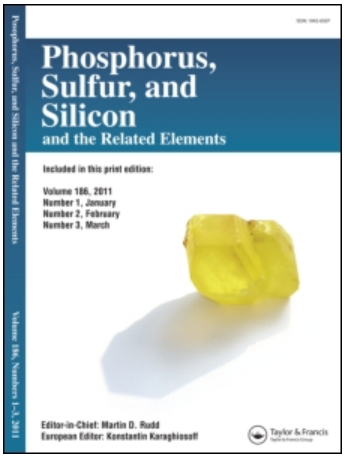


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Facile Protocol for the Convenient Preparation of Phosphino-and Phosphono-Containing Trans-1,2-Difluorovinylsilanes

Hou-Jen Tsai[a]; Chi-Wei Hsieh[a]; Shyi-Chen Wu[b]
[a] Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, R.O.C. [b] Department of Chemistry, R.O.C. Military Academy, Kaohsiung, Taiwan, R.O.C.

To cite this Article Tsai, Hou-Jen , Hsieh, Chi-Wei and Wu, Shyi-Chen(2007) 'A Facile Protocol for the Convenient Preparation of Phosphino-and Phosphono-Containing Trans-1,2-Difluorovinylsilanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 2, 491 — 501
To link to this Article: DOI: 10.1080/10426500600977346
URL: http://dx.doi.org/10.1080/10426500600977346

Phosphorus, Sulfur, and Silicon, 182:491–501, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600977346

Taylor & Francis
Taylor & Francis Group

A Facile Protocol for the Convenient Preparation of Phosphino- and Phosphono-Containing Trans-1,2-Difluorovinylsilanes

Hou-Jen Tsai
Chi-Wei Hsieh
Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan, Taiwan, R.O.C.

Shyi-Chen Wu
Department of Chemistry, R.O.C. Military Academy, Fengshan, Kaohsiung, Taiwan, R.O.C.

Attempted preparation of phosphono containing trans-*1,2-difluoro-1-phenyldimethylsilyl ethylenes* $R_2P(O)CF{=}CFSiMePh$ **3** *by deprotonation of* $HFC{=}CFSiMe_2Ph$ **2** *followed by acylation with* $R_2P(O)Cl$ *was unsuccessful. However, acylation of the lithium salt of* **2** *with* R_2PCl *gave* $R_2PCF{=}CFSiMe_2Ph$ **4**, *which on subsequent oxidation with hydrogen peroxide or* tert-*butylhydroperoxide afforded a series of compounds* trans-$R_2P(O)CF{=}CFSiMe_2Ph$ **3** *in good yields.*

Keywords Acylation; deprotonation; *trans*-1,2-difluoroethylene; oxidation

INTRODUCTION

Fluorinated organic compounds continue to attract the interest of pharmaceutical chemists and agrochemists due to the unique properties of compounds, which contain one or more fluorine atoms at strategic positions in the molecule.[1] Many natural products, such as pheromones and juvenile hormones, contain double bonds and conjugated polyenes as essential features of their structures. Synthetic and biological activities of several fluorinated analogs have been reported.[2–8] In most cases, only hydrogens at saturated carbon atoms or one vinyl hydrogen have been replaced by fluorine atoms. Although the introduction

Received July 19, 2006; accepted July 28, 2006.
The authors would like to thank the National Science Council of the Republic of China for supporting this work.
Address correspondence to Hou-Jen Tsai, Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan, Taiwan, 335 Republic of China. E-mail: hjtsai@ccit.edu.tw

of the *trans*-1,2-difluoroethylene unit into organic compounds using readily available fluoromonomers as starting materials has been studied by Normant and coworkers,[9] the preparation of organic compounds containing the 1,2-difluoroethene unit is still a challenging problem.[10–13] The first successful preparation of 1,2-difluoro-1-alkenes through the fluorination of bromoketones with potassium fluoride and sulfur tetrafluoride followed by dehydrofluorination of trifluoroalkanes with potassium *tert*-butoxide was reported by Leroy,[10] but this method required toxic or expensive fluorinating agents. However, there are no reports in the literature concerning the synthesis of phosphino- and phosphono-containing *trans*-1,2-difluorovinylsilanes. Herein, we present a novel and convenient method for the preparation of a series of phosphino-containing *trans*-1,2-difluoro-1-phenyl-dimethylsilyl ethylenes $R_2PCF{=}CFSiMe_2Ph$ and phosphono-containing *trans*-1,2-difluoro-1-phenyldimethylsilyl ethylenes $R_2P(O)CF{=}CFSiMe_2Ph$.

RESULTS AND DISCUSSION

Phenyldimethylsilyl trifluoroethylene $F_2C{=}CFSiMe_2Ph$ **1** was prepared from chlorotrifluoroethylene and phenyldimethylsilyl chloride in the presence of *n*-butyllithium at a low temperature.[14] Figure 1 shows the reaction apparatus for the preparation of **1**.

