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Phosphorus–Fluorine Chemistry. XIII.[1] The Adduct of Nitrosyl Fluoride with Phenyltetrafluorophosphorane. New Fluorophosphates

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Nitrosyl fluoride was found to react with phenyltetrafluorophosphorane to form a solid, thermally unstable 1:1 adduct. Evidence for the formulation of this adduct as a nitrosyl salt, $NO^+C_6H_5PF_5^-$, based on various chemical reactions, is presented. The novel fluoroanions, $R(Ar)PF_5^-$, together with alkyl(aryl)dialkylaminotrifluorophosphoranes, $R(Ar)PF_3NR_2$, are also obtained in the form of stable dialkylammonium salts upon dialkylaminolysis of tetrafluorophosphoranes, $R(Ar)PF_4$. The stereochemistry of the $R(Ar)PF_5^-$ anions, and of the alkyl(aryl)dialkylaminotrifluorophosphoranes, based on n.m.r. spectroscopic studies, is discussed. In contrast to nitrosyl fluoride, nitryl fluoride reacted with phenyltetrafluorophosphorane with direct nitration of the aromatic ring.

Introduction

It is now firmly established that phosphorus pentafluoride is a Lewis acid whose acceptor properties are comparable to those of boron trifluoride.[2] It thus may be expected that derivatives of phosphorus pentafluoride, containing, for instance, hydrocarbon substituents such as alkyl or aryl groups, also possess some Lewis acid character. Indeed, there is evidence that the behavior of aromatic tetrafluorophosphoranes and, to a lesser extent, of tetrafluorophosphoranes containing aliphatic substituents toward certain donor molecules is similar to that of the parent compound, phosphorus pentafluoride.

In connection with the problem of separating nitrosyl fluoride from reaction mixtures we turned our attention to its reaction with phosphorus(V) fluorides. Thus, in his first report on a salt of the novel hexafluorophosphoric acid, Lange[3] already suggested that nitrosyl fluoride may be capable of combining with phosphorus pentafluoride to form nitrosyl hexafluorophosphate. It was shown later on[4] that nitrosyl hexafluorophosphate seems to be in equilibrium with its components, NOF and PF_5, and the compound was found to be thermally less stable and more readily sublimable than the fluoroborate, $NO^+BF_4^-$.[4,5]

We have considered an analogous system, involving phenyltetrafluorophosphorane, $C_6H_5PF_4$, instead of phosphorus pentafluoride as the Lewis acid. Phenyl tetrafluorophosphorane is a particularly readily accessible liquid, which can be handled with ease, and thus seemed preferable over the gaseous phosphorus pentafluoride. A 1:1 adduct between nitrosyl fluoride and phenyl tetrafluorophosphorane was indeed readily formed, but neither NOF nor $C_6H_5PF_4$ was recovered upon its thermal decomposition. Based on various chemical reactions of the thermally unstable adduct, which irreversibly decomposed above 0°, evidence for the formation of a nitrosyl salt, $NO^+C_6H_5PF_4^-$, was found. Thermally stable salts containing the novel alkyl(aryl)pentafluorophosphate anion could be prepared by an independent route.

In contrast to nitrosyl fluoride, nitryl fluoride immediately nitrated the aromatic nucleus of phenyltetrafluorophosphorane, no 1:1 adduct, corresponding to a nitryl salt, $NO_2^+C_6H_5PF_5^-$, being isolated.

Experimental

Since most of the preparations described in this paper involve highly moisture-sensitive materials, all reactions were conducted in an atmosphere of dry nitrogen. Organic solvents were dried by standard procedures. Nitrosyl and nitryl fluoride were obtained from the Ozark-Mahoning Co. The Freon[6] fluorocarbon solvents were obtained from Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc. The fluorophosphoranes were obtained according to published routes.[7,8]

Nitrosyl and nitryl fluoride were stored in Monel cylinders and were transferred *via* a Monel high-vacuum line.

The P^{31} and F^{19} n.m.r. spectra were obtained on a Varian Associates 4311B high resolution spectrometer at 24.3 and 56.4 Mc./sec., respectively. The H^1 spectra were recorded on a Varian A-60 analytical spectrometer. For P^{31} spectra either pure liquids or saturated solutions in CH_3CN (in the case of solids) were used and the calibrations were carried out by the superposition technique using 85% phosphoric acid as external reference. The F^{19} and H^1 spectra were calibrated with $CFCl_3$ and $Si(CH_3)_4$, respectively, as internal references using the sideband technique.

(I) **The Adduct between Nitrosyl Fluoride and Phenyltetrafluorophosphorane.**—The preparation was conducted under variable conditions at temperatures between −78 and 0°, employing inert solvents, especially Freon 113 refrigerant (b.p. 46.6°) and Freon 12 (b.p. −30°). Owing to the instability of the adduct above 0°, it proved somewhat difficult to remove the Freon 113 solvent completely from the product. The freezing point of Freon 113 is as high as −35°.

(1) **Preparation of $NOF–C_6H_5PF_4$ Adduct in Freon 113.**—A typical run was as follows: A 500-ml. wide-neck polyethylene bottle was equipped with a Kel-F inlet tube, ending 20 mm. above the bottom of the bottle, and a short outlet tube, which was connected to two polyethylene tubes, filled with Drierite. Air was removed from the system by flushing with dry nitrogen, and in a countercurrent of nitrogen, 46 g. (0.25 mole) of phenyltetrafluorophosphorane and 250 ml. of Freon 113 were placed in the bottle. Nitrosyl fluoride (12.9 g., 0.266 mole) was condensed in a 30-ml. Monel cylinder, connected to the gas inlet tube

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(1) Previous paper in this series: R. Schmutzler, *Chem. Ber.*, in press.

(2) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

(3) W. Lange, *Ber.*, **61**, 799 (1928).

(4) F. Seel and Th. Gössl, *Z. anorg. allgem. Chem.*, **263**, 253 (1950).

(5) E. Wilke-Dörfurt and G. Balz, *ibid.*, **159**, 219 (1927); G. Balz, *ibid.*, **217**, 161 (1934).

(6) Du Pont's registered trademark.

(7) R. Schmutzler, *Chem. Ind.* (London), 1868 (1962).

(8) R. Schmutzler, *Inorg. Chem.*, **3**, 410, 421 (1964).

