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Synthesis and Characterization of Methylaminotetrafluorophosphorane

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We have reported that alkylaminotetrafluorophosphoranes, $RNHPF_4$ (R = C_2H_5, *tert*-C_4H_9)[1] and R_2NPF_4 (R = CH_3, C_2H_5, *n*-C_3H_7),[2] are conveniently prepared by the thermal decomposition of the 1:1 amine–phosphorus pentafluoride adducts. However, the reaction between methylamine and phosphorus pentafluoride gave only a 2:1 adduct; this decomposed on heating to give methylaminotetrafluorophosphorane and methylamine which underwent further reaction before they could be separated.[1] Methylaminotetrafluorophosphorane can, however, be prepared by the reaction between methylaminotrimethylsilane and phosphorus pentafluoride, a preparation analogous to that of $(CH_3)_2NPF_4$ from $(CH_3)_3SiN(CH_3)_2$ and PF_5.[3]

Experimental Section

Apparatus.—Reactions were carried out in a Pyrex vacuum system with standard vacuum techniques.

Reagents.—Commercial phosphorus pentafluoride (Matheson Co.) was purified by low-temperature distillation. Methylaminotrimethylsilane was prepared by the method of Sauer and Hasek;[4] it was contaminated with traces of $((CH_3)Si)_2NCH_3$ and $((CH_3)_3Si)_2O$.

Technique.—$(CH_3)_3SiNHCH_3$ (1.35 g, 13.1 mmol) was condensed with excess of PF_5 into an ampoule and the mixture was then allowed to warm slowly up to room temperature. A reaction was indicated by the formation of white solids. The ampoule was then placed in a −100° bath and the excess of PF_5 was pumped off; reweighing the ampoule indicated that 1.33 g (10.6 mmol) of PF_5 had been absorbed. The remaining volatile components were fractionated through a −100° bath and identified by ir spectroscopy as $(CH_3)_3SiF$ (1.14 g, 12.4 mmol)[5] and a mixture of CH_3NHPF_4, $((CH_3)_3Si)_2O$,[6] and $(F_3PNCH_3)_2$[3] (0.10 g). The solid remaining (1.38 g) was heated up to 140° to give CH_3NHPF_4 (1.04 g, 60% yield) contaminated with traces of $(CH_3)_3SiF$, $((CH_3)_3Si)_2O$, and $(F_3PNCH_3)_2$; final purification was achieved by fractional distillation. The solid residue was identified by its ir and nmr spectra (in acetonitrile solution) as $CH_3NH_3^+PF_6^-$.[1]

The molecular weight of CH_3NHPF_4 was determined by vapor density measurements to be 141; the theoretical value is 137. Its vapor pressure is 133 mm at 20°.

Anal. Calcd for CH_4F_4NP: C, 8.8; H, 2.9; F, 55.6; N, 10.2; P, 22.6. Found (Bernhardt): C, 9.0; H, 3.1; F, 55.8; N, 10.4; P, 22.0.

Spectroscopy. A. Nmr Spectra.—The ^{19}F and ^1H spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 56.4 and 60 MHz, respectively, using either trichlorofluoromethane or tetramethylsilane as the external standard. The parameters obtained are listed in Table I.

B. Infrared Spectrum.—The spectrum was obtained on a Perkin-Elmer 225 spectrophotometer.

C. Mass Spectrum.—The spectrum was obtained with an AEI MS 12 mass spectrometer operating at 70 eV. Peaks were recorded at the following mass numbers (with relative abundance and probable ion, respectively): 137, 27, $CH_4NPF_4^+$; 136, 8, $CH_3NPF_4^+$; 118, 37, $CH_4NPF_3^+$; 117, 2, $CH_3NPF_3^+$; 116, 6, $CH_2NPF_3^+$; 107, 100, PF_4^+; 104, 2, POF_3^+ and $H_2NPF_3^+$; 103, 2, $HNPF_3^+$; 98, trace, $CH_3NPF_2^+$; 89, 1, HPF_3^+; 88, 9, PF_3^+; 85, 2, POF_2^+ and $H_2NPF_2^+$; 84, 2, $HNPF_2^+$; 69, 10, PF_2^+; 58.5, 2, CH_3NPF^+; 51, trace, HPF^+; 50, 2, PF^+; 30, 2, CH_4N^+; 29, 9, CH_3N^+; 28, 19, CH_2N^+; 27, 1, CHN^+; 19, trace, F^+; 15, 2, CH_3^+ and HN^+.

