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REACTION OF MES*NPCl WITH TRIPHENYLCARBENIUM TETRAFLUOROBORATE

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 STANLEY CAMERON

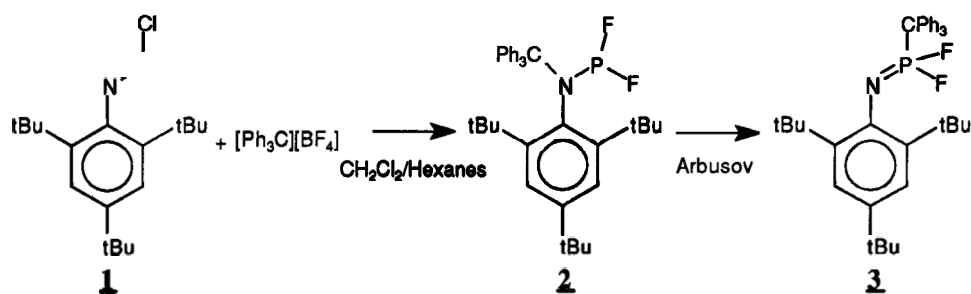
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Abstract Reaction of Mes*NPCl with triphenylcarbenium salts (BF₄ or PF₆) produces a difluorophosphine and not the expected iminophosphenium cation. This compound then undergoes an Arbusov-type rearrangement to generate a difluoroiminophosphorane.

Reaction of Mes*NPCl **1** with AlCl₃ or GaCl₃ gives the iminophosphenium cation, Mes*NP⁺. In contrast, reaction with NaBPh₄ gives the covalent iminophosphine Mes*NPPH¹ quantitatively. We now report the reaction with [Ph₃C][BF₄⁻] in 3:1 CH₂Cl₂/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 hindrance³.

EXPERIMENTAL

Mes*NPCl (0.41 g, 1.26 mmol) in ≈10 mL of 3:1 CH₂Cl₂/hexane was added over a period of 10 minutes to a solution of [Ph₃C][BF₄⁻] (0.42 g, 1.28 mmol) in ≈10 mL of a similar solvent mixture. The solution turned bright yellow after 10 minutes and slow



removal of solvent yielded yellow crystals which were characterized as Mes*NPF₂CPh₃ (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

³¹P nmr studies of [Ph₃C][BF₄] or [Ph₃C][PF₆] indicate immediate quantitative formation of **2** (³¹P: 146 ppm triplet; ¹J_{PF}: 1105 Hz) which then decays over three days to give **3** (³¹P: -38 ppm triplet; ¹J_{PF}: 1221 Hz) in a solution yield of > 90%.

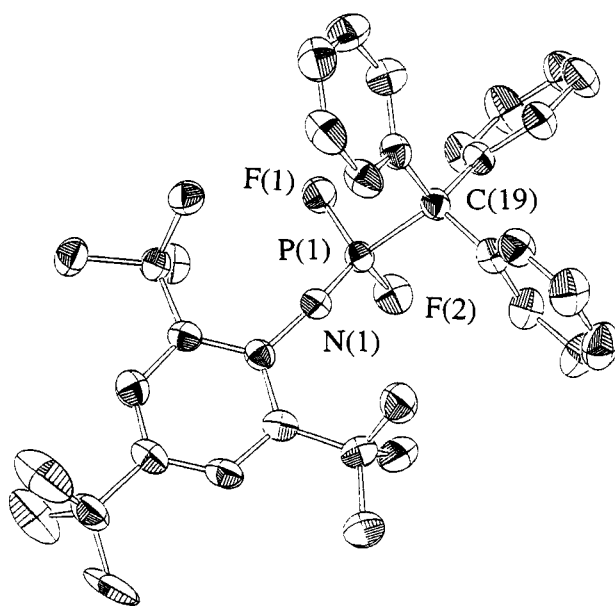


FIGURE 1 ORTEP view of **3**. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.475(4), P(1)-C(19) 1.847(4), P(1)-F(1) 1.557(3), P(1)-F(2) 1.562(3), C_{Mes*}-N(1) 1.563(3), P(1)-N(1)-C_{Mes*} 156.3(3).

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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 C₃₇H₄₄F₂NP: 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) Å³, Z = 2, D_{calc.} = 1.178 g cm⁻³, μ_{MoKα} = 1.17 cm⁻¹, Observations [I>3σ(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.