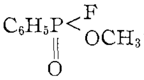
via a flow meter which was constructed of Monel, Teflon[6] fluorocarbon resin, and Tygon parts only, and filled with halocarbon oil. The temperature of the solution of phenyltetrafluorophosphorane in Freon 113 was maintained at -30 to $-40°$, while nitrosyl fluoride was added at a rate of *ca.* 3 g./hr. with magnetic stirring. A light orange solid precipitated immediately, its amount increasing steadily. The addition being completed after 4.5 hr., the precipitate was filtered immediately under a nitrogen blanket through a polyethylene Büchner funnel which could be cooled with Dry Ice from the outside. The crude product thus obtained, containing Freon solvent, was transferred under nitrogen protection to a 250-ml. round-bottom quartz flask, which was attached immediately to a rotating evaporator. Material volatile at 0.1 mm. was pumped off while the flask was immersed in a bath held at *ca.* -20 to $-10°$, in order to prevent decomposition of the adduct. After 3 hr. pumping the now dust-dry material was transferred to a polyethylene storage bottle and stored at $-40°$.

Anal. Calcd. for $NOF \cdot C_6H_5PF_4$: C, 30.9; H, 2.2; F, 40.8; N, 6.0; P, 13.3. Found: C, 30.9; H, 2.4; F, 39.9; N, 4.7[9]; P, 13.2.

(2) **Preparation of $NOF–C_6H_5PF_4$ Adduct in Freon 12.**—The apparatus employed was as described in the above experiment. After the polyethylene reaction vessel had been flushed with dry nitrogen, 27.6 g. (0.15 mole) of phenyltetrafluorophosphorane was charged in a countercurrent of nitrogen. *Ca.* 200 ml. of Freon 12 (miscible with the fluorophosphorane) was then condensed into the reaction vessel; 9.6 g. (0.196 mole) of nitrosyl fluoride was employed in the experiment. The reaction proceeded equally well at -40 or $-80°$, clearly showing the advantage of the Freon 12 solvent over Freon 113, the former being highly mobile even at $-80°$. The adduct, almost colorless at $-80°$ and faintly orange-yellow at $-20°$, was recovered as in the preceding experiment. Volatile products were again pumped off, first at 100 mm., then at 1 mm., to leave the adduct in quantitative yield, based on the amount of fluorophosphorane employed.

Anal. Calcd. for $NOF \cdot C_6H_5PF_4$: C, 30.9; H, 2.2; F, 40.8; N, 6.0; P, 13.3. Found (two independent preparations): C, 31.1, 31.1; H, 2.8, 2.4; F, 40.3; N, 6.0, 4.1[9]; P, 13.3, 13.3.

(3) **Reactions of the $NOF–C_6H_5PF_4$ Adduct (I).** (A) **Hydrolysis of $NOF–C_6H_5PF_4$.**—A 2.4-g. (0.01 mole) sample of I was added in portions with vigorous stirring to 30 ml. of water cooled below 0° and was dissolved immediately with evolution of heat. After repeated evaporation of the hydrolysate on a steam bath the residue was crystallized from water to give 1.3 g. (82%) of phenylphosphonic acid, m.p. 158–159° (lit.[10] m.p. 156–161°).

(B) **Reaction of $NOF–C_6H_5PF_4$ (I) with Methanol.** (a) **Stoichiometric Amount of Methanol.**—A solution of 1.0 g. (0.03 mole) of methanol in 15 ml. of carbon tetrachloride was added dropwise to 7.4 g. (0.03 mole) of I, suspended in 60 ml. of carbon tetrachloride, at $-15°$ over 30 min. The mixture darkened, and evolution of methyl nitrite occurred when the temperature was allowed to rise, 0.95 g. (52%) being collected in a Dry Ice trap. The infrared spectrum (gas) of the methyl nitrite thus obtained was identical with that reported in the literature.[11] A v.p.c. check on the higher boiling products left after removal of the carbon tetrachloride indicated two components, phenylphosphonic difluoride, $C_6H_5POF_2$ (collected and identified by infrared), and a less volatile product, tentatively identified as methyl phenylphosphonofluoridate,  $C_6H_5P(=O)(F)OCH_3$, a known compound.[12] This is suggested by a strong P=O absorption in the infrared spectrum at 1300 cm.$^{-1}$ (intermediate between $C_6H_5PO(OCH_3)_2$ (1260 cm.$^{-1}$) and $C_6H_5POF_2$ (1336 cm.$^{-1}$)).

(b) **Excess Methanol.**—To a suspension of 9.3 g. (0.04 mole) of I in 30 ml. of carbon tetrachloride was added 6.4 g. (0.2 mole; *ca.* 6 molar excess) of methanol at $-15°$. An immediate reaction occurred, and a colorless two-phase mixture resulted. No product was condensed in an attached Dry Ice trap (b.p. of CH_3ONO $-17°$). A check by v.p.c. for other products revealed the presence of a single, high-boiling compound (b.p. >200°), which was collected by preparative v.p.c.

Anal. Calcd. for $C_6H_5PO(OCH_3)_2$: C, 51.5; H, 6.0. Found: C, 50.9; H, 6.2.

The infrared spectrum was identical with that of an authentic sample of dimethyl phenylphosphonate.[13] The proton n.m.r. spectrum showed a doublet at -3.78 p.p.m. (tetramethylsilane as external reference), $J_{P-H} = 11$ c.p.s., and an aromatic multiplet, centered at -7.55 p.p.m., area ratio aliphatic:aromatic protons 6:5, confirming the structure.[14]

(C) **Reaction of $NOF–C_6H_5PF_4$ (I) with 2,4-Dimethylaniline.**—In an atmosphere of dry nitrogen, 5.2 g. (0.043 mole) of freshly distilled 2,4-dimethylaniline was dissolved in 70 ml. of dichloromethane. The solution was cooled to $-80°$, and 10 g. of I (0.043 mole) was added in small portions in a countercurrent of nitrogen with stirring over 2 hr. The dark brown mixture was allowed to warm up to room temperature (1 hr.). A dark brown residue, left after removal of products volatile at 200 mm. and 25°, was washed with water and extracted three times with 50 ml. of ether, the extract being worked up as usual. Distillation through a 5-in. Vigreux column *in vacuo* gave 2.6 g. (48.7%) of a colorless liquid, b.p. 60–61° (39 mm.); $n^{25}D$ 1.4739; purity by v.p.c. 100%.

Anal. Calcd. for $(CH_3)_2C_6H_3F$: C, 77.4; H, 7.3; F, 15.3. Found: C, 77.2; H, 7.6; F, 14.8. Infrared spectrum (cm.$^{-1}$) (pure liquid): 2916 (s, sym. triplet); 1598 (m); 1502 (vs); 1450 (m, b); 1377 (m); 1250, 1212 (vs), 1137 (m); 1118 (vs); 1099 (vw); 1038 (w); 928 (w), 872 (m); 810, 760 (vs); 715 (m); 702 (vw); 664 (m).