Table I

Nmr Spectrum of CH_3NHPF_4 at −80°

Chemical Shifts, Ppm

δ_{F_a}	$\delta_{F_{a'}}$	δ_{F_e}	δ_{CH_3}	δ_{NH}
60	70	83	−2.7	−3.3 br

Coupling Constants, Cps

$J(PF_a)$	$J(PF_a')$	$J(PF_e)$	$J(F_aF_e)$	$J(F_a'F_e)$	$J(F_aF_a')$
755	770	920	~68	~69	2.8

$J(F_a'CH_3)$	$J(F_eCH_3)$	$J(F_a'NH)$	$J(PNH)$	$J(PCH_3)$
2.1,[a] 2.8[b]	2.1[a,b]	~21,[a] 27.6[b]	~21	15.2

[a] Obtained from the ^1H nmr spectrum. [b] Obtained from the ^{19}F nmr spectrum.

Results and Discussion

Methylaminotetrafluorophosphorane can be prepared by the reaction

$$(CH_3)_3SiNHCH_3 + PF_5 \longrightarrow (CH_3)_3SiF + CH_3NHPF_4 \quad (1)$$

The $(F_3PNCH_3)_2$ which features as a by-product in this reaction is probably obtained from two sources: (i) from the reaction of the $((CH_3)_3Si)_2NCH_3$ impurity with PF_5[3] and (ii) from the CH_3NHPF_4, through either its reaction with PF_5 (which could be confirmed by a separate reaction) or its disproportionation (with the concurrent formation of $CH_3NH_3^+PF_6^-$). CH_3NHPF_4 is thermally stable for short periods, but $(F_3PNCH_3)_2$ is identified in samples that have been kept over an extended period.

A variable-temperature ^{19}F nmr study shows that at 70° there is only one fluorine atom environment for the axial and equatorial fluorine atoms in CH_3NHPF_4 (δ_F 74 ppm; $J(PF)$ = 847 cps). At 30° no resonance is observed but three fluorine atom environments are present at −80° (see Figure 1). These results are consistent with this compound adopting a trigonal-bipyramidal structure with nonequivalent axial fluorine atoms

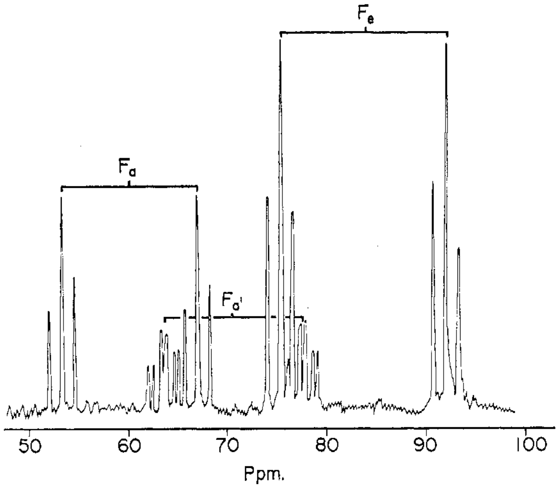
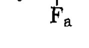


Figure 1.—The ^{19}F nmr spectrum of CH_3NHPF_4.



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Nonequivalent axial fluorine atoms have previously been observed in the nmr spectra of some di- and trifluorophosphoranes containing alkylamino substituents[7] and were briefly mentioned to be present in the room-temperature nmr spectrum of 2,6-$(C_2H_5)_2C_6H_3$-$NHPF_4$.[8] There is no evidence for nonequivalent equatorial fluorine atoms, which might be expected if the CNH–P skeleton were rigid and nonplanar; a recent crystal structure shows that the C_2N–P skeleton in $(CH_3)NPF_2$ is planