoms bonded to carbon on the two-

fold axis were omitted from the refinement. The final agreement factors[41] were R = 0.060 and $R_w$ = 0.088 for the 1519 reflections with $I > 2\sigma_I$.

*X-Ray Study for Ph(1-Np)$_2$PF$_2$* (**3**). The colorless irregular crystal used for the study was cut from a fused mass of lath-shaped crystals and had approximate dimensions of 0.20 × 0.40 × 0.45 mm.

*Crystal Data:* $C_{26}H_{19}F_2P$, monoclinic space group $P2_1/c$ (No. 14), a = 15.868(2) Å, b = 7.434(1) Å, c = 18.213(4) Å, $\beta$ = 112.34(2)°, V = 1987.1 Å$^3$, and Z = 4. A total of 3479 independent reflections was measured. The 29 independent non-hydrogen atoms were refined anisotropically. The 19 independent hydrogen atoms were treated as described for **1**. The final agreement factors[41] were R = 0.040 and $R_w$ = 0.051 for the 2469 reflections with $I > 2\sigma_I$.

## RESULTS

The molecular geometry and the atom-labeling scheme for **1** is shown in the ORTEP plot of Figure 1, while selected bond distances and angles are given in Table I. The corresponding information for **2** and **3** is given in Figures 2 and 3 and in Tables II and III. Refined atomic coordinates are listed in Tables IV–VI for **1**–**3**. Anisotropic thermal parameters, expanded tables of bond distances and angles, and hydrogen atom parameters for all three compounds will be deposited with the Cambridge Crystallographic Data Centre (CCDC), U.K.



## DISCUSSION

All of the organodifluorophosphoranes, whose NMR spectra are listed in Table VII, were prepared by the fluorination of the precursor organophosphine with the

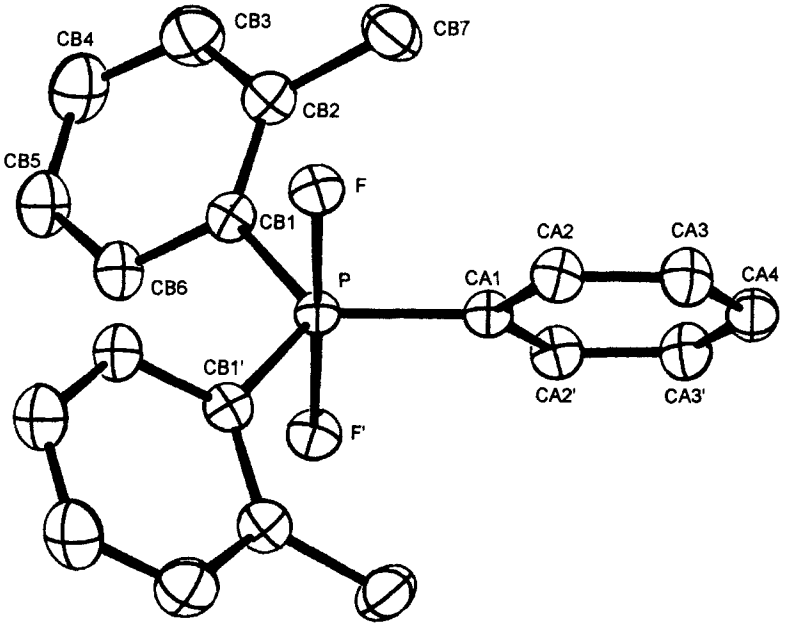



FIGURE 1 ORTEP plot of Ph(*o*-Tol)$_2$PF$_2$ (**1**) with thermal ellipsoids at the 30% probability level. Primed atoms are related to unprimed ones with the same name by the crystallographic two-fold axis passing through P, CA1 and CA4. Hydrogen atoms are omitted for clarity.