(D) **Reaction of I with Boron Trifluoride.**—A 250-ml. three-necked quartz flask, equipped with a gas inlet tube, a thermometer, and a reflux condenser, protected by a drying tube, was charged with a solution of 1.7 g. (0.05 mole) of I in 150 ml. of nitromethane. The brownish solution was held below $-10°$. Boron trifluoride was passed through the solution until it was present in excess. The color of the solution became lighter, and a white precipitate settled which was filtered under nitrogen protection; yield 2.96 g. (51%, as $NOBF_4$). The salt was stored in a vacuum desiccator. There was presumably much handling loss, due to the tendency of the fluoroborate to stick to the walls of the flask.

The product showed the typical behavior of a nitrosyl salt, *e.g.*, vigorous reaction with formation of brown fumes upon dropwise addition of water. The infrared spectrum (Nujol mull) was identical with that of an authentic specimen and was in agreement with the literature report,[15] characteristic absorptions (cm.$^{-1}$) appearing at 2326 ($N\equiv O$), 1808 ($N=O$), and 1025, 1064 (BF_4^-).

A v.p.c. investigation of the filtrate obtained above, after removal of the nitromethane solvent, indicated formation of phenyltetrafluorophosphorane to an extent of 75 ± 10%, part of which had been converted to phenylphosphonic difluoride.

(E) **Reaction of $NOF–C_6H_5PF_4$ (I) with Secondary Amines.** (a) **I + Dimethylamine.**—This reaction was studied most extensively with respect to both products formed.

Under nitrogen protection, 4.1 g. (*ca.* 0.09 mole) of dry dimethylamine was dissolved in 70 ml. of ether, cooled to $-10°$, in a three-necked flask, equipped with thermometer, dropping funnel, and reflux condenser, the latter being topped by a drying tube. I (10.0 g., *ca.* 0.043 mole) was added to this solution with stirring in small portions, a white precipitate being formed which gradually turned to a light brown oil, separating from the ether

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[9] Nitrogen analyses by the Dumas method were erratic.

[10] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, New York and London, 1950.

[11] P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

[12] L. M. Yagupol'skii and Zh. M. Ivanova, *Zh. Obshch. Khim.*, **30**, 1284 (1960).

[13] A. Michaelis, *Ann.*, **181**, 275 (1876).

[14] T. H. Siddall and C. A. Prohaska, *J. Am. Chem. Soc.*, **84**, 3467 (1962).

[15] G. L. Cote and H. W. Thompson, *Proc. Roy. Soc.* (London), **A210**, 217 (1951).

solution when the mixture was allowed to warm up to room temperature. The ether solution was decanted from the oil, and the ether was distilled off. Vacuum distillation of the residue through a 5-in. Vigreux column gave 2.45 g. (76%) of dimethylnitrosamine as a light yellow liquid, b.p. 54° (21 mm.). The refractive index (n^{25}_{D} 1.4343; lit.[16] n^{18}_{D} 1.4374) and the infrared spectrum[17] were in agreement with the literature reports.

Anal. Calcd. for $(CH_3)_2N\cdot NO$: C, 32.4; H, 8.2; N, 37.8. Found: C, 32.3; H, 8.5; N, 37.5.

The above-mentioned oily residue was distilled at 140–142° (0.5 mm.); yield 7.2 g. (67%). The product solidified readily on standing.

Anal. Calcd. for $(CH_3)_2NH_2{}^+C_6H_5PF_5{}^-$: C, 38.6; H, 5.3; N, 5.6. Found: C, 38.2; H, 5.5; N, 5.75.

The infrared (in KBr) and F^{19} n.m.r. spectra of the product proved its identity to the independently obtained dimethylammonium phenylpentafluorophosphate (*vide infra*). No products other than this salt and the nitrosamine were detected.

(b) **I + Diethylamine.**—As described in the preceding experiment, 9.6 g. (0.04 mole) of I was added to the solution of 5.85 g. (0.08 mole) of diethylamine in 75 ml. of ether between −5 and +5°. Work-up by distillation gave 2.2 g. (54%) of diethylnitrosamine; b.p. 74.5° (21 mm.). The refractive index (n^{25}_{D} 1.4356; lit.[18] $n^{19.9}_{D}$ 1.4386) and the infrared spectrum[17] were in agreement with the literature report; purity by v.p.c. >98%.

Anal. Calcd. for $(C_2H_5)_2N\cdot NO$: C, 47.0; H, 9.9. Found: C, 47.4; H, 9.8.

The solid reaction residue, containing diethylammonium phenylpentafluorophosphate, was not investigated further in this run.

(c) **I + Piperidine.**—From 10.0 g. (0.043 mole) of I and 6.8 g. (0.09 mole) of piperidine in 70 ml. of ether at −10° was obtained 2.3 g. (49%) of piperidinenitrosamine; b.p. 94° (7 mm.) n^{25}_{D} 1.4863 (lit.[18] $n^{18.5}_{D}$ 1.4933). The infrared spectrum was also identical with that reported in the literature.[17]

Anal. Calcd. for $C_5H_{10}N\cdot NO$: C, 52.6; H, 8.9; N, 24.5. Found: C, 52.9; H, 9.1; N, 23.8.

(II) **Reaction of Nitryl Fluoride with Phenyltetrafluorophosphorane.**—In a 250-ml. two-necked quartz flask, equipped with a gas inlet tube and a drying tube at the outlet, 18.4 g. (0.1 mole, 13.4 ml.) of phenyltetrafluorophosphorane was dissolved in 150 ml. of Freon 113 refrigerant under nitrogen protection. Nitryl fluoride (9.0 g., 0.14 mole) was passed through the solution at −20 to −30°, and formation of a dense precipitate commenced almost immediately. After the addition of the nitryl fluoride was completed (1 hr.), nitrogen was passed through the reaction mixture in order to remove excess nitryl fluoride. The precipitate was filtered off in a special apparatus preventing any contact with the atmosphere and was washed with Freon 113 and dried overnight *in vacuo* (25° at 0.5 mm.).

A strong absorption in the infrared spectrum (Nujol mull) at 1545 cm.$^{-1}$ suggested the presence of a nitro group, while no evidence for nitryl ion, $NO_2{}^+$, was found (characteristic infrared absorption at 2360 cm.$^{-1}$).[19] Chemical analysis suggested formation of a nitrated phenyltetrafluorophosphorane.