Treatment of **1** with lithium aluminum hydride[15] resulted in the formation of *trans*-1,2-difluoro-1-phenyl-dimethylsilyl ethylene **2** as the

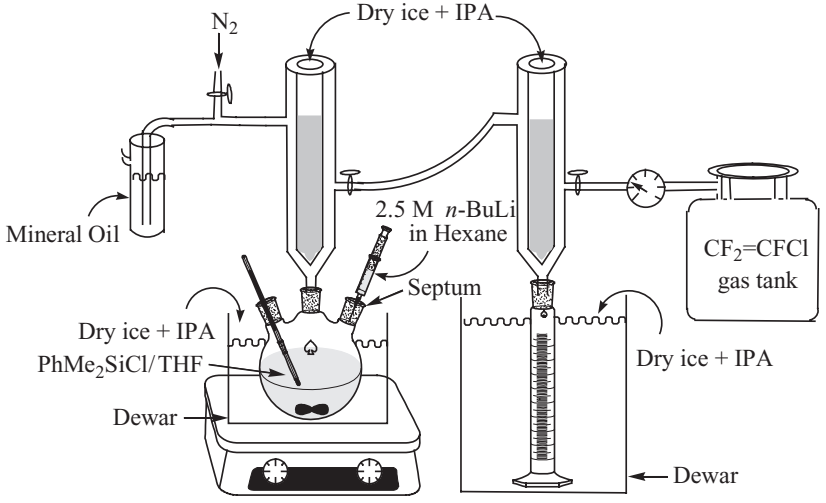


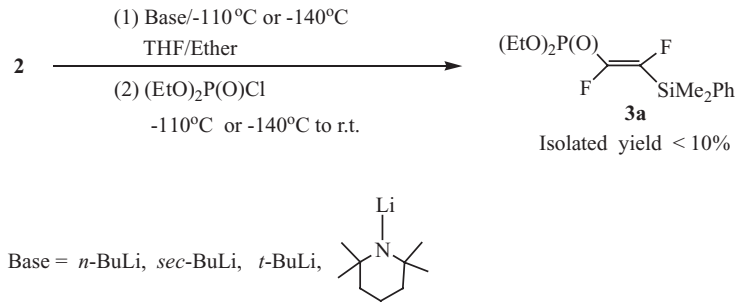
FIGURE 1 Reaction apparatus for the preparation of $F_2C{=}CFSiMe_2Ph$.

predominant isomer (*trans*:*cis* = 96:4 by ^{19}F NMR analysis). The two isomers were easily identified by ^{19}F NMR spectroscopy due to the large difference in the $^{2}J_{FF}$ coupling constants[16] between the *cis* isomer (0–20 Hz) and the *trans* isomer (120–140 Hz).

$$F_2C{=}CFCl + PhMe_2SiCl \xrightarrow[-78^\circ C \text{ to R.T.}]{n\text{-BuLi/THF}} F_2C{=}CFSiMe_2Ph$$

$$1 + LiA1H_4 \xrightarrow[-5^\circ C \text{ to R.T.}]{THF} HFC{=}FSiMe_2Ph$$

Observations in our laboratory indicate that direct conversion of $HFC{=}CFSiMe_2Ph$ **2** to *trans*-$(EtO)_2P(O)CF{=}CFSiMe_2Ph$ **3a** proceeds with very low yields when deprotonation and acylation is performed with *n*-butyllithium and diethyl chlorophosphate $(EtO)_2P(O)Cl$, respectively (Scheme 1). The use of different bulky alkyl lithium reagents such as *sec*-butyllithium and *tert*-BuLi and of a proton-selective base such as lithium 2,2,6,6-tetramethyl piperidide (LTMP) at different temperatures and with different solvent ratios did not improve the yield of the conversion of **2** to **3a**. Before work-up, ^{19}F NMR analysis of the reaction mixture indicated the complete consumption of **2** and the presence of **3a** as a minor product. Some unexpected byproducts could not be isolated and identified. After work-up, only trace amounts of *trans*-$(EtO)_2P(O)CF{=}CFSiMe_2Ph$ **3a** were isolated.



SCHEME 1

Deprotonation of $HFC{=}CFSiMe_2Ph$ **2** afforded the lithium salt $[PhMe_2SiCF{=}CF]^-Li^+$ **2a**, which could not be isolated at r.t. In the acylation of **2a** with $(EtO)_2P(O)Cl$, the lithium salt was stable in THF/Et_2O solvent below $-110^\circ C$, but if the reaction temperature was allowed to rise to $-90^\circ C$, it rapidly produced a white material. In this situation, the potential instability of the lithium salt can be explained by the

TABLE I Preparation of *Trans*-$(EtO)_2P(O)CF{=}CFSiMe_2Ph$ 3a From 2 and $(EtO)_2P(O)Cl$