TABLE I
Selected distances (Å) and angles (deg) for $Ph(o\text{-}Tol)_2PF_2$ (**1**)[a]

| | | | |
|---|---|---|---|
| P–F | 1.683(2) | CA1–CA2 | 1.412(5) |
| P–CA1 | 1.803(3) | CA2–CA3 | 1.370(6) |
| P–CB1 | 1.827(4) | CA3–CA4 | 1.393(5) |
| CB1–CB2 | 1.395(6) | CB4–CB5 | 1.359(7) |
| CB2–CB3 | 1.391(6) | CB5–CB6 | 1.383(6) |
| CB3–CB4 | 1.392(7) | CB6–CB1 | 1.397(5) |
| | | CB2–CB7 | 1.532(7) |
| F–P–CA1 | 90.74(9) | CA1–P–CB1 | 120.7(1) |
| F–P–CB1 | 89.2(1) | CB1–P–CB1′ | 118.6(3) |
| F–P–F′ | 178.5(2) | F–P–CB1′ | 90.0(1) |
| P–CA1–CA2 | 117.5(5) | CB1–CB2–CB7 | 124.3(4) |
| CA1–CA2–CA3 | 121.1(4) | CB3–CB2–CB7 | 118.5(4) |
| CA2–CA3–CA4 | 120.3(5) | CB2–CB3–CB4 | 122.2(4) |
| CA3–CA4–CA3′ | 119.7(6) | CB3–CB4–CB5 | 119.6(5) |
| P–CA1–CA3 | 121.3(3) | CB4–CB5–CB6 | 120.0(4) |
| P–CB1–CB2 | 123.7(3) | CB5–CB6–CB1 | 120.5(4) |
| CB1–CB2–CB3 | 117.2(4) | CB6–CB1–CB2 | 120.4(4) |
| | | P–CB1–CB6 | 115.9(3) |

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 1.

use of dimethylaminosulfur trifluoride[42] in ether solution at room temperature. The products, which are new compounds, formed in yields ranging from 45 to 80%. The $^{31}P$ chemical shifts of **1**–**3** are indicative of retention of pentacoordination in solution in agreement with the trigonal bipyramidal structures found in the solid state by X-ray analysis for these phosphoranes. $^{31}P$ chemical shifts of the other members also are found in the pentacoordinate region. All of the triaryl substituted phosphoranes have chemical shifts listed in Table VII that are downfield from the value of −58.1 ppm observed for $Ph_3PF_2$.[43–45] This decrease may suggest the presence of a steric effect operating between the equatorially positioned aryl substituents and the axial fluorine atoms. Some support for this assertion is obtained by noting that $(p\text{-}Tol)_3PF_2$ has a shift of −56.1 ppm, comparable to that of $Ph_3PF_2$, whereas $(o\text{-}Tol)_3PF_2$ has a shift of −34.3 ppm. The same effect is seen in the