Anal. Calcd. for $NO_2F\cdot C_6H_5PF_4$: C, 29.0; H, 2.0; F, 38.1; N, 5.6; P, 12.4. Calcd. for $O_2N\cdot C_6H_4\cdot PF_4$: C, 31.4; H, 1.8; F, 33.2; N, 6.1; P, 13.5. Found: C, 31.9; H, 2.2; F, 30.6; N, 6.5; P, 13.7.

The product could be kept for short periods when stored in a polyethylene container, but decomposed gradually on prolonged storage.

Hydrolysis of $O_2N\cdot C_6H_4\cdot PF_4$.—A 3.75-g. (0.015 mole) sample of $O_2N\cdot C_6H_4\cdot PF_4$ was readily soluble in 30 ml. of water, no evolution of fumes of nitrogen oxides being observed, as might have been expected if the product were a nitryl salt. Repeated evaporation of the solution to dryness on a steam bath left 2.7 g. of a residue, which was dried *in vacuo* over phosphorus pentoxide. Recrystallization from ethanol–hexane furnished white crystals, m.p. 195–197° (softening from 189°). *p*-Nitrophenylphosphonic acid, obtained by a different route, was reported to have m.p. 197–198°.[20]

Anal. Calcd. for $O_2N\cdot C_6H_4PO(OH)_2$: C, 35.5; H, 3.0; N, 6.9. Found: C, 35.5; H, 3.2; N, 6.9.

The infrared spectrum (KBr) shows the presence of the nitro group, absorbing at 1540 cm.$^{-1}$.

(III) **Reaction of Tetrafluorophosphoranes with Secondary Amines.** The general procedure is illustrated by the following example.

(1) **Reaction of Dimethylamine with Phenyltetrafluorophosphorane.**—A three-necked flask was equipped with a gas inlet tube, a thermometer, and a reflux condenser, protected by a drying tube. The system was flushed with dry nitrogen and charged with a solution of 44 g. (0.24 mole) of phenyltetrafluorophosphorane in 150 ml. of ether. Dimethylamine (11.0 g., 0.24 mole), dried over sodium hydroxide pellets, was passed through the solution at 0° for 2 hr. A precipitate was formed temporarily, but disappeared after removal of the ether solvent by distillation at atmospheric pressure. The remaining two-phase liquid mixture was distilled *in vacuo* through an 8-in. glass-helix packed column. Material boiling at 48–49° (0.4 mm.), n^{25}_{D} 1.4796, was collected first; yield 19.6 g. (79%). The residue solidified on standing and was distilled at a higher temperature, again solidifying readily during the distillation; b.p. 128–129° (0.15 mm.); white solid, m.p. *ca.* 50° (sealed capillary); yield 24.9 g. (83%). The low boiling product was identified as phenyldimethylaminotrifluorophosphorane, while the higher boiling material was the salt, dimethylammonium phenylpentafluorophosphate. Analytical data on this and the following reactions are presented in Table I. Infrared spectrum (cm.$^{-1}$) of $C_6H_5PF_3N(CH_3)_2$ (pure liquid): 3060 (sh); 2950 (m); 2882 (sh); 2817 (w, N–CH_3); 1595 (w); *ca.* 1470 (m, b); 1442 (s); 1290 (s); 1195 (m); 1122 (s); 1060 (m); 1020 (vs); 1000 (w); 860 (vs, b); 779, 764, 748 (vs); 693 (s); 666 (m).

(2) **Diethylamine with Phenyltetrafluorophosphorane.**—Phenyldiethylaminotrifluorophosphorane, b.p. 81° (1.35 mm.), $n^{24.6}_{D}$ 1.4689, was obtained in 78% yield from the reaction of 14.6 g. (0.2 mole) of diethylamine with 36.8 g. (0.2 mole) of phenyltetrafluorophosphorane in 150 ml. of ether at 0°. Diethylammonium phenylpentafluorophosphate precipitated from the ether reaction medium and was collected in essentially quantitative yield by filtration in a drybox. The salt was dried *in vacuo*. For analytical data see Table I. Infrared spectrum (cm.$^{-1}$) of $C_6H_5PF_3N(C_2H_5)_2$ (pure liquid): 3055 (sh); 2978 (vs); 2960 (sh); 1595 (m); 1486, 1469, 1440, 1380, 1348 (s); 1298 (w); 1208, 1176, 1121 (vs); 1090, 1081, 1071 (s); 1048 (vs); 999 (m); 960 (vs); 852 (vs); 776, 755, 739, 692, 659 (vs).

(3) **Piperidine with Phenyltetrafluorophosphorane.**—The aminolysis was conducted as described in the preceding experiments, employing 17.0 g. (0.2 mole) of piperidine, which was added dropwise with stirring at 0° to 36.8 g. (0.2 mole) of phenyltetrafluorophosphorane in 150 ml. of ether. The precipitate formed was filtered off in a drybox, washed with ether, and dried *in vacuo* (25° at 0.1 mm.). The yield was quantitative. The product was insoluble in nonpolar solvents and very soluble in acetonitrile. It was, as the other dialkylammonium alkyl(aryl)pentafluorophosphates, strongly deliquescent and liquefied rapidly upon exposure to the atmosphere. For analytical data see Table I.

Work-up of the ethereal filtrate obtained above by high-vacuum distillation (10-in. helix-packed column) gave 11.5 g. (46%) of phenylpiperidyltrifluorophosphorane, b.p. 69° (0.05 mm.); n^{25}_{D} 1.4928. Infrared spectrum (cm.$^{-1}$) of $C_6H_5PF_3NC_5H_{10}$ (pure liquid; 700–1000 cm.$^{-1}$ region in benzene): 2930 (m); 2860 (w); 1598 (m); 1477 (m); 1440 (s); 1334 (m); 1284 (s); 1206, 1168 (m); 1136 (s); 1070 (m); 1038 (s); 995 (w); 970 (m); 872 (vs); 849 (vs, b); 790 (vs, b); 729 (vs); 694 (s).