Base	Solvent (THF/Et_2O)	Temperature (°C)	Isolated Yield (%)[a]
n-BuLi	1:1	−110 to r. t.	<5
s-BuLi	1:2	−110 to r. t.	<10
t-BuLi	2:1	−140 to r. t.	<10
LTMP	3:1	−140 to r.t.	<8

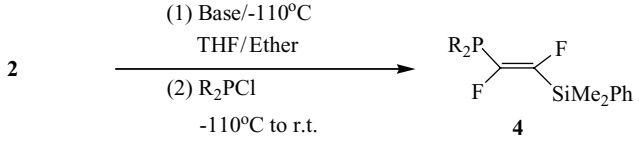
[a]Isolated yields are based on $HCF{=}CFSiMe_2Ph$.

possibility of lithium fluoride elimination [15] leading initially to alkynes, which may then react further.

Results for the direct synthesis of *trans*-$(EtO)_2P(O)CF{=}CFSiMe_2Ph$ **3a** from $HFC{=}CFSiMe_2Ph$ **2** and $(EtO)_2P(O)Cl$ with different bases and at different temperatures and solvents are summarized in Table I. Cooling was accomplished with an external dewar bath consisting of an ethanol/liquid N_2 mixture at −110°C or an isopentane/liquid N_2mixture at −140°C.

However, we found that if chlorophosphines such as diethyl chlorophosphite $(EtO)_2PCl$, diphenyl chlorophosphine Ph_2PCl, bis(diethylamino) chlorophosphine $(Et_2N)_2PCl$, dicyclohexyl chlorophosphine $(c\text{-}C_6H_{11})_2PCl$, diethyl chlorophosphine Et_2PCl, diisopropyl chlorophosphine $(i\text{-}C_3H_7)_2PCl$, di-*tert*-butyl chlorophosphine $t\text{-}Bu_2PCl$, or 1,2-phenylene phosphorochloridate $(C_6H_4O_2)PCl$ were used as acylating reagents to react with the lithium salt of $HFC{=}CFSiMe_2Ph$ **2**, the phosphino-containing *trans*-1,2-difluoro-1-phenyl dimethylsilyl ethylenes $R_2PCF{=}CFSiMe_2Ph$ **4** were obtained (Scheme 2) in 90–94% yields (according to ^{19}F NMR).

Yields of products **4** obtained using different bases and different THF/Et_2O solvent ratios at −110°C are given in Table II.



Base = *n*-BuLi, *sec*-BuLi, *t*-BuLi R = EtO (**4a**), Ph (**4b**), Et_2N (**4c**), c-C_6H_{11} (**4d**), Et (**4e**), *i*-C_3H_7 (**4f**), *t*-Bu (**4g**), -OC_6H_4O- (**4h**)

SCHEME 2

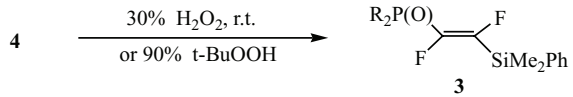
TABLE II Preparation of *Trans*-$R_2PCF{=}CFSiMe_2Ph$ 4

	R	Base	Solvent (THF/Et_2O)	Yield (%)[a]
4a	EtO	*n*-BuLi	3:1	92
4b	Ph	*n*-BuLi	2:1	90
4c	Et_2N	*s*-BuLi	3:1	94
4d	*c*-C_6H_{11}	*t*-BuLi	3:1	91
4e	Et	*n*-BuLi	2:1	88
4f	*i*-C_3H_7	*t*-BuLi	1:1	84
4g	*t*-Bu	*n*-BuLi	2:1	80
4h	-OC_6H_4O-	*s*-BuLi	1:1	82

[a]Determined by ^{19}F NMR; $C_6H_5CF_3$ as internal standard.

^{19}F NMR and ^{31}P NMR data of compounds $R_2PCF{=}CFSiMe_2Ph$ **4** are shown in Table III.

Trans-1,2-difluoro-1-phenyldimethylsilyl ethylenes **4** can be directly oxidized to afford *trans*-$R_2P(O)CF{=}CFSiMe_2Ph$ **3**. In situ oxidation of $R_2PCF{=}CFSiMe_2Ph$ **4** with hydrogen peroxide or *tert*-butylhydroperoxide afforded *trans*-**3** in 80–85% isolated yields (Scheme 3). The results illustrate that this methodology can be used to prepare difluoro ethylenes **3** in good yields.