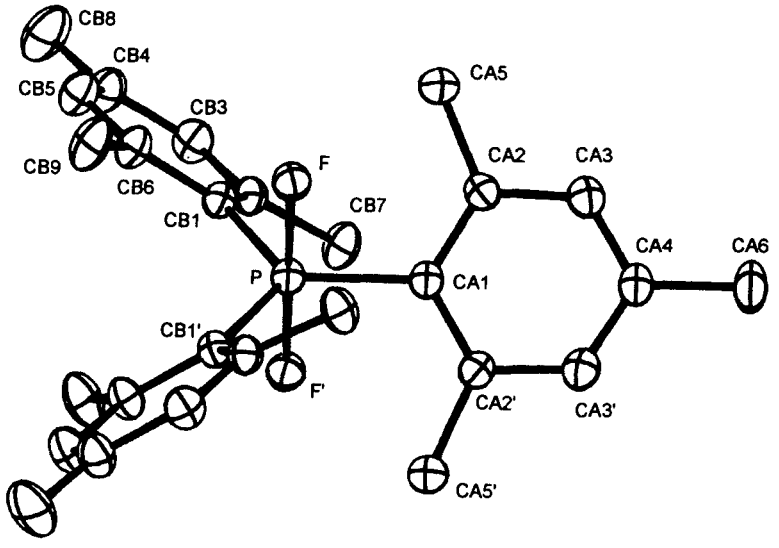



FIGURE 2 ORTEP plot of $Mes_3PF_2$ (**2**) with thermal ellipsoids at the 30% probability level. Primed atoms are related to unprimed ones with the same label by the crystallographic two-fold axis passing through P, CA1, CA4 and CA6. Hydrogen atoms are omitted for clarity.

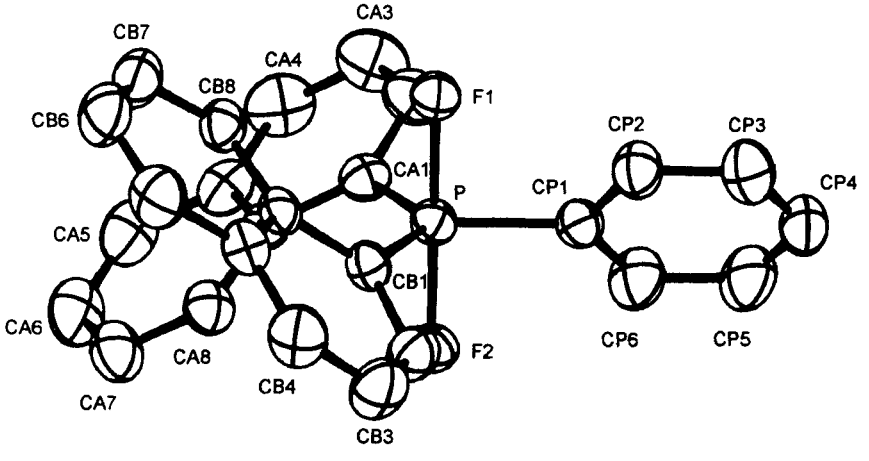



FIGURE 3 ORTEP plot of $Ph(1\text{-}Np)_2PF_2$ (**3**), with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

TABLE II
Selected distances (Å) and angles (deg) for $Mes_3PF_2$ (2)[a]

| | | | |
|---|---|---|---|
| P–F | 1.673(2) | CB1–CB2 | 1.426(5) |
| P–CA1 | 1.854(6) | CB2–CB7 | 1.511(6) |
| P–CB1 | 1.844(4) | CB2–CB3 | 1.395(6) |
| CA1–CA2 | 1.408(5) | CB3–CB4 | 1.388(6) |
| CA2–CA3 | 1.400(6) | CB4–CB8 | 1.519(6) |
| CA2–CA5 | 1.525(6) | CB4–CB5 | 1.390(6) |
| CA3–CA4 | 1.373(5) | CB5–CB6 | 1.397(6) |
| CA4–CA6 | 1.536(8) | CB6–CB9 | 1.524(6) |
| | | CB6–CB1 | 1.411(5) |
| F–P–CA1 | 89.81(9) | CB1′–P–CB1 | 117.9(3) |
| F–P–CB1 | 90.2(5) | CA1–P–CB1 | 121.0(1) |
| F–P–CB1′ | 89.9(2) | F–P–F′ | 179.6(2) |
| P–CA1–CA2 | 120.2(3) | CB1–CB2–CB7 | 125.2(4) |
| CA1–CA2–CA5 | 125.8(4) | CB7–CB2–CB3 | 115.8(4) |
| CA5–CA2–CA3 | 115.6(4) | CB2–CB3–CB4 | 122.8(4) |
| CA1–CA2–CA3 | 118.6(4) | CB3–CB4–CB8 | 120.9(5) |
| CA2–CA3–CA4 | 122.8(4) | CB3–CB4–CB5 | 117.5(4) |
| CA3–CB4–CA6 | 121.3(3) | CB5–CB4–CB8 | 121.6(4) |
| CA3–CA4–CA′3 | 117.7(6) | CB4–CB5–CB6 | 122.4(4) |
| P–CB1–CB2 | 120.5(3) | CB5–CB6–CB9 | 125.2(4) |
| P–CB1–CB6 | 120.7(3) | CB5–CB6–CB1 | 119.6(4) |
| CB2–CB1–CB6 | 118.7(4) | CB9–CB6–CB1 | 115.2(4) |
| CB1–CB2–CB3 | 119.0(4) | | |

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 2.