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(20) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

TABLE I

ANALYTICAL DATA FOR ALKYL(ARYL)DIALKYLAMINOTRIFLUOROPHOSPHORANES AND DIALKYLAMMONIUM ALKYL(ARYL)PENTAFLUOROPHOSPHATES

	Analyses, %									
	C		H		F		N		P	
Compound	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_2H_5PF_3N(C_2H_5)_2$	38.1	38.0	8.0	8.1	30.1	29.3	7.4	7.6	16.4	17.3
$(C_2H_5)_2NH_2{}^+C_2H_5PF_5{}^-$	31.4	31.2	7.5	7.6	41.4	40.0	6.1	6.3	13.5	13.8
$C_6H_5PF_3N(CH_3)_2$	45.9	45.8	5.3	5.5	27.2	27.8	6.7	7.0	14.8	14.7
$(CH_3)_2NH_2{}^+C_6H_5PF_5{}^-$	38.6	38.4	5.3	5.5	38.1	37.7	5.6	5.6	12.4	12.7
$C_6H_5PF_3N(C_2H_5)_2$	50.6	50.5	6.4	6.0	24.0	23.8	5.9	5.9	13.1	13.5
$(C_2H_5)_2NH_2{}^+C_6H_5PF_5{}^-$	43.4	43.2	6.2	6.3	34.2	33.2	5.1	5.2	11.2	10.9
$C_6H_5PF_3NC_5H_{10}$ ($C_5H_{10}N$ = piperidyl)	53.0	53.1	6.1	6.0	...	...	5.6	5.8	...	...
$C_5H_{10}NH_2{}^+C_6H_5PF_5{}^-$	45.7	45.1	5.9	6.0	32.8	30.6	4.8	4.8	10.7	10.7

(4) **Diethylamine with Ethyltetrafluorophosphorane.**—Upon addition of 14.7 g. (0.2 mole) of diethylamine to 27.2 g. (0.2 mole) of ethyltetrafluorophosphorane in 120 ml. of ether at 0° over a 1-hr. period, a precipitate was formed immediately. After the solvent had been distilled off partially, the liquid was decanted from the solid product and distilled, finally *in vacuo*, through a 5-in. Vigreux column; 7.0 g. (37%) of a colorless liquid, b.p. 66.5° (30 mm.); $n^{25}{}_D$ 1.3869 was obtained.

Recovery of the solid product by distillation was difficult, because it readily solidified during the distillation in the condenser. Vacuum sublimation at *ca.* 120° (0.1 mm.) gave 16.5 g. (72%) of the deliquescent diethylammonium ethylpentafluorophosphate. Analytical data are given in Table I. Infrared spectrum (cm.$^{-1}$) of $C_2H_5PF_3N(C_2H_5)_2$ (pure liquid): 2977 (s); 1486 (m); 1469 (s); 1380, 1350 (s); 1295, 1240 (m); 1208, 1177 (vs); 1090, 1073 (s); 1048 (vs); 957 (s); 859 (vs); 797, *ca.* 755 (vs).

(5) **Reaction of Methylamine with Phenyltetrafluorophosphorane.**—With careful exclusion of moisture, 36.8 g. (0.2 mole) of phenyltetrafluorophosphorane was dissolved in 150 ml. of ether in a 250-ml. three-necked flask, equipped with a thermometer, gas-inlet tube, and reflux condenser, the latter being protected with a drying tube. *Ca.* 15 g. (0.48 mole) of methylamine (dried over sodium hydroxide pellets) was passed through the solution at approximately 0° (ice cooling) within 1 hr. A white precipitate was formed and was filtered off in a drybox and washed with ether. The H^1 n.m.r. spectrum of the product (as a supercooled liquid) exhibited a single resonance signal at -1.25 p.p.m. (due to CH_3 protons) and a broad resonance at *ca.* -3.7 p.p.m. (due to NH_3 protons); area ratio 1:1, indicating CH_3NH_3F.

Distillation of the filtrate, after removal of the ether, afforded 15.0 g. of a colorless liquid; b.p. 66–69° (1.5 mm.), which was once redistilled through a 5-in. Vigreux column; b.p. 42° (0.25 mm.); $n^{26}{}_D$ 1.4732.

Anal. Calcd. for $C_6H_5PF_3NHCH_3$: C, 43.1; H, 4.7; F, 29.2; N, 7.2; P, 15.9. Found: C, 43.5; H, 4.8; F, 28.8; N, 7.2; P, 16.0.

Infrared spectrum (cm.$^{-1}$) (pure liquid): 3450 (m); 3070, 2940 (vw); 1597 (w); 1481 (w); 1439, 1330 (m); 1160 (s); 1136 (w); 904 (vs); 880 (w); 823 (vs); 765, 752 (vs, b); 692 (s).

Results and Discussion

Nitrosyl fluoride was found to react readily when passed through a solution of phenyltetrafluorophosphorane in Freon 113 or Freon 12 refrigerants, a solid 1:1 adduct precipitating immediately. The reaction could be conducted with identical results over the temperature range 0 to −78°. Freon 12 (b.p. −29.8°; f.p. −158°) was preferred over Freon 113 (b.p. 46.6°; f.p. −35°), since the latter tended to turn viscous near its freezing point, while Freon 12 was mobile at −78°. The adduct, $NOF{\cdot}C_6H_5PF_4$ (I), was obtained as a light orange, highly deliquescent solid, which was stable over extended periods when stored at temperatures below 0°. Between 0 and 10°, I was found to undergo a sudden, irreversible decomposition with formation of an undefined, tarry, purple product, whose identity was not established. Neither NOF nor $C_6H_5PF_4$ could be recovered during this decomposition, which may involve attack of NO^+ on the aromatic nucleus. Because of its thermal instability and its deliquescent character, the spectroscopic investigation of I did not provide unambiguous proof of its structure as a nitrosyl salt, NO^+-$C_6H_5PF_5{}^-$. In particular, no reproducible F^{19} n.m.r. spectrum of I, which would readily establish the presence of $C_6H_5PF_5{}^-$ ion, could be obtained. Indirect evidence for the formulation of I as $NO^+C_6H_5PF_5{}^-$, however, was obtained from a study of some of its properties and chemical reactions.

Thus, the nitrosyl fluoride–phenyltetrafluorophosphorane adduct is insoluble in nonpolar solvents, such as the Freon solvents used during its preparation. On the other hand, the salt-like character of I is suggested by its excellent solubility in polar solvents such as liquid hydrogen fluoride, acetonitrile, or nitromethane.

The formation of phenylphosphonic acid upon hydrolysis of I indicates that the phenyl group of phenyltetrafluorophosphorane remains unaffected during the reaction with nitrosyl fluoride.

Boron trifluoride, when passed through a solution of I at low temperature, displaces $C_6H_5PF_4$ as follows.

$$NOF{\cdot}C_6H_5PF_4 + BF_3 \xrightarrow{<0^\circ} NOBF_4 + C_6H_5PF_4$$

Conceivably, BF_3 is a stronger Lewis acid than phenyltetrafluorophosphorane. It is interesting to note that liquid BF_3 does not react at all with nitrosyl hexafluorophosphate, but effects complete conversion to (the thermally more stable) nitrosyl fluoroborate when passed over the fluorophosphate at temperatures above 150°[4].