R = EtO (**3a**), Ph (**3b**),

Et_2N (**3c**), c-C_6H_{11}(**3d**)

SCHEME 3

TABLE III ^{19}F and ^{31}P NMR Data of $R_2PCF{=}CFSiMe_2Ph$ (4); Coupling Constants J in Hz

	δ ^{19}F (ppm)					
	1-F	2-F	$^3J_{FF}$	$^2J_{PF}$	$^3J_{PF}$	δ ^{31}P (ppm)
4a	−157.0 (dd)	−162.9 (dd)	139.2	77.9	22.4	134.6 (dd)
4b	−170.9 (dd)	−179.5 (dd)	132.3	78.4	11.9	29.0 (dd)
4c	−171.1 (dd)	−179.4 (dd)	130.7	81.6	11.3	−4.6 (dd)
4d	−151.9 (dd)	−157.9 (dd)	136.9	56.9	6.0	46.3 (dd)
4e	−152.9 (dd)	−154.9 (dd)	144.3	78.0	3.2	−32.1 (dd)
4f	−145.9 (d)	−150.4 (dd)	147.1	83.2	0.0	−7.4 (d)
4g	−170.9 (d)	−179.4 (d)	130.6	30.9	0.0	66.8 (d)
4h	−144.3 (dd)	−147.5 (dd)	144.2	90.1	6.7	1.4 (d)

TABLE IV Preparation of *Trans*-$R_2P(O)CF{=}CFSiMe_2Ph$ 3

	R	Oxidation Reagent	Isolated Yield (%)[a]
3a	EtO	30% H_2O_2	85
3b	Ph	95% *t*-BuOOH	84
3c	Et_2N	30% H_2O_2	80
3d	*c*-C_6H_{11}	95% *t*-BuOOH	84
3h	-OC_6H_4O-	95% *t*-BuOOH	46[b]

[a]Isolated yields are based on $R_2PC{=}CFSiMe_2Ph$.
[b]Determined by ^{19}F NMR; $C_6H_5CF_3$ as internal standard.

Results for the synthesis of *trans*-$R_2P(O)CF{=}CFSiMe_2Ph$ **3** by oxidation of *trans*-$R_2PCF{=}CFSiMe_2Ph$ **4** with hydrogen peroxide or *tert*-butylhydroperoxide are summarized in Table IV.

Additional work is in progress to explore the possible application of difluoro ethylenes **3** and **4** in organic synthesis.

In conclusion, deprotonation of $HFC{=}CFSiMe_2Ph$ **2** followed by acylation of the lithium salt $[PhMe_2SiCF{=}CF]^-Li^+$ **2a** with R_2PCl gave *trans*-$R_2PCF{=}CFSiMe_2Ph$ **4**. Oxidation of the resulting phosphino-substituted ethylenes **4** with hydrogen peroxide or *tert*-butylhydroperoxide afforded *trans*-$R_2P(O)CF{=}CFSiMe_2Ph$ **3** in good yields.

EXPERIMENTAL

^{31}P, ^1H, and ^{13}C NMR spectra were recorded on a Bruker AM-300WB spectrometer. ^{19}F NMR spectra were recorded on a Bruker MSL-300 spectrometer. All chemical shifts are reported in ppm downfield (positive) from the standard. ^{19}F NMR spectra are referenced against internal $CFCl_3$. ^1H, and ^{13}C NMR spectra are referenced against internal $(CH_3)_4Si$, and ^{31}P NMR spectra are referenced against an external 85% H_3PO_4 capillary. Mass spectra were recorded with a Finingan MAT TSQ-46C spectrometer. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl. Diethyl chlorophosphate $(EtO)_2P(O)Cl$ and diethyl chlorophosphite $(EtO)_2PCl$ were distilled from calcium hydride (CaH_2) under reduced pressure. LTMP was prepared from *n*-butyl lithium and 2,2,6,6-tetramethyl piperidine. Phenyldimethylsilyl chloride, 1,2-phenylene phosphorochloridate $(C_6H_4O_2)PCl$, diisopropyl chlorophosphine $(i\text{-}C_3H_7)_2PCl$, diethyl chlorophosphine Et_2PCl, bis(diethylamino) chlorophosphine $(Et_2N)_2PCl$, di-*tert*-butyl chlorophosphine $t\text{-}Bu_2PCl$,

dicyclohexyl chlorophosphine $(c\text{-}C_6H_{11})_2PCl$, lithium aluminum hydride ($LiAlH_4$), dry ether, *tert*-butylhydroperoxide (*t*-BuOOH), and the lithium reagents (*n*-BuLi, *sec*-BuLi, *t*-BuLi) were obtained from commercial sources and were used without further purification.

Preparation of Phenyldimethylsilyl Trifluoroethylene $F_2C{=}CFSiMe_2Ph$ (1)

