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 $\text{H}_3\text{N}\cdot\text{PF}_5$ AND H_2NPF_5^- , NEW COMPOUNDS IN THE SYSTEM $\text{H}_3\text{N}/\text{PF}_5$

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Phosphorus pentafluoride was reported long ago to give adducts $2\text{PF}_5 \cdot 5\text{NH}_3$ (1) and $n\text{NH}_3 \cdot \text{PF}_5$ ($n = 1 - 4$) (2). None of the compounds was characterized in detail. Repeating the reaction of PF_5 and NH_3 we found the adduct $\text{H}_3\text{N}\cdot\text{PF}_5$, 1, in 8% yield, besides $(\text{H}_2\text{N})_2\text{PF}_3$ (3) and NH_4PF_6 . However, HF and $(\text{F}_2\text{P}=\text{N})_3$ gave 1 in 41% yield. The ^1H , ^{19}F , and ^{31}P n.m.r. spectra of 1 exhibit $^1\text{N}-\text{H}$, $^{14}\text{N}-\text{P}-\text{F}$ (cis), and $^{14}\text{N}-\text{P}$ coupling. The x-ray structure determination shows almost perfect octahedral geometry at phosphorus with a P-N bond length of 1.842 Å. Compound 1 is soluble in water without decomposition. Treatment with NH_3 leads to the anion H_2NPF_5^- . Upon heating 1 forms in good yield H_2NPF_4 and NH_4PF_6 . Without a solvent 1 and NH_3 react to give $(\text{H}_2\text{N})_2\text{PF}_3$. A mechanism for the ammonolysis of PF_5 is proposed.

(1) T. E. Thorpe, Proc. Roy. Soc. (London), 25, 122 (1876); Liebigs Ann. Chem. 182, 201 (1876)
 (2) S. Johnson, Ph. D. Thesis, Purdue University, 1953. (3) M. Lustig and H. W. Roesky, Inorg. Chem. 9, 1289 (1970).

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STRUCTURAL AND CHEMICAL STUDIES RELATING TO
CYCLOTETRAMETHYLENE TRIFLUOROPHOSPHORANE (1.1.1-TRIFLUORO- $\lambda^5\text{P}$ -PHOSPHOLANE)G. Bettermann^a, H. Buhl^a, R. Gereke^a, H. Oberhammer^b, R. Schmutzler^{a*}, M. Sell^a,
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The title compound, $(\text{CH}_2)_4\text{PF}_3$, 1 holds a special position amongst stereochemically nonrigid fluorophosphoranes, due to the incorporation of $\lambda^5\text{P}$ into a five-membered ring system; thus, 1 has served as a model in the rationalization of the mechanism of hydrolysis of cyclic phosphate esters (F.H. Westheimer, Acc. Chem. Res., 1, 70 (1968)). Compound 1, prepared by a new, efficient method, has been converted into two solid spiro-monofluorophosphoranes, involving the $\lambda^5\text{P}$ -phospholane ring system. Both in the gas phase (electron diffraction study of 1) and in the solid state (single crystal X-ray structure determination on two spiro-monofluorophosphoranes) the $(\text{CH}_2)_4$ unit is bridging two equatorial positions at trigonal-bipyramidal $\lambda^5\text{P}$. The static and dynamic stereochemistry of 1 and of its derivatives will be discussed on the basis of the above structural studies as well as by n.m.r. spectroscopy. Some further derivative chemistry of 1 will be described.