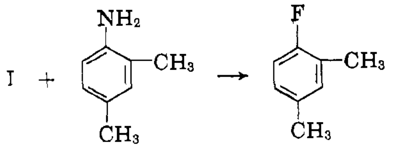
A number of further reactions of I were observed which are quite typical of nitrosyl salts.

The reaction of I with methanol, for instance, depended on the molar ratio I:methanol. If a 1:1 ratio of reactants was employed, methyl nitrite was formed, as expected, in 52% yield, phenylphosphonic difluoride, and, presumably, methyl phenylphosphonofluoridate being the other products of the reaction.

Reaction of I with a sixfold molar excess of methanol at −15° in carbon tetrachloride produced dimethyl phenylphosphonate as the only new product, while formation of methyl nitrite was not observed.

In a separate experiment it was shown that an alkyl nitrite such as isoamyl nitrite would react vigorously with phenyltetrafluorophosphorane with formation of brown fumes and tarry materials, in contrast to the observations made during the reaction of I with methanol.

Next, I was studied as a nitrosating agent for aromatic amines. In a liquid hydrogen fluoride medium at −50 to 0°, for instance, *p*-fluorotoluene was not obtained from *p*-toluidine, which was recovered unchanged. Addition of solid I in small portions to the solution of 2,4-dimethylaniline in dichloromethane at −78° (1:1 molar ratio), however, gave rise to the expected Schiemann-type reaction, 2,4-dimethylfluorobenzene being obtained in 49% yield.



The reaction of nitrosyl salts of fluoro acids with aromatic amines has previously been used relatively rarely as a route to diazonium and/or aromatic fluorine compounds; *cf.*, for instance, ref. 21–23.

Especially revealing as to the nature of I was its reaction with secondary aliphatic amines, which was investigated in most detail. Dimethyl- and diethylamine and piperidine were chosen as secondary amines and were found to react with I in accordance with the following stoichiometry

$$\mathrm{NOF\cdot C_6H_5PF_4(\sim NO^+C_6H_5PF_5^-) + 2R_2NH \rightarrow R_2N\cdot NO + R_2NH_2^+C_6H_5PF_5^-}$$

The reaction proceeded smoothly upon addition of solid I to the solution of the secondary amine in ether at −10 to −20°. From the clear solution which was formed the dialkylammonium phenylpentafluorophosphates separated, while the dialkylnitrosamines were recovered by distillation.

The dialkylammonium phenylpentafluorophosphates were completely identical with those obtained upon direct, controlled aminolysis of tetrafluorophosphoranes

$$\mathrm{2RPF_4 + 2R'_2NH \xrightarrow[\text{ether}]{0^\circ} RPF_3NR'_2 + R'_2NH_2^+RPF_5^-}$$

The above dialkylaminolysis seems to be a general reaction of aliphatic and aromatic tetrafluorophosphoranes, providing easy access both to alkyl(aryl)dialkylaminotrifluorophosphoranes and to the novel dialkylammonium alkyl(aryl)pentafluorophosphates. Some of the aryldialkylaminotrifluorophosphoranes have recently been obtained independently by Russian workers[24] by the following route.

$$\mathrm{ArPCl_2 \xrightarrow{KHF_2} ArPF_3H \xrightarrow{Cl_2} ArPF_3Cl \xrightarrow{R_2NH} ArPF_3NR_2}$$

The present route does not involve corrosive intermediates such as $\mathrm{ArPF_3H}$, which cannot be handled in glass apparatus.

It may be noted that, when a primary amine such as methylamine was allowed to react with phenyltetrafluorophosphorane in ether at 0°, the aminolysis took the following course.

$$\mathrm{C_6H_5PF_4 + 2CH_3NH_2 \rightarrow C_6H_5PF_3NHCH_3 + CH_3NH_3^+F^-}$$

No evidence for the formation of methylammonium phenylpentafluorophosphate was found in this case.

The identity both of the alkyl(aryl)dialkylaminotrifluorophosphoranes and of the alkyl(aryl)pentafluorophosphate species was established especially by the $\mathrm{F^{19}}$ n.m.r. spectra, which are rather indicative. The positive identification of dialkylammonium phenylpentafluorophosphates, resulting from the reaction of I with secondary amines, also provides significant support for the formulation of the $\mathrm{NOF–C_6H_5PF_4}$ adduct as a nitrosyl salt, $\mathrm{NO^+C_6H_5PF_5^-}$.

The dialkylammonium alkyl(aryl)pentafluorophosphates are deliquescent, colorless solids, all of which are volatile under high vacuum. $\mathrm{(CH_3)_2NH_2^+C_6H_5PF_5^-}$, for instance, may even be distilled and is obtained as a rapidly solidifying liquid, which sometimes tends to supercool. The fluorophosphates are rapidly decomposed in aqueous solution, in contrast to the "parent" hexafluorophosphate ion, $\mathrm{PF_6^-}$, which is of high stability even toward aqueous alkali.[3] Unless kept rigorously anhydrous, the fluorophosphates were found to attack glass gradually, and were preferably stored in plastic containers.

Only a few complex fluoroanions containing only organic hydrocarbon groups in addition to fluorine atoms as substituents have been reported. Thus, triphenylfluoroborates were obtained more than 20 years ago upon combination of tetraalkylammonium fluorides with the ammonia adduct of triphenylboron[25]

$$\mathrm{NR_4F + H_3N\cdot B(C_6H_5)_3 \rightarrow NR_4^+B(C_6H_5)_3F^- + NH_3}$$

A trifluoromethyltrifluoroborate was obtained as follows.[26]

$$\mathrm{(CH_3)_3SnCF_3 + BF_3 \rightarrow (CH_3)_3Sn^+CF_3BF_3^-}$$

Most recently, alkyl- and alkenyltrifluoroborates were described for the first time[27]

$$\mathrm{KF\cdot 2H_2O + RBF_2 \rightarrow K^+RBF_3^- + 2H_2O}$$
$$\mathrm{(R = CH_3,\ CH_2{=}CH-)}$$

In connection with the dialkylaminolysis of the tetrafluorophosphoranes, it may be noted that as early as 1929 a similar reaction between another Lewis acid, boron trifluoride, and ammonia was suggested.

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(21) S. A. Voznesenskii and P. P. Kurskii, *Zh. Obshch. Khim.*, **8**, 524 (1938).

(22) U. Wannagat and G. Hohlstein, *Chem. Ber.*, **88**, 1839 (1955).

