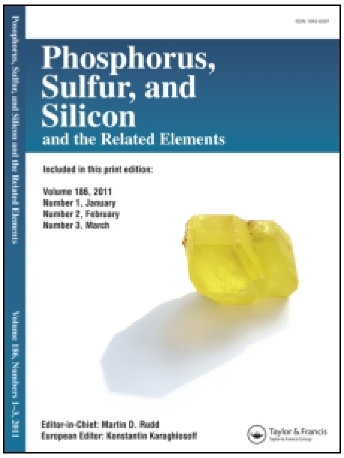

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TRIMETHYLSILYL CARBODIIMIDO FLUOROPHOSPHINES

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N,N′-Bis(trimethylsilylcarbodiimido)fluorophosphine, **3** was obtained in the reaction of N,N′-bis(trimethylsilyl)carbodiimide, **1** with dichlorofluorophosphine. Compound **3** is unstable, both thermally and in solution. Upon warming neat **3** to 50°C, **1** and other decomposition products are formed. In solution in dichloromethane, formation of the difluorophosphine $F_2P{-}N{=}C{=}N{-}SiMe_3$, **2** and of **1**, besides further decomposition products, takes place. Reaction of **2** with tetrachloro-o-benzoquinone furnished the fluorophosphorane, **5** which was found to decompose in solution with formation of Me_3SiF.

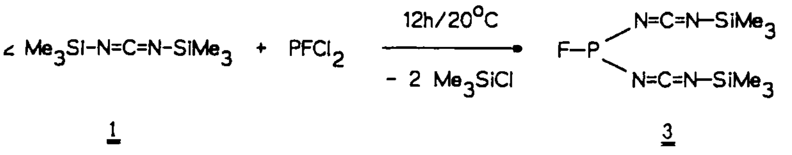
Key words: Fluorophosphines; scrambling reaction; N,N′-bis(trimethylsilylcarbodiimido)fluorophosphine; N-trimethylsilylcarbodiimido,N′-difluorophosphine.

REACTION OF N,N′-BIS(TRIMETHYLSILYL)CARBODIIMIDE, 1 WITH DICHLOROFLUOROPHOSPHINE

Formation of NN′-bis(trimethylsilylcarbodiimido)fluorophosphine, 3

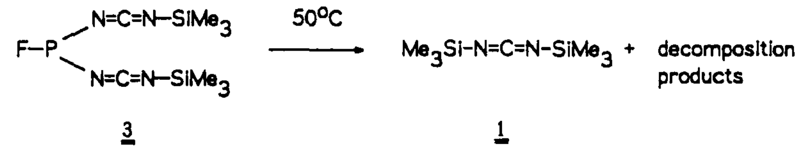
The smooth synthesis and isolation of the difluorophosphine, $F_2P{-}N{=}C{=}N{-}SiMe_3$, **2**[1] (Equation (1)), encouraged us to attempt the synthesis of the related monofluorophosphine, **3** (Equation (2)).

$$\underset{\underline{1}}{Me_3Si{-}N{=}C{=}N{-}SiMe_3} + PF_2Cl \xrightarrow[-\ Me_3SiCl]{12h/20^{o}C} \underset{\underline{2}}{F_2P{-}N{=}C{=}N{-}SiMe_3} \qquad (1)$$



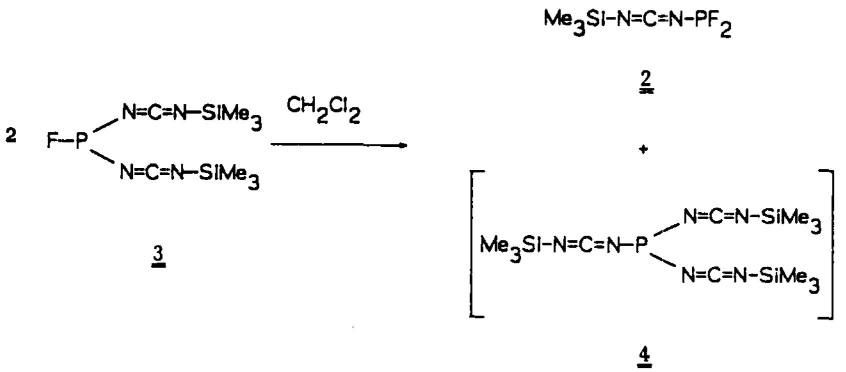
(2)

In analogy to the synthesis of **2** a mixture of N,N′–bis(trimethylsilyl)carbodiimide, **1** and $PFCl_2$ was stirred for 12 h at room temperature in a sealed glass tube. Compound **3** could not be isolated by distillation (5×10^{-4} mm Hg) and was found to undergo a transformation within 1 h with formation of a brown, sticky product and **1**. In no case formation of Me_3SiF was noted (Equation (3)),

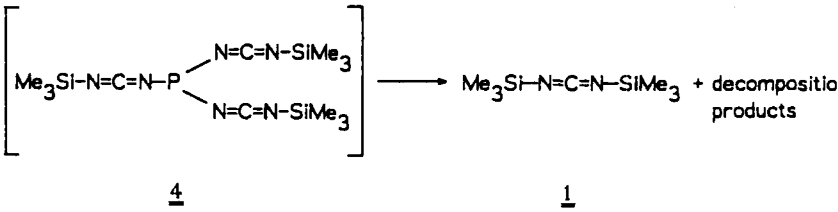


(3)

In contrast to the difluorophosphine, **2** N,N′-bis(trimethylsilylcarbodiimido)-fluorophosphine, **3** is unstable in solution, undergoing a scrambling reaction with formation of **2** and, presumably, of N-tris(trimethylsilylcarbodiimido)phosphine, **4** (Equation (4a)). The latter compound decomposes with formation of **1** (^{1}H, ^{13}C n.m.r. spectra), and other poorly soluble products (Equation (4b)).