A 500-mL three-necked, round-bottomed flask equipped with a septum port, a low temperature thermometer, a telflon-coated magnetic stirring bar, and a dry-ice isopropyl alcohol condenser topped with a nitrogen T-tube leading to a source of nitrogen and mineral-oil bubbler was charged sequentially with 180-mL dry THF and 293 mmol (50.0 g) phenyldimethylsilyl chloride. The contents of the flask were cooled to −78°C in a dry ice/*i*-PrOH slush bath, and then 343 mmol (40.0 g, 31 mL, b.p. = −27°C) of chlorotrifluoroethylene was condensed into the solution. To the cooled solution, 315 mmol (126 mL) of a 2.5 M *n*-hexane solution of *n*-butyllithium was added dropwise via a syringe, maintaining an internal temperature below −75°C. After the addition was complete, the resulting mixture was stirred at −78°C for 2 h, was allowed to warm to r. t. over a time of 5 h, and it was stirred at that temperature overnight. ^{19}F NMR analysis of the reaction mixture indicated the formation of **1**. The reaction mixture was poured into water (80 mL), and the water layer was extracted with ether (3 × 120 mL). The combined organic phases were washed with diluted HCl until the washings were neutral to litmus paper. The resulting solution was washed successively with brine (60 mL) and water (80 mL), dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude residue then was fractionally distilled through a 6-cm Vigreux column at 80–82°C and 9.0 mm Hg to yield 58.2 g (92%) of $F_2C{=}CFSiMe_2Ph$ (97% pure by GLPC analysis). ^{19}F NMR ($CDCl_3$): δ −190.7 (dd, $^3J_{FF} = 117.3$ Hz, $^3J_{FF} = 25.6$ Hz), −115.3 (dd, $^3J_{FF} = 117.3$ Hz, $^3J_{FF} = 65.9$ Hz), −86.3 (dd, $^3J_{FF} = 65.9$ Hz, $^3J_{FF} = 25.6$ Hz); ^1H NMR ($CDCl_3$): δ 7.55–7.52 (m, 2H), 7.36–7.30 (m, 3H), 0.47 (d, $^4J_{FH} = 1.3$ Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 161.7 (ddd, $^1J_{CF} = 310.0$ Hz, $^1J_{CF} = 277.0$ Hz, $^2J_{CF} = 40.0$ Hz), 134.3 (s), 133.8 (s), 132.5 (m), 130.1 (s), 128.2 (s), −4.8 (s, ^{29}Si satellites, $^1J_{SiC} = 28.1$ Hz).

Preparation of *Trans*-1,2-Difluoro-1-Phenyldimethylsilyl Ethylene $HFC{=}CFSiMe_2Ph$ (2)

A 500-mL three-necked, round-bottomed flask was charged with 150 mL of dry THF and 187 mmol (7.1 g) of powder lithium aluminum hydride.

The contents of the flask were cooled to −5°C in an ice/salt bath. To the cooled solution, 231 mmol (50.0 g) of phenyldimethylsilyl trifluoroethylene in 150 mL of dry THF was added via a pressure-equalizing funnel maintaining an internal temperature of 0°C. After the addition, the resulting mixture was allowed to warm to r. t. over a time of 3 h. ^{19}F NMR analysis of the reaction mixture revealed the complete consumption of $F_2C{=}CFSiMe_2Ph$ and the presence of product **2**. The solution was cooled to −20°C and was quenched cautiously by a dropwise addition of 80 mL 2N HCl. After the addition of the acid was completed, the solution was allowed to slowly warm up to r. t. and the liquid fraction was decanted from the solids. The solids were rinsed with ether (3 × 150 mL), and any remaining solid in the organic layer was filtered by water aspiration. The combined organic phases were washed with aqueous $NaHCO_3$ until the washings were neutral to litmus paper. The resulting solution was washed successively with brine (50 mL) and water (40 mL), dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude residue then was fractionally distilled through a 6-cm Vigreux column at 80–81°C and 7.2 mm Hg to yield 39.3 g (86%) of *trans* and *cis*-1,2- difluoro-1-phenyldimethylsilyl ethylene (99% pure by GLPC analysis). *Trans/cis* = 96/4. ^{19}F NMR ($CDCl_3$): *trans* isomer: δ −179.2 (dd, $^3J_{FF} = 131.8$ Hz, $^3J_{FH} = 12.2$ Hz), −170.8 (dd, $^3J_{FF} = 131.8$ Hz, $^2J_{FH} = 78.1$ Hz), *cis* isomer: −157.4 (dd, $^3J_{FH} = 21.9$ Hz, $^3J_{FF} = 19.5$ Hz), −143.9 (dd, $^2J_{FH} = 75.7$ Hz, $^3J_{FF} = 19.5$ Hz); ^{1}H NMR ($CDCl_3$): δ 7.57 (dd, $^2J_{FH} = 79.1$ Hz, $^3J_{FH} = 10.8$ Hz, 1H), 7.59–7.54 (m, 2H), 7.38–7.31 (m, 3H), 0.51 (dd, $^4J_{FH} = 1.25$ Hz, $^4J_{FH} = 0.78$ Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 160.6 (dd, $^1J_{CF} = 260.0$ Hz, $^2J_{CF} = 56.0$ Hz), 154.2 (dd, $^1J_{CF} = 244.0$ Hz, $^2J_{CF} = 56.0$ Hz), 134.8 (s), 133.8 (s), 129.9(s), 128.1 (s), −4.1 (s, ^{29}Si satellites, $^1J_{SiC} = 28.1$ Hz).