TABLE III
Selected distances (Å) and angles (deg) for $Ph(1\text{-}Np)_2PF_2$ (**3**)[a]

| | | | |
|---|---|---|---|
| P–F1 | 1.675(1) | CA10–CA5 | 1.417(4) |
| P–F2 | 1.675(1) | CA5–CA6 | 1.349(4) |
| P–CP1 | 1.812(2) | CA6–CA7 | 1.409(4) |
| P-CA1 | 1.822(2) | CA7–CA8 | 1.373(3) |
| P–CB1 | 1.817(2) | CA8–CA9 | 1.414(3) |
| CP1–CP2 | 1.389(3) | CA9–CA10 | 1.418(3) |
| CP2–CP3 | 1.384(4) | CA9–CA1 | 1.439(3) |
| CP3–CP4 | 1.373(4) | CB1–CB2 | 1.371(3) |
| CP4–CP5 | 1.371(4) | CB2–CB3 | 1.404(4) |
| CP5–CP6 | 1.384(4) | CB3–CB4 | 1.355(4) |
| CP6–CP1 | 1.395(3) | CB4–CB10 | 1.409(4) |
| CA1–CA2 | 1.365(1) | CB10–CB9 | 1.424(3) |
| CA2–CA3 | 1.412(4) | CB10–CB5 | 1.420(4) |
| CA3–CA4 | 1.361(4) | CB5–CB6 | 1.357(4) |
| CA4–CA10 | 1.413(4) | CB6–CB7 | 1.395(4) |
| CB8–CB9 | 1.421(3) | CB7–CB8 | 1.372(3) |
| CB9–CB1 | 1.441(3) | | |
| | | | |
| F1–P-F2 | 178.99(8) | CA1–P–CP1 | 118.5(1) |
| F1–P–CB1 | 89.88(9) | CA1–P–CB1 | 125.3(1) |
| F2–P–CA1 | 89.05(9) | CB1–P–F2 | 90.8(1) |
| F1–P–CP1 | 90.10(9) | CB1–P–CP1 | 116.2(1) |
| F1–P–CA1 | 89.95(9) | CF2–P–CP1 | 90.27(9) |
| P–CP1–CP2 | 120.6(2) | CP3–CP4–CP5 | 119.6(3) |
| P–CP1–CP6 | 121.2(2) | CP4–CP5–CP6 | 120.3(3) |
| | | | |
| CP2–CP1–CP6 | 118.3(2) | CP5–CP6–CP1 | 120.7(3) |
| CP1–CP2–CP3 | 120.2(2) | P–CA1–CA2 | 116.3(2) |
| CP2–CP3–CP4 | 120.9(3) | P–CA1–CA9 | 123.8(2) |

TABLE III (*Continued*)

