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The Reaction of Chlorotetrafluorophosphorane with Trimethylamine

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The reaction of chlorotetrafluorophosphorane with trimethylamine affords a 1 1 Lewis acid–base complex of composition $ClF_4P{\cdot}NMe_3$ *It has been established by* ^1H *and* ^{19}F *NMR spectroscopy that the Cl and* Me_3N *ligands occupy mutually* trans *positions in a locally octahedral geometry around phosphorus*

Introduction

One of the most useful and well recognized properties of the pentahalides of Group VA relates to their acceptor behavior However, while numerous complexes of the type Base → MX_5 (M = P, As, Sb, X = halogen) have been characterized [1, 2], we are not aware of the synthesis of any complexes featuring mixed halophosphoranes of the type Base →MF_4X (X ≠ F) Such complexes are of interest because of the possibility of geometrical isomerism The present study concerns the reactions of PF_4Cl with Me_3N

Experimental

Preparations

Due to the moisture and/or oxygen sensitivity of boron and phosphorus halides it was necessary to perform all operations in an inert atmosphere or in a Pyrex vacuum system of standard design Boron trichloride and PF_5 were procured commercially and used without subsequent purification Chlorotetrafluorophosphorane was prepared by the vapor-phase reaction of PF_5 with BCl_3 [3], and purified by trap-to-trap distillation until the infrared spectrum conformed to the one reported in the literature [4]

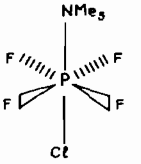
In a typical preparation of $ClF_4P{\cdot}NMe_3$, 5 5 mmol of PF_4Cl and 10 0 mmol of Me_3N were condensed into the side-arm of an evacuated 2-L reaction bulb at −196 °C and allowed to warm slowly to room temperature Formation of a white solid was apparent as soon as the reaction mixture melted Excess of Me_3N (beyond that required for formation of the 1 1 complex) was removed quantitatively from the reaction mixture after allowing it to stand for 30 minutes at room temperature The white solid product, which fumes in moist air, partially sublimes at ~80 °C in a sealed melting point capillary, leaving a residual infusible (<300 °C) brown mass With rapid heating, samples darken at ~80 °C and decompose rapidly at ~90 °C, with evidence of sublimation *Anal* Calcd for $C_3H_9ClF_4NP$ C, 17 88, H, 4 50, N, 6 95, Cl, 17 60% Found C, 17 90, H, 4 50, N, 6 90, Cl, 17 59%

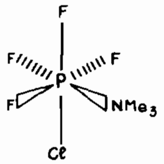
Spectroscopic Measurements

^1H and ^{19}F NMR measurements were made on Varian A60 and Varian A56/60 spectrometers, respectively NMR samples were prepared by dissolving $ClF_4P{\cdot}NMe_3$ in CD_3CN The NMR tubes were sealed off in vacuo with the sample held at −196 °C It was found that the samples decomposed (with slight etching of the Pyrex glass) upon standing for two weeks at ambient temperature

Results and Discussion

The analytical data establish that the reaction of PF_4Cl with Me_3N results in the formation of a 1 1 complex Assuming a locally octahedral geometry about the hexacoordinate phosphorus atom, two geometrical isomers are possible for this compound, *trans* (I) and *cis* (II)


(I)


(II)

The fact that the ^{19}F NMR spectrum of $ClF_4P{\cdot}N(CH_3)_3$ exhibits only one type of resonance (Table I) clearly establishes the preference for the *trans* geometry, (I) The equivalence of the fluoride ligands is also apparent from the ^1H NMR spectrum which

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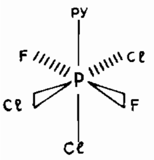
TABLE I. Nuclear Magnetic Resonance Parameters for $ClF_4P{\cdot}NMe_3$.

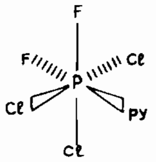
Nucleus observed (splitting pattern)	J_{XP} (Hz)	J_{XF} (Hz)	Shift (ppm)[a]
^1H (doublet of quintets)	9.2	2.2	$\delta = 3.28$
^{19}F (doublet of unresolved multiplets)	970	–	$\delta = 31.7$

[a] Relative to external Me_4Si or CCl_3F for ^1H, and ^{19}F respectively (Upfield +, downfield –).

consists of a doublet of quintets. In a previous study, Holmes and Gallagher [5] noted that the ^{19}F NMR spectrum of the pyridine (py) complex of PF_2Cl_3 comprised 'only one doublet'. It can be implied therefore that the preferred geometry for this complex is (III) rather than (IV).



(III)



(IV)

Note that the preferred geometries, (I) and (III), both feature chloride ligands *trans* to the Lewis base, while the disfavored isomers, (II) and (IV) both have fluoride ligands *trans* to the Lewis base. This *trans* chloride preference may be a consequence of minimizing steric repulsions between the Lewis base and halide ligands. Alternatively, the observed isomeric preferences may result from the operation of subtle electronic effects.

The one-bond P–F coupling constant, J_{PF}, in $ClF_4P{\cdot}N(CH_3)_3$ (Table 1) is smaller than that in the free phosphorane (1000 Hz) [5]. The same trend is apparent when PF_5 coordinates to Me_3N [6], Me_3P [7], or F^- [8, 9]. Such a trend is anticipated on the basis of the Fermi contact term since in a free phosphorane, the average %P (3s) character in the dsp^3 hybrid orbitals is ~20%, while for octahedral hybrid orbitals the %P (3s) character is ~16.7%. This generalization should be applied cautiously, however, because $^1J_{PF}$ is 996 and 1049 Hz in PCl_4F and $Cl_4FP{\cdot}NC_5H_5$ [5] respectively.

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