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$H_3N{\cdot}PF_5$ AND $H_2NPF_5^-$, NEW COMPOUNDS IN THE SYSTEM H_3N/PF_5

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Phosphorus pentafluoride was reported long ago to give adducts 2 $PF_5{\cdot}5\ NH_3$ (1) and n $NH_3{\cdot}PF_5$ (n= 1 - 4) (2). None of the compounds was characterised in detail. Repeating the reaction of PF_5 and NH_3 we found the adduct $H_3N{\cdot}PF_5$, 1, in 8% yield besides $(H_2N)_2PF_3$ (3) and NH_4PF_6. However, HF and $(F_2P{=}N)_3$ gave 1 in 41% yield. The ^1H, ^{19}F, and ^{31}P n.m.r. spectra of 1 exhibit ^{14}N-H, ^{14}N-P-F(cis), and ^{14}N-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 $(H_2N)_2PF_3$. A mechanism for the ammonolysis of PF_5 is proposed.

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STRUCTURAL AND CHEMICAL STUDIES RELATING TO CYCLOTETRAMETHYLENE TRIFLUOROPHOSPHORANE (1.1.1-TRIFLUORO-λ^5P-PHOSPHOLANE)

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The title compound, $(CH_2)_4PF_3$, 1 holds a special position amongst stereochemically nonrigid fluorophosphoranes, due to the incorporation of λ^5P 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 spiromonofluorophosphoranes, involving the λ^5P-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 spiromonofluorophosphoranes) the $(CH_2)_4$ unit is bridging two equatorial positions at trigonal-bipyramidal λ^5P. 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.