| | |
|---|---|
| CA2–CA1–CA9 | 119.9(2) |
| CA1–CA2–CA3 | 121.7(3) |
| CA2–CA3–CA4 | 119.4(3) |
| CA3–CA4–CA10 | 121.1(3) |
| CA4–CA10–CA5 | 120.7(3) |
| CA4–CA10–CA9 | 119.9(2) |
| CA5–CA10–CA9 | 119.4(3) |
| CA10–CA5–CA6 | 121.3(3) |
| CA5–CA6–CA7 | 120.1(3) |
| CA6–CA7–CA8 | 120.0(3) |
| CA7–CA8–CA9 | 121.4(2) |
| CA8–CA9–CA10 | 117.8(2) |
| CA8–CA9–CA1 | 124.2(2) |
| P–CB1–CB2 | 116.0(2) |
| P–CB1–CB9 | 124.6(2) |
| CB2–CB1–CB9 | 119.3(2) |
| CB1–CB2–CB3 | 122.0(2) |
| CB2–CB3–CB4 | 119.7(3) |
| CB3–CB4–CB10 | 121.1(3) |
| CB4–CB10–CB5 | 120.9(2) |
| CB4–CB10–CB9 | 119.9(2) |
| CB9–CB10–CB5 | 119.2(3) |
| CB10–CB5–CB6 | 121.0(3) |
| CB5–CB6–CB7 | 120.2(2) |
| CB6–CB7–CB8 | 121.0(3) |
| CB7–CB8–CB9 | 120.6(2) |
| CB8–CB9–CB10 | 118.1(2) |
| CB8–CB9–CB1 | 117.9(2) |
| CB1–CB9–CB10 | 124.0(2) |

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 3.

TABLE IV
Atomic coordinates in crystalline $Ph(o\text{-}Tol)_2PF_2$ (**1**)[a]

| Atom Type[b] | Coordinates | | |
|---|---|---|---|
| | $10^4x$ | $10^4y$ | $10^4z$ |
| P | 0[c] | 7548(1) | 7500[c] |
| F | -1222(2) | 7570(2) | 7974(2) |
| CA1 | 0[c] | 5774(5) | 7500[c] |
| CA4 | 0[c] | 3016(6) | 7500[c] |
| CA2 | 1034(4) | 5053(4) | 7614(3) |
| CA3 | 1032(4) | 3705(4) | 7625(3) |
| CB1 | -723(3) | 8466(4) | 6456(3) |
| CB2 | -734(4) | 8076(4) | 5498(3) |
| CB3 | -1311(5) | 8882(5) | 4778(3) |
| CB4 | -1818(5) | 10062(5) | 4987(4) |
| CB5 | -1808(4) | 10417(4) | 5925(4) |
| CB6 | -1267(4) | 9627(4) | 6664(3) |
| CB7 | -191(5) | 6803(5) | 5198(3) |

[a] Estimated standard deviations in parentheses.

[b] Atom labeling scheme is shown in Figure 1.

[c] Fixed.



pattern of $^{19}F$ chemical shifts which are shifted 10–20 ppm to lower fields relative to either of these values for $Ph_3PF_2$, −40.4 ppm, or $(p\text{-}Tol)_3PF_2$, −40.8 ppm.

Table VIII lists the P—F bond and P—C bond lengths for fluorophosphoranes studied by a variety of structural methods. The data are also suggestive of a steric effect in the case of **1–3**. They all have trigonal bipyramidal geometries (Figures 1–3) as is common for acyclic derivatives of main group elements.[46] The $P—F_{ax}$ distances are among the longest for **1–3**. However, an electronegativity effect is present among the entries in Table VIII. This is most notable in the series $Me_nPF_{5-n}$ (n = 0–3)[13-15,20] whose geometries are in agreement with the VSEPR theory.[47] Due to the inductive ability of the methyl group, the $P—F_{ax}$ length goes from 1.579 Å in $PF_5$ to 1.685 Å in $Me_3PF_2$, over an entire angstrom increase. To compare **1–3** on a common electronegativity scale, the structure of $Ph_3PF_2$ is needed. Even without this information, the presence of a steric effect is supported. This is provided from an examination of $P—C_{eq}$ bond lengths. These lengths for the two difluorophosphoranes, $(C_6F_5)_3PF_2$ and $Me_3PF_2$, which have markedly dis-

