7.1 Synthesis of Tetramethylfluoroformamidinium Hexafluorophosphate (TFFH) (7)[10]

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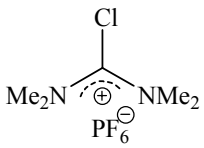
Step 1: Synthesis of Tetramethylchloroformamidinium Hexafluorophosphate (TCFH) (71)

Starting amounts:

5.80 g	(0.05 mol) Tetramethylurea (**70**)
8.67 g	(0.07 mol) Oxalylchloride
15.0 g	(0.08 mmol) KPF_6
94 ml	Toluene
250 ml	Diethyl ether
250 ml	Dichloromethane
35 ml	Water

Procedure: A 20% solution of oxalyl chloride in toluene was added dropwise and under dry conditions to a solution of tetramethylurea (**70**) in toluene. The reaction mixture was refluxed for 2 h, and then anhydrous diethyl ether (175 ml) was added with vigorous stirring. The precipitated salt was filtered and washed with anhydrous diethyl ether (3 x 25 ml). The highly hygroscopic material was immediately dissolved in dichloromethane (250 ml) and to this solution a saturated solution of KPF_6 (15 g/15 ml) was added with continuous stirring for 10-15 min. The organic phase was washed with water (20 ml), dried with $MgSO_4$ and the solvent was removed under reduced pressure.

Yield: 5.27 g (40 %) of **71** as colourless solid



71

Melting point: 91-93 °C

^{1}H-NMR (250 MHz, CD_3OD): δ = 3.32 (s, Me).

In accordance with the data from literature.

Step 2: Synthesis of Tetramethylfluoroformamidinium Hexafluorophosphate (TFFH) (7)

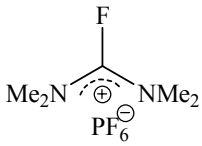
Starting amounts:

5.27 g	(20.0 mmol) TCFH (**71**)
1.09 g	(20.0 mmol) KF
28 ml	Acetonitrile

Procedure: To a solution of TCFH (**71**) in dry acetonitrile was added KF (dried under reduced pressure and upon heating overnight) portionwise and the reaction mixture was stirred at room temperature for 3 h. The insoluble solid (KCl) was filtered and the filtrate was evaporated under reduced pressure.

Purification: Recrystallization from acetonitrile/diethyl ether

Yield: 3.06 g (62 %) of **7** as colourless crystals



7

Melting point: 107-109 °C

^{1}H-NMR (250 MHz, CD_3OD): δ = 3.18 (bs, Me).

In accordance with the data from literature.