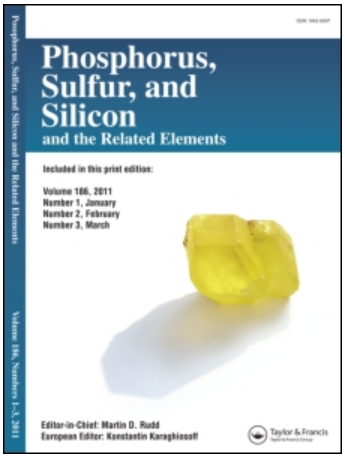

Phosphorus, Sulfur, and Silicon and the Related Elements

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Reaction of Mes NPC1 with Triphenylcarbenium Tetrafluoroborate

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REACTION OF MES*NPCl WITH TRIPHENYLCARBENIUM TETRAFLUOROBORATE

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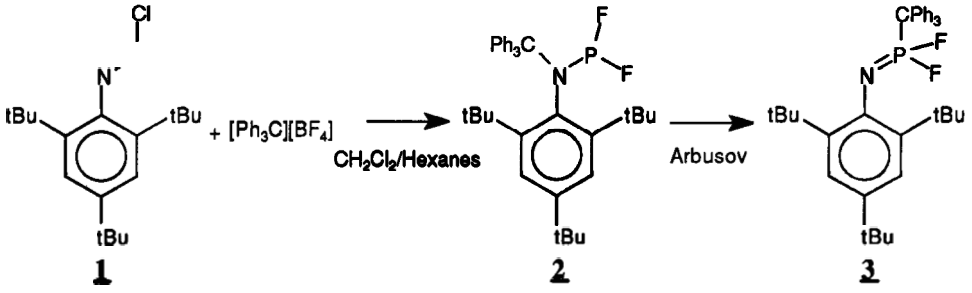
Abstract Reaction of Mes*NPCl with triphenylcarbenium salts (BF_4 or PF_6) produces a difluorophosphine and not the expected iminophosphenium cation. This compound then undergoes an Arbusov-type rearrangement to generate a difluoro-iminophosphorane.

Reaction of Mes*NPCl **1** with $AlCl_3$ or $GaCl_3$ gives the iminophosphenium cation, Mes*NP$^+$. In contrast, reaction with $NaBPh_4$ gives the covalent iminophosphine Mes*NPPh[1] quantitatively. We now report the reaction with $[Ph_3C][BF_4^-]$ in 3:1 CH_2Cl_2/hexane solution (Scheme 1) which gives the (dialkyl)amino-difluorophosphine **2** quantitatively. This extremely sterically hindered phosphine then readily undergoes an Arbusov-type rearrangement to generate the difluoroiminophosphorane **3** which has been structurally characterized (Figure 1)[2]. Compounds such as **3** typically dimerize, but this is prevented by steric hinderance[3].

EXPERIMENTAL

Mes*NPCl (0.41 g, 1.26 mmol) in ≈10 mL of 3:1 CH_2Cl_2/hexane was added over a period of 10 minutes to a solution of $[Ph_3C][BF_4^-]$ (0.42 g, 1.28 mmol) in ≈10 mL of a similar solvent mixture. The solution turned bright yellow after 10 minutes and slow



1 **2** **3**

removal of solvent yielded yellow crystals which were characterized as $Mes^*NPF_2CPh_3$ (0.56 g, 0.98 mmol, 78%), mp 157.0-158.5 °C.

Elemental analysis:	Calc.	C, 77.73	H, 7.76	N, 2.45
	Found	C, 76.53	H, 8.34	N, 2.59

^{31}P nmr studies of $[Ph_3C][BF_4]$ or $[Ph_3C][PF_6]$ indicate immediate quantitative formation of **2** (^{31}P: 146 ppm triplet; $^1J_{PF}$: 1105 Hz) which then decays over three days to give **3** (^{31}P: -38 ppm triplet; $^1J_{PF}$: 1221 Hz) in a solution yield of > 90%.

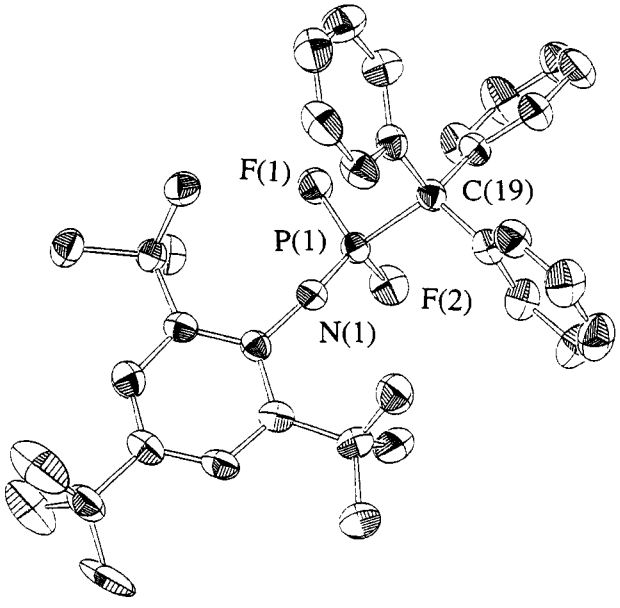


FIGURE 1 ORTEP view of **3**. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.475(4), P(1)-C(19) 1.847(4), P(1)-F(1) 1.557(3), P(1)-F(2) 1.562(3), C_{Mes^*}-N(1) 1.563(3), P(1)-N(1)-C_{Mes^*} 156.3(3).

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1. E. Niecke, J. F. Nixon, P. Wenderoth, B. F. Trigo Passos, M. Nieger, J. Chem. Soc. Chem. Commun., 846, (1993).
2. Crystal data $C_{37}H_{44}F_2NP$: M=571.73; space group P1 (#2), a = 13.728(3), b = 23.808(5), c = 10.125(2), α = 95.69(1), β = 101.37(1), γ = 91.62(2), V = 3224(1) Å^3, Z = 2, $D_{calc.}$ = 1.178 g cm^{-3}, $\mu_{MoK\alpha}$ = 1.17 cm^{-1}, Observations [I>3s(I)] 5430, 100R = 4.98, $100R_w$ = 4.98, GoF = 1.532. Positional parameters have been deposited (CSD).
3. N. Burford, J. A. C. Clyburne, D. P. Gates, M. J. Schriver, and J. F. Richardson, J. Chem. Soc., Dalton Trans., 997 (1994), and references therein.