TABLE V

Atomic coordinates in crystalline $Mes_3PF_2$ (2)[a]

| | Coordinates | | |
|---|---|---|---|
| Atom Type[b] | $10^4x$ | $10^4y$ | $10^4z$ |
| P | 5000[c] | 4121(1) | 2500[c] |
| F | 3380(2) | 4125(2) | 2410(1) |
| CA1 | 5000[c] | 5585(4) | 2500[c] |
| CA4 | 5000[c] | 7810(5) | 2500[c] |
| CA6 | 5000[c] | 9022(5) | 2500[c] |
| CA2 | 4075(4) | 6144(3) | 1945(2) |
| CA3 | 4115(4) | 7249(3) | 1958(3) |
| CA5 | 3015(4) | 5656(4) | 1308(3) |
| CB1 | 4767(4) | 3371(3) | 1604(2) |
| CB2 | 5407(4) | 3690(3) | 1033(2) |
| CB3 | 5272(4) | 3069(4) | 382(3) |
| CB4 | 4542(5) | 2145(4) | 266(2) |
| CB5 | 3915(5) | 1849(4) | 825(3) |
| CB6 | 4006(4) | 2441(3) | 1487(2) |
| CB7 | 6228(5) | 4675(4) | 1063(3) |
| CB8 | 4444(6) | 1483(5) | -445(3) |
| CB9 | 3264(5) | 1991(4) | 2040(3) |

[a] Estimated standard deviations in parentheses.

[b] Atom labeling scheme is shown in Figure 2.

[c] Fixed.

TABLE VI

Atomic coordinates in crystalline $Ph(1\text{-}Np)_2PF_2$ (3)[a]

| | Coordinates | | |
|---|---|---|---|
| Atom Type[b] | $10^4x$ | $10^4y$ | $10^4z$ |
| P | 6869.4(4) | 8762.9(9) | 1668.8(3) |
| F1 | 7148.0(8) | 7105(2) | 2341.7(7) |
| F2 | 6589.8(9) | 10395(2) | 983.6(7) |
| CA1 | 6945(2) | 7197(3) | 927(1) |
| CA2 | 6431(2) | 5673(4) | 809(2) |
| CA3 | 6374(2) | 4424(4) | 208(2) |
| CA4 | 6864(2) | 4714(4) | -253(2) |
| CA5 | 7933(2) | 6538(4) | -625(1) |
| CA6 | 8462(2) | 8009(5) | -532(2) |
| CA7 | 8520(2) | 9291(4) | 55(2) |
| CA8 | 8041(2) | 9043(4) | 536(1) |
| CA9 | 7472(2) | 7529(3) | 449(1) |
| CA10 | 7421(2) | 6253(4) | -145(1) |
| CB1 | 7805(1) | 10110(3) | 2332(1) |
| CB2 | 7594(2) | 11843(4) | 2456(2) |
| CB3 | 8221(2) | 12965(4) | 3022(2) |
| CB4 | 9070(2) | 12347(4) | 3454(2) |
| CB5 | 10243(2) | 9991(4) | 3763(2) |
| CB6 | 10515(2) | 8335(4) | 3628(2) |
| CB7 | 9905(2) | 7196(4) | 3067(2) |
| CB8 | 9023(2) | 7719(4) | 2644(1) |
| CB9 | 8711(1) | 9441(3) | 2767(1) |
| CB10 | 9339(2) | 10598(4) | 3339(1) |
| CP1 | 5783(1) | 9025(3) | 1769(1) |
| CP2 | 5714(2) | 8785(4) | 2500(1) |
| CP3 | 4883(2) | 9003(5) | 2574(2) |
| CP4 | 4114(2) | 9430(4) | 1928(2) |
| CP5 | 4168(2) | 9645(5) | 1200(2) |
| CP6 | 4996(2) | 9465(4) | 1118(2) |

[a] Estimated standard deviations in parentheses.

[b] Atom labeling scheme is shown in Figure 3.