Attempted Preparation of *Trans*-$(EtO)_2P(O)CF{=}CFSiMe_2Ph$ (3a) from $(EtO)_2P(O)Cl$ and $HFC{=}CFSiMe_2Ph$ (2)

A 500-mL three-necked, round-bottomed flask was charged with 60 mL of dry THF, 60 mL of dry ether, and 50.0 mmol (9.90 g) $HFC{=}CFSiMe_2Ph$. The contents of the flask were cooled to −110°C in a pentane/liquid nitrogen slush bath. To the cooled solution, 55 mmol (22 mL) of a 2.5 M *n*-hexane solution of *n*-butyllithium was added dropwise via a syringe, maintaining the temperature of the reaction mixture at −90 to −110°C. After the addition was complete, the resulting mixture was stirred at −110°C for 40 min, and then 60.0 mmol (10.4 g) of freshly distilled diethyl chlorophosphate in 20 mL of dry THF was added dropwise via a pressure-equalizing funnel. The resulting mixture was stirred at −110°C for 1 h and then allowed to warm

up to r. t. over a time of 4 h. The reaction mixture was poured into water (80 mL), and the water layer was extracted with ether (3×80 mL). The combined organic phases were washed with diluted HCl until the washings were neutral to litmus paper. The resulting solution was washed successively with brine (60 mL) and water (50 mL), dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by flash chromatography (120 g silica gel, 200–425 mesh) eluting with *n*-hexane/ethyl acetate (3/1) to give 0.69 g (4%) of **3a**. ^{19}F NMR ($CDCl_3$): δ −162.2 (dd, $^3J_{FF} = 139.2$ Hz, $^2J_{PF} = 96.7$ Hz), −150.6 (d, $^3J_{FF} = 139.2$ Hz); ^{31}P NMR ($CDCl_3$): δ 0.41 (d, $^2J_{PF} = 96.7$ Hz); ^1H NMR ($CDCl_3$): δ 7.57–7.54 (m, 2H), 7.42–7.33 (m, 3H), 4.16 (q, $^3J_{HH} = 7.4$ Hz, 4H), 1.31 (t, $^3J_{HH} = 7.4$ Hz, 6H), 0.58 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 133.9 (s), 133.6 (s), 133.0 (ddd, $^1J_{CF} = 187.4$ Hz, $^1J_{CF} = 116.6$ Hz, $^2J_{CF} = 5.5$ Hz), 131.6 (dd, $^1J_{CF} = 210.6$ Hz, $^2J_{CF} = 4.9$ Hz), 128.2 (s), 127.7 (s), 63.4 (s), 16.2 (s), −4.14 (s, ^{29}Si satellites, $^1J_{SiC} = 28.1$ Hz); GC-MS m/z (relative intensity): 319 ($M^+ - CH_3$, 1.4), 258 ($M^+ - C_6H_5 +$ H, 1.6), 245 ($M^+ - 2$ C_2H_5O + H, 10.8), 243 ($M^+ - C_6H_5 - CH_3 +$ H, 7.0), 137 ($(C_2H_5O)_2P(O)$, 11.0), 135 ($Si(CH_3)_2C_6H_5$, 7.9), 62 (C_2F_5, 2.5); FTIR: 3095 (m), 3054 (m, Ar—H), 2908 (m), 2870 (m, C—H), 1741 (m), 1653 (m, C=C), 1456, 1336 (m, C—F), 1202 (s, P=O), 1164 (s), 1052 (m) cm^{-1}.

General Procedure for Preparation of *Trans*-$R_2PCF{=}CFSiMe_2Ph$ (4)

A solution of 5.0 mmol (0.99 g) $HFC{=}CFSiMe_2Ph$ with 12 mL of dry THF and 3 mL of dry ether was cooled to −110°C via a pentane/liquid nitrogen slush bath under nitrogen. To the cooled solution, 5.5 mmol (2.2 mL) of a 2.5 M *n*-hexane solution of *n*-butyllithium was added dropwise via a syringe, maintaining the reaction mixture at −90 to –110°C. After the addition was completed, the resulting mixture was stirred at –110°C for 40 min, and then 5.7 mmol of freshly distilled R_2PCl was added dropwise via a pressure-equalizing funnel. The resulting mixture was stirred at –110°C for 1 h and then was allowed to warm up to r. t. over a time of 4 h. ^{19}F NMR analysis of the reaction mixture revealed the complete consumption of $HFC{=}CFSiMe_2Ph$. The reaction mixture was filtered through a Schlenck funnel to give the products of *trans*-$R_2PCF{=}CFSiMe_2Ph$ **4**. ^{19}F and ^{31}P NMR data of **4a–4h** in the solvent of THF/Et_2O are given in Table III.