(4a)

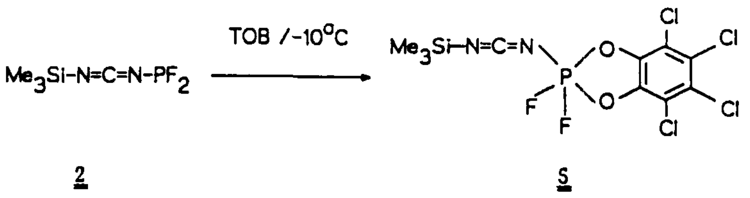


(4b)

Scrambling reactions of the above type have previously been observed, e.g., for $(Me_2N)_2PF$ which was found to yield Me_2NPF_2 and $(Me_2N)_3P$[2].

OXIDATION OF N-TRIMETHYLSILYLCARBODIIMIDO-N′-DIFLUOROPHOSPHINE, 2 WITH TETRACHLORO-O-BENZOQUINONE (TOB)

The oxidative addition of o-benzoquinones to λ^3P phosphorus compounds is known,[3] and the reaction of **2** with TOB is no exception here. The reaction was conducted at −10°C (Equation (5)).



(5)

Compound **5** could be isolated as a solid whose solutions in organic solvents were found to decompose with formation of Me_3SiF. NMR spectra were therefore recorded at $-20°C$ on solutions of **5** in $CDCl_3$. The identity of **5** could be established by mass spectrometry, a parent peak of relative intensity 5% was observed.

EXPERIMENTAL

All experiments described were conducted with careful exclusion of air and moisture. Solvents were dried by standard procedures.[4] Starting materials: N,N′-Bis(trimethylsilyl)carbodiimide, **1**[5]; Dichlorofluorophosphine.[6]

NMR spectra were recorded on a Bruker AC-200 spectrometer, employing the following standards and conditions: ^1H (200.1 MHz, $CDCl_3$, TMS internal), ^{19}F (188.3 MHz, $CDCl_3$, $CFCl_3$ external), ^{31}P (81.0 MHz, $CDCl_3$, H_3PO_4 external). In the case of **3**, a coaxial n.m.r. tube was used ($CDCl_3$ external). The mass spectra were recorded on a Finnigan MAT 8430 instrument under E.I. conditions.

Reaction of **1** *with dichlorofluorophosphine: Formation of* **3**. A mixture of 8.35 g (44.8 mmol) of **1** and 2.7 g (22.3 mmol) of $PFCl_2$ was condensed at $-196°C$ into a glass tube, fitted with a TEFLON® stopcock. The mixture was magnetically stirred at room temperature for 12 h. A yellow solid was subsequently removed from the reaction mixture by filtration. This solid product was poorly soluble in dichloromethane but very well soluble and reactive in methanol and water. Trimethylchlorosilane (4.9 g = 100%) was pumped off at 1 mm, was condensed in a trap cooled with liquid nitrogen, and identified by ^1H n.m.r. spectroscopy.

Upon an attempt at the distillation of the remaining product in *high vacuo* (5×10^{-4} mm) it was found to turn yellow at 50°C, and at 60°C decomposition was evident. A brown, sticky residue was left, and in a trap 1.5 g of **1** could be identified (^1H, ^{13}C n.m.r. spectroscopy).

^{19}F-NMR spectrum of **3**: δ -71.99 ppm (d, $^1J(PF)$ 1165 Hz).
$^{31}P\{^1H\}$-NMR spectrum of **3**: δ 142.18 ppm (d, $^1J(PF)$ 1165 Hz).

Reaction of **2** *with TOB: Preparation of the difluorophosphorane,* **5**. In the temperature range, -10 to 0°C, solutions of 3.0 g (12.2 mmol) of **2** in 20 ml of dichloromethane and of 1.9 g (11.5 mmol) TOB in 15 ml of dichloromethane were combined within 20 min dropwise. The colour of the TOB solution faded gradually during this process and precipitation of a solid product was noted after ca. 1/4 of the TOB solution had been added. After the addition of the TOB solution had been completed the reaction mixture was stirred at 0°C for 10 min.

Subsequently, the supernatant red solution was removed (pipette), was cooled to $-30°C$, and 5 ml of dichloromethane were added. The supernatant solution was again removed from the solid product, and cooled to $-50°C$ after the addition of 3 ml of dichloromethane. The white solid, formed during this process, was collected by filtration, and was washed with small amounts of dichloromethane until the filtrate was colourless. The product, **5** was collected by filtration and dried *in vacuo* (0.1 mm; 20°C). Yield 2.3 g (47%).

$C_{10}H_9Cl_4F_2N_2O_2PSi$ (428.05)	found:	C 27.12	H 2.31	Cl 33.65
	calc.:	C 28.06	H 2.12	Cl 33.13

^1H-NMR spectrum (253 K): δ 0.34 ppm (s, $Si(CH_3)_3$).
^{19}F-NMR spectrum (253K): δ -46.66 ppm (d, $^1J(PF)$ 868 Hz).
$^{31}P\{^1H\}$-NMR spectrum (253 K): δ -48.2 ppm (t, $^1J(PF)$ 868 Hz).
Mass spectrum (100°C; related to ^{35}Cl): $[M]^+$ 426 (5%), $[M-Me]^+$ 411 (2%), $[Me_2SiF]^+$ 77 (100%).

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