(23) G. G. Yakobson, A. I. D'yachenko, and F. A. Bel'chikova, *Zh. Obshch. Khim.*, **32**, 849 (1962).

(24) Zh. M. Ivanova and A. V. Kirsanov, *ibid.*, **32**, 2592 (1962).

(25) D. L. Fowler and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 1143 (1940).

(26) R. D. Chambers, H. C. Clark, and C. J. Willis, *ibid.*, **82**, 5298 (1960).

(27) S. L. Stafford, *Can. J. Chem.*, **41**, 807 (1963).

$$2BF_3 + 2NH_3 \rightarrow \underbrace{NH_4BF_4 + F_2BNH_2}_{\text{analyzes as } F_3B\cdot NH_3}$$

However, no definite proof was given.[28]

More recently, evidence has been presented that the reaction between boron trifluoride and diethylamine takes a course identical with that given above, diethylammonium fluoroborate positively being identified as a reaction product.[29]

In the course of the present work we have obtained evidence that the interaction of phosphorus pentafluoride with a secondary amine such as diethylamine proceeds principally identical with that involving tetrafluorophosphoranes, although the reaction is definitely more complex. F^{19} n.m.r. spectroscopy suggests formation of a 1:1 adduct between PF_5 and diethylamine as the first stage of the reaction, which then undergoes further transformation.[30] The formation of hexafluorophosphate, PF_6^-, is observed when the initial reaction product is allowed to warm up to room temperature, while the only other defined product which can be obtained is bis(diethylamino)trifluorophosphorane.[30]

It may be worthwhile, in the light of the above observations, to reinvestigate the reaction of phosphorus pentafluoride with ammonia, which was studied first nearly 90 years ago.[31-33] More recently, when the gas phase reaction of PF_5 with NH_3 was followed by manometric measurements at room temperature, three adducts, $(NH_3)_n\cdot PF_5$ (n = 1, 2, 3), were found, while a further adduct, $4NH_3\cdot PF_5$, was obtained at $-64°$.[34]

The melting points of the various adducts were found to be very close (*ca.* 195–200°), and it was suggested that the solid phase at the higher temperature was the same in all four instances.[34] The adducts were not characterized further by physical means, and it is likely that an F^{19} n.m.r. study, for instance, might readily reveal their actual nature. A reaction such as

$$2PF_5 + 2NH_3 \rightarrow NH_4PF_6 + [H_2N\cdot PF_4]$$

the latter presumably undergoing further condensation, seems entirely possible.

Finally, it was found that the behavior of nitryl fluoride toward phenyltetrafluorophosphorane is different from that of nitrosyl fluoride, in that the former even at $-40°$ smoothly nitrates the aromatic nucleus of the fluorophosphorane. The nitrated compound is obtained as a highly deliquescent, colorless solid, which gradually decomposes on storage at room temperature. Its hydrolysis was found to give mainly *p*-nitrophenylphosphonic acid,[20] which suggests that nitration of the fluorophosphorane also occurred in the position *para* to the PF_4 group. This is somewhat surprising, if the NO_2 group of NO_2F attacks as NO_2^+. The PF_4 substituent might be expected to direct the entering NO_2^+ in *meta*, rather than *para* (or *ortho*) position.

No evidence was found for the formation of a nitryl salt, $NO_2^+C_6H_5PF_5^-$, in the reaction of NO_2F with $C_6H_5PF_4$. This behavior is different from that of phosphorus pentafluoride, which is known to react with nitryl fluoride to give nitryl hexafluorophosphate, $NO_2^+PF_6^-$.[19]

F^{19} and P^{31} N.m.r. Spectra of $RPF_3NR'_2$ and RPF_5^-.—The nuclear magnetic resonance spectral data for the compounds of the type $R'_2NP(R)F_3$ are summarized in Table II. Both P^{31} and F^{19} spectra of $C_6H_5PF_3N(C_2H_5)_2$ are shown in Figure 1 as representative spectra.

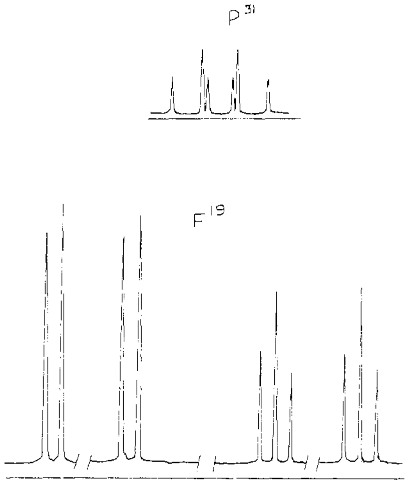
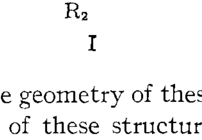


Figure 1.—P^{31} (24.3 Mc.) and F^{19} (56.4 Mc.) n.m.r. spectra of $C_6H_5PF_3N(C_2H_5)_2$.

All the remaining compounds give the same general type of spectra. All the spectra contain two doublets and two triplets in the F^{19} resonance. The phosphorus resonance shows two sets of triplets. This shows that there are two equivalent and one different fluorine atoms in these molecules. Further, the coupling constant between phosphorus and the two equivalent fluorines is much smaller than that between phosphorus and the third fluorine.



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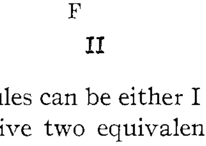

II

The geometry of these molecules can be either I or II. Both of these structures can give two equivalent and one different fluorines as is shown by their n.m.r. spectra. However, the three equatorial bonds are formed from the sp^2 hybridized orbitals of the phosphorus while the two axial bonds are the result of p–d hybridization. Hence, the equatorial bonds have large s-character. It is an accepted fact that the larger the s-character in a bond, the larger the spin–spin coupling constant between the two nuclei forming that bond. This is because the spin–spin interactions between two nuclei are transmitted through the spins of the electrons shared by the two atoms, and the s-

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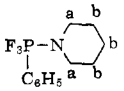
(28) C. A. Kraus and E. H. Brown, *J. Am. Chem. Soc.*, **51**, 2690 (1929).
(29) I. G. Ryss and D. B. Donskaya, *Zh. Neorgan. Khim.*, **5**, 2251 (1960).
(30) R. Schmutzler, to be published.
(31) T. E. Thorpe, *Chem. News*, **32**, 232 (1875).
(32) T. E. Thorpe, *Proc. Roy. Soc.* (London), **25**, 122 (1876).
(33) T. E. Thorpe, *Ann.*, **182**, 201 (1876).
(34) S. Johnson, Ph.D. Dissertation, Purdue University, June 1953.