General Procedure for Preparation of *Trans*-$R_2P(O)CF{=}CFSiMe_2Ph$ (3)

A prepared solution of 5.0 mmol *trans*-$R_2PCF{=}CFSiMe_2Ph$ in 15 mL of dry THF and 3 mL of dry ether was cooled to 0°C via an ice-water bath

under nitrogen. To the cooled solution, 7.0 mmol of a 90% *t*-BuOOH solution or a 30% H_2O_2 was added dropwise via a syringe, maintaining the reaction mixture at 0°C. After the addition was completed, the resulting mixture was stirred at r. t. for 4 h. The reaction mixture was quenched by the addition of water (20 mL), and the water layer was extracted with ether (3×20 mL), dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by flash chromatography (60 g silica gel, 200–425 mesh) eluting with *n*-hexane/ethyl acetate to give *trans*-$R_2P(O)CF{=}CFSiMe_2Ph$ **3**.

Trans-$Ph_2P(O)CF{=}CFSiMe_2Ph$ (3b)

Yield: 84%; ^{19}F NMR ($CDCl_3$): δ −155.8 (dd, $^3J_{FF} = 144.0$ Hz, $^2J_{FP} = 75.0$ Hz), −145.6 (d, $^3J_{FF} = 144.0$ Hz); ^{31}P NMR ($CDCl_3$): δ 16.5 (d, $^2J_{PF} = 75.0$ Hz); ^1H NMR ($CDCl_3$): δ 7.77–7.70 (m, 4H), 7.62–7.45 (m, 6H), 7.43–7.34 (m, 5H), 0.58 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 133.9 (s), 132.6 (s), 131.7 (s), 131.5 (s), 130.8 (dd, $^1J_{CF} = 222.1$ Hz, $^2J_{CF} = 12.9$ Hz), 130.3 (s), 129.3 (ddd, $^1J_{CF} = 211.8$ Hz, $^1J_{CP} = 166.9$ Hz, $^2J_{CF} = 9.8$ Hz), 128.7 (s), 128.5 (s), 128.1 (s), −4.1 (s, ^{29}Si satellites, $^1J_{SiC} = 28.1$ Hz); GC-MS m/z (relative intensity): 400 (M^++1, 0.3), 399 (M^+, 0.9), 398 ($M^+ - 1$, 3.3), 322 ($M^+ - C_6H_5$, 0.6), 263 ($M^+ - Si(CH_3)_2Ph$, 0.6), 201 ($Ph_2P(O)$, 11.0), 186 ($M^+ - Si(CH_3)_2Ph - C_6H_5$, 12.5), 77 ($C_6H_5^+$, 14.0); FTIR: 3061 (m), 3003 (m, Ar-H), 2964 (m), 2904 (m, C—H), 2360 (m), 1950 (m), 1620 (m, C=C), 1438 (m, C—F), 1254 (s, P=O), 1028 (m, P-O-C) cm^{-1}.

Trans-$(Et_2N)_2P(O)CF{=}CFSiMe_2Ph$ (3c)

Yield: 80%; ^{19}F NMR ($CDCl_3$): δ −171.3 (dd, $^3J_{FF} = 147.0$ Hz, $^2J_{FP} = 70.8$ Hz), −158.7 (d, $^3J_{FF} = 147.0$ Hz); ^{31}P NMR ($CDCl_3$): δ 14.0 (d, $^2J_{PF} = 70.8$ Hz); ^1H NMR ($CDCl_3$): δ 7.49–7.43 (m, 2H), 7.34–7.24 (m, 3H), 3.00 (q, $^3J_{HH} = 7.2$ Hz, 8H), 0.99 (t, $^3J_{HH} = 7.2$ Hz, 12H), 0.81 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 149.8 (s), 149.6 (dd, $^1J_{CF} = 216.3$ Hz, $^2J_{CF} = 11.7$ Hz), 149.3 (s), 149.1 (ddd, $^1J_{CF} = 201.2$ Hz, $^1J_{CP} = 156.1$ Hz, $^2J_{CF} = 10.2$ Hz), 148.1 (s), 147.9 (s), 37.9 (s), 13.4 (s), −4.1 (s, ^{29}Si satellites, $^1J_{SiC} = 28.1$ Hz); GC-MS m/z (relative intensity): 358 ($M^+ - 2CH_3$, 1.6), 253 ($M^+ - Si(CH_3)_2C_6H_5$, 7.2), 239 ($M^+ - Si(CH_3)_2C_6H_5 - CH_3 - H$, 20.8), 196 ($(Et_2N)_2P(O)$, 9.3), 72 ($(Et_2N)_2$, 43.0); FTIR : 3450 (s), 2974 (s), 2874 (m), 1654 (m), 1464 (m), 1382 (m), 1239 (s), 1128 (m), 1022 (m) cm^{-1}.

