Formation of a Carbon–Phosphorus Bond between a C–F Compound and Phosphorus(III) Fluorides: a Fluorine Analogue of the Kinnear–Perren Reaction Furnishing 1-Adamantylfluorophosphoranes

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Summary Insertion of phosphorus trifluoride into the C–F bond of 1-adamantyl fluoride in the presence of phenyltetrafluorophosphorane leads to formation of the otherwise inaccessible 1-adamantyltetrafluorophosphorane; the formation of a carbon–phosphorus bond is also observed in the systems 1-adamantyl fluoride–Bu^tPF_2–$PhPF_4$ and 1-adamantyl fluoride–1-adamantyldifluorophosphine–$PhPF_4$ from which the new compounds 1-adamantyl-t-butyltrifluorophosphorane and bis-(1-adamantyl)trifluorophosphorane, respectively, are obtained.

THE condensation of alkyl chlorides with phosphorus trichloride and aluminium chloride is a major preparative method for creating phosphorus–carbon bonds;[1] the adducts thus obtained serve as versatile intermediates in organophosphorus chemistry.[2] In contrast, no such reaction involving a carbon–fluorine compound and a P^{III} fluoride has yet been reported.

We have found that 1-adamantyltetrafluorophosphorane (**3**) is obtained in 80% yield when 1-adamantylfluoride (**1**) and PF_3 (**2**) in the presence of PhPF_4 are kept in a sealed tube for 5 days at room temperature. In a separate experiment, involving the same quantities of (**1**) and (**2**) under identical conditions, but in the absence of PhPF_4, only the formation of a trace of 1-adamantylphosphonic difluoride[3] [<3%, based on (**1**)] was observed by ^{19}F n.m.r. spectroscopy; the phosphonic difluoride probably originates from partial hydrolysis of (**3**) formed under these conditions. It appears reasonable to formulate the reaction [equation (1)] as resembling a Kinnear–Perren reaction[1] [equation (2)].

$$\underset{(\mathbf{1})}{\text{1-AdF}} + \underset{(\mathbf{2})}{\text{PF}_3} \xrightarrow{\text{PhPF}_4} \underset{(\mathbf{3})}{\text{1-AdPF}_4} \qquad (1)$$

1-Ad = 1-adamantyl

$$\text{RCl} + \text{PCl}_3 + \text{AlCl}_3 \rightarrow [\text{RPCl}_3][\text{AlCl}_4] \qquad (2)$$

While in the Kinnear–Perren reaction, a stable complex of the chlorophosphorane with the aluminium halide is obtained, the fluorophosphorane (**3**) is recovered directly in the adamantyl fluoride–PF_3 reaction. PhPF_4 is believed to function as a Lewis acid sufficiently strong to activate the C–F bond in (**1**) but too weak to form an adduct with (**3**) stable at room temperature. Compound (**3**) is a volatile solid (m.p. 43 °C; b.p. 77 °C at 2 Torr).

It is worth noting that fluorination of 1-adamantyl phosphonic difluoride[3] with SF_4 has failed to give the tetrafluorophosphorane, although the fluorination of phosphoryl compounds with SF_4[4] is an otherwise generally applicable route for the synthesis of fluorophosphoranes.[5]

Identification of (**3**) was straightforward from ^{31}P and ^{19}F n.m.r. data: δ_{P} +35·6 p.p.m. (ext. H_3PO_4); δ_{F} +59·9 p.p.m. (int. CCl_3F); J_{PF} 1040 Hz. The n.m.r. spectra are typical of a tetrafluorophosphorane undergoing pseudorotation;[5] the appearance of the ^{19}F n.m.r. spectrum was unchanged at temperatures down to −100 °C, and no effect of the bulky adamantyl substituent on the pseudorotation process was observed. The tetrafluorophosphorane (**3**) was characterized further by mass spectroscopy, the most intense fragment being the adamantyl cation (*m/e* 135). The PF_4 fragment (*m/e* 107) was also intense, while a molecular ion, as for other tetrafluorophosphoranes,[6] was absent.

This preparative method has been extended to reactions of (**1**) with other P^{III} fluorides; the examples in equations (3) and (4) are typical.

$$\text{1-AdF} + \text{Bu}^{\text{t}}\text{PF}_2 \xrightarrow{\text{PhPF}_4} \text{1-Ad(Bu}^{\text{t}}\text{)PF}_3 \qquad (3)$$

$$\text{1-AdF} + \text{1-AdPF}_2 \xrightarrow{\text{PhPF}_4} (\text{1-Ad})_2\text{PF}_3 \qquad (4)$$

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