TABLE II
N.M.R. SPECTRAL DATA FOR SOME $\underset{R}{\underset{|}{R'_2NPF_3}}$ COMPOUNDS[a]

Compound	δ_P, p.p.m. from H_3PO_4	δ_F, p.p.m. from $CFCl_3$	δ_H, p.p.m. from TMS	J_{P-F}, c.p.s.	J_{FF}, c.p.s.
$\underset{C_6H_5}{\underset{\vert}{F_3P}}—N(CH_3)_2$	+53.0	+39.5 (axial) +68.3 (equatorial)	−1.12 (CH_3) −3.10 (CH_2)	819 (axial) 959 (equatorial)	56
$\underset{C_6H_5}{\underset{\vert}{F_3P}}—N(C_2H_5)_2$	+52.0	+43.4 (axial) +66.5 (equatorial)	−1.10 (CH_3) −3.05 (CH_2)	819 (axial) 962 (equatorial)	53
$\underset{C_2H_5}{\underset{\vert}{F_3P}}—N(C_2H_5)_2$	+35.5	+41.5 (axial) +70.0 (equatorial)	. . . . . .	830 (axial) 984 (equatorial)	55
	. . .	+43.6 (axial) +68.0 (equatorial)	−1.47 (b) −2.93 (a)	820 (axial) 964 (equatorial)	58
$\underset{C_6H_5}{\underset{\vert}{F_3P}}—NHCH_3$	. . .	+39.7 (axial) +71.8 (equatorial)	. . . . . .	770 (axial) 953 (equatorial)	52
$F_3P[N(C_2H_5)_2]_2$	+64.5	+59.5 (axial) +67.5 (equatorial)	−1.13 (CH_3) −3.10 (CH_2)	750 (axial) 875 (equatorial)	44
$[(C_2H_5)_2NH_2]^+[C_6H_5PF_5]^-$	+136.0	56.0 (equatorial) 60.0 (axial)	. . .	820 (equatorial) 700 (axial)	~40
$[C_5H_{10}NH_2]^+[C_6H_5PF_5]^-$	+135.0	56.0 (equatorial) 59.0 (axial)	. . .	820 (equatorial) 700 (axial)	~40

[a] The estimated uncertainties are 1 p.p.m. for δ_P, 0.5 p.p.m. for δ_F, 0.05 p.p.m. for δ_H, 3 c.p.s. for J_{PF}, and 1 c.p.s. for J_{FF}.

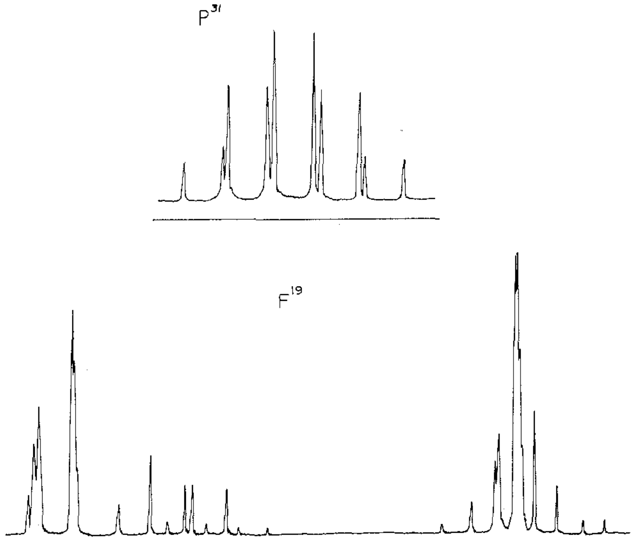
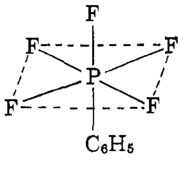


Figure 2.—P^{31} (24.3 Mc.) and F^{19} (56.4 Mc.) n.m.r. spectra of $C_5H_{10}NH_2{}^+C_6H_5PF_5{}^-$.

electrons are more effective because of their large Fermi contact term. The data in Table II clearly show that $J_{P-F(equatorial)}$ is much larger than $J_{P-F(axial)}$. This suggests the structure of these molecules to be as in II. Also, the four C_2H_5 groups in $[(C_2H_5)_2N]_2PF_3$ are all equivalent as shown by their proton resonance spectra while the fluorine atoms still fall into two groups, clearly indicating that both the $N(C_2H_5)_2$ groups are in the equatorial positions. These observations are in complete agreement with those of Muetterties, *et al.*,[35] in the series R_2PF_3 with R a hydrocarbon group. In general, it can be noticed from Table II that in the series $R'_2NP(R)F_3$, J_{P-F} decreases with increasing electronegativity of the atoms attached to the phosphorus atom, and this is in contrast to the observations in trivalent phosphorus compounds.[36] It can also be noticed that replacement of an alkyl group with a second NR'_2 group increases $\delta_{F(axial)}$ considerably while $\delta_{F(equatorial)}$ remains practically unchanged. This may reflect the greater electronegativity of nitrogen and also its capability to form double bonds, which distorts the d orbitals of phosphorus and hence changes the nature of the axial bonds much more than that of the equatorial bonds.

The P^{31} and F^{19} spectra of $[C_5H_{10}NH_2]^+[C_6H_5PF_5]^-$ shown in Figure 2 are identical with those of $[(C_2H_5)_2NH_2]^+[C_6H_5PF_5]^-$. It can be seen that the P^{31} spectrum consists of two quintets while the F^{19} spectrum is typical of an AB_4X system with only the AB_4 part showing (here X is P^{31}). This clearly indicates that in the $[C_6H_5PF_5]^-$ anion there are four equivalent and one different fluorine atoms, and the structure of the ion can unequivocally be written in octahedral form as



This is in complete agreement with the observations of Muetterties, *et al.*,[2,37] on PF_5–base adducts and also with the findings of Ragsdale and Stewart on $[TiF_5(ROH^-)]$.[38]

It is noticed that both $J_{P-F(equatorial)}$ and $J_{P-F(axial)}$ in $[C_6H_5PF_5]^-$ are considerably smaller than in the other compounds included in Table II. However, $J_{P-F(equatorial)}$ is larger than $J_{P-F(axial)}$ by the same amount of about 120 c.p.s. as in the other compounds.

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[35] E. L. Muetterties W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[36] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, in press.

[37] Evidence for the presence of $[RPF_5]^-$ has also been obtained by K. J. Packer and E. L. Muetterties [*J. Am. Chem. Soc.*, **85**, 3035 (1963)] in an F^{19} n.m.r. spectroscopic study of the system RPF_4–$(CH_3)_2SO$.

[38] R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).