Trans-$(c\text{-}C_6H_{11})_2P(O)CF{=}CFSiMe_2Ph$ (3d)

Yield: 84%; ^{19}F NMR ($CDCl_3$): $\delta - 158.0$ (dd, $^3J_{FF} = 145.0$ Hz, $^2J_{FP} = 60.3$ Hz), −151.8 (d, $^3J_{FF} = 145.0$ Hz); ^{31}P NMR: δ 46.5 (d,

$^2J_{PF} = 60.3$ Hz); ^{1}H NMR ($CDCl_3$): δ 7.53–7.51 (m, 2H), 7.37–7.31 (m, 3H), 1.98–1.80 (m, 2H), 1.77–1.64 (m, 8H), 1.36–1.15 (m, 12H), 0.51 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 133.9 (s), 133.6 (dd, $^1J_{CF} = 213.8$ Hz, $^2J_{CF} = 9.6$ Hz), 133.0 (s), 129.9 (ddd, $^1J_{CF} = 224.9$ Hz, $^1J_{CP} = 139.8$ Hz, $^2J_{CF} = 11.3$ Hz), 127.9 (s), 127.8 (s), 34.7 (s), 34.4 (s), 26.2 (s), 25.8 (s), −4.2 (s, ^{29}Si satellites, $^1J_{SiC} = 28.1$ Hz); GC-MS m/z (relative intensity): 333 ($M^+ - C_6H_5$, 4.5), 275 ($M^+ - Si(CH_3)_2C_6H_5$, 12.0), 197 ($M^+ - (C_6H_{11})_2P(O)$, 7.5), 135 ($Si(CH_3)_2C_6H_5$, 13.5), 77 (C_6H_5, 10); FTIR : 2920 (m), 2878 (m), 1920 (m), 1648 (m), 1430 (m), 1320 (m), 1248 (m), 1121 (m), 1031 (m) cm^{-1}.

REFERENCES

[1] J. T. Welch, *Tetrahedron*, **43,** 3123 (1987).

[2] (a) J. F. Carvalho and G. D. Prestwich, *J. Org. Chem.*, **49,** 1251 (1984); (b) W. C. Sun, C. S. Ng, and G. D. Prestwich, *J. Org. Chem.*, **57,** 132 (1992).

[3] W. C. Sun and G. D. Prestwich, *Tetrahedron Lett.*, **31,** 801 (1990).

[4] G. D. Prestwich, W. C. Sun, M. S. Mayer, and J. C. Dickens, *J. Chem. Ecol.*, **16,** 1761 (1990).

[5] (a) M. Masnyk, J. Fried, and W. Roelofs, *Tetrahedron Lett.*, **30,** 324 (1989); (b) P. Y. Kwok, F. W. Muellner, C. K. Chen, and J. Fried, *J. Am. Chem. Soc.*, **109,** 3684 (1987).

[6] F. Camps, J. Coll, G. Fabrias, and A. Guerrero, *Tetrahedron*, **40,** 2871 (1984).

[7] F. Camps, G. Fabrias, and A. Guerrero, *Tetrahedron*, **42,** 3623 (1986).

[8] P. H. Buist, J. M. Findlay, G. Leger, and R. A. Pon, *Tetrahedron Lett.*, **28,** 3891 (1987).

[9] (a) J. F. Normant, *J. Organomet. Chem.*, **400,** 19 (1990); (b) F. Tellier, R. Sauvetre, and J. F. Normant, *J. Organomet. Chem.*, **362,** 23 (1989).

[10] J. Leroy, *J. Org. Chem.*, **46,** 206 (1981).

[11] P. Martinet, R. Sauvetre, and J. F. Normant, *Bull. Soc. Chem. Fr.*, **127,** 86 (1990).

[12] T. Dubuffet, C. Bidon, P. Martinet, R. Sauvetre, and J. F. Normant, *J. Organomet. Chem.*, **393,** 161 (1990).

[13] T. Spawn, P. Heinze, A. Bailey, S. Shinya, and D. J. Burton, *J. Fluorine Chem.*, **38,** 131 (1988).

[14] (a) S. Martin, R. Sauvetre, and J. F. Normant, *Tetrahedron Lett.*, **24,** 5615 (1983); (b) S. Martom, R. Sauvetre, and J. F. Normant, *J. Organomet. Chem.*, **264,** 155 (1984); (c) P. Martinet, R. Sauvetre, and J. F. Normant, *J. Organomet. Chem.*, **367,** 1 (1989).

[15] (a) J. Kvicala, R. Harbal, J. Czernek, I. Bartosova, O. Paleta, and A. Pelter, *J. Fluorine Chem.*, **113,** 211 (2002); (b) L. Lu and D. J. Burton, *Tetrahedron Lett.*, **44,** 7673 (1997); (c) S. A. Fontana, C. R. Davis, Y. B. He, and D. J. Burton, *Tetrahedron*, **52,** 37 (1996); (d) L. Lu, S. D. Pedersen, Q. Liu, R. M. Narske, and D. J. Burton, *J. Org. Chem.*, **62,** 1064 (1997).

[16] A. E. Asato and R. S. H. Liu, *Tetrahedron Lett.*, **27,** 3337 (1986).