TABLE VII

$^{31}P$ and $^{19}F$ NMR data for organodifluorophosphoranes

| | yield (%) | $^{31}P$, ppm | $J_{P-F}$, Hz | $^{19}F$, ppm | $J_{P-F}$, Hz |
|---|---|---|---|---|---|
| Ph(*o*-Tol)$_2PF_2$ (1) [a] | 60 | -41.2 | 630 | -30.1 | 628 |
| $Mes_3PF_2$ (2) [a] | 68 | -40.4 | 654 | -25.8 | 647 |
| Ph(*1*-Np)$_2PF_2$ (3) [b] | 54 | -41.6 | 644 | -21.3 | 644 |
| (*o*-Tol)$_3PF_2$ [a] | 45 | -34.3 | 621 | -26.0 | 620 |
| $PhMes_2PF_2$ [a] | 80 | -44.2 | 636 | -31.4 | 635 |
| (*p*-Tol)$_3PF_2$ [b] | 57 | -56.1 | 656 | -40.8 | 654 |
| Ph(*t*-Bu)$_2PF_2$ [b] | --- [c] | -31.2 | 741 | -60.9 | 741 |
| $(Ph_2PF_2)_2CH_2$ [b] | --- [c] | -46.9 | 640-680 | -26.9 | -644 |

[a] $^{31}P$ and $^{19}F$ NMR spectra obtained in $CDCl_3$ solution.

[b] $^{31}P$ and $^{19}F$ NMR spectra obtained in $C_6D_6$ solution.

[c] Not isolated.



parate electronegativities, as well as the lengths for the P—$C_{eq}$ bonds to the phenyl groups of **1** and **3**, are all in the range of 1.803–1.817 Å, whereas those for the larger aryl groups have P—$C_{eq}$ lengths considerably longer, in the range 1.820–1.849 Å.

A comparison is made with isoelectronic anionic fluorosilicates in Table IX.[48] Compared to the Si—$F_{ax}$ bond length for $Ph_2SiF_3^-$ of 1.688 Å, this length for trifluorosilicates having larger aryl groups of comparable electronegativity, (*o*-Tol)$_2SiF_3^-$, $Mes_2SiF_3^-$, and $Xyl_2SiF_3^-$, all show longer distances. Thus, the presence of some measure of a steric effect among these members is indicated here as well.

The range of Si—$F_{ax}$ bond lengths in Table IX from 1.646 Å to 1.720 Å over a similar class of compounds as that presented in Table VIII for fluorophosphoranes, is narrower by ~0.3 Å. Although the methyl series is not available for the fluorosilicates, it is noted that the upper end of the range for P—$F_{ax}$ distances of fluorophosphoranes is found for $Me_3PF_2$ and Ph(*o*-Tol)$_2PF_2$ (**1**). The latter phosphorane should be somewhat comparable to the silicate *1*-$NpPh_2SiF_2^-$ in steric size which has the longest Si—$F_{ax}$ distance. A value having some uncertainty of 1.72–1.73 Å has been reported for $Me_3SiF_2^-$.[49]

A final feature of note that most likely pertains to the enhanced reactivity ascribed to pentacoordinate silicon[9,23-35] is the longer axial fluorine distances found at either end of the bond distance spectrum for the fluorosilicates relative to the fluorophosphoranes present in Tables IX and VIII, respectively. After a correction is applied for electronegativity differences, *e.g.*, between $SiF_5^-$ and $PF_5$, the Si—$F_{ax}$ bond is still longer than expected. Relative to a P—F distance, the Si—F bond length is expected to be no greater than about 0.05 Å longer based on this bond

TABLE VIII
P—F and P—C bond lengths (Å) for fluorophosphoranes

| No. | Compound | Ave. P–$F_{ax}$ | Ave. P–$F_{eq}$ | Ref. |
|---|---|---|---|---|
| 4 | $PF_5$ | 1.579 [a] | 1.530 [a] | 13, 20 |
| 5 | $ClPF_4$ | 1.581 | 1.535 | 19 |
| 6 | $HPF_4$ [b] | 1.594 | 1.55 | 18 |
| 7 | $MePF_4$ [c] | 1.612 | 1.543 | 14 |
| 8 | $Cl_2PF_3$ [c] | 1.593 | 1.538 | 19 |
| 9 | $(CH_2)_4PF_3$ [c] | 1.635 | 1.547 | 21 |
| 10 | $(CH_2)_5PF_3$ [c] | 1.637 | 1.562 | 21 |
| 11 | $Me_2PF_3$ [c] | 1.643 | 1.553 | 14 |
| | | | Ave. P–C | |
| 12 | $Cl_3PF_2$ [c] | 1.596 | | 19 |
| 13 | $(Me_2N)_3PF_2$ [c] | 1.632 | | 17 |
| 14 | $(C_6F_5)_3PF_2$ [d] | 1.636 | 1.817 | 16 |
| 15 | $Me_3PF_2$ [c] | 1.685 | 1.813 | 15 |
| | | | Ave. P–C | |
| 2 | $Mes_3PF_2$ | 1.673 | 1.849 | this work |
| 3 | $Ph(1\text{-}Np)_2PF_2$ | 1.675 | 1.812 (Ph) | this work |
| | | | 1.820 | |
| 1 | $Ph(o\text{-}Tol)_2PF_2$ | 1.683 | 1.803 (Ph) | this work |
| | | | 1.827 | |
| 16 | $Cl_4PF$ [c] | 1.597 | | 19 |

[a] Values from two electron diffraction studies,[13,20b] a crystal structure,[20a] a study of vibration–rotation bands,[20d] and a force field analysis.[20c]

[b] A microwave study.

[c] An electron diffraction study.

[d] An X-ray study.

TABLE IX
Si—F bond lengths (Å) for anionic fluorosilicates[a]

| No. | Compound | Ave. Si-$F_{ax}$ (Å) | Ave. Si-$F_{eq}$ (Å) | Ref. |
|---|---|---|---|---|
| 17 | $SiF_5^-$ | 1.646 | 1.591 | 6 |
| 18 | $PhSiF_4^-$ | 1.669 | 1.601 | 7 |
| 19 | $MesSiF_4^-$ | 1.672 | 1.606 | 10 |
| 20 | $(TTBP)SiF_4^-$ [b] | 1.677 | 1.622 | 10 |
| 21 | $Ph_2SiF_3^-$ | 1.688 | 1.648 | 6 |
| 22 | $PhMeSiF_3^-$ | 1.695 | 1.621 | 8 |
| 23 | $(t\text{-Bu})PhSiF_3^-$ | 1.700 | 1.639 | 11 |
| 24 | $(o\text{-Tol})_2SiF_3^-$ | 1.701 | 1.640 | 11 |
| 25 | $Mes_2SiF_3^-$ | 1.703 | 1.641 | 9 |
| 26 | $Xyl_2SiF_3^-$ | 1.714 | 1.652 | 11 |
| 27 | $1\text{-NpPh}_2SiF_2^-$ | 1.720 | | 8 |

[a] All are $K^+$, 18-crown-6 salts except $[SiF_5][PhCH_2NMe_3]$ (17), $[PhSiF_4][Pr_4N]$ (18), $[Ph_2SiF_3][Me_4N]$ (21), $[PhMeSiF_3][n\text{-}Bu_4N]$ (22), and $[1\text{-NpPh}_2SiF_2][(NMe_2)_3S]$ (27).

[b] TTBP = 2,4,6-tri-*tert*-butylphenyl.



distance correction. The difference between these two isoelectronic molecules is ~0.07 Å. However, many of the reactions exhibiting enhanced reactivity for pentacoordinate silicon[9,23–35] most likely proceed via hexacoordinate states where the bond length differences between silicon and phosphorus may be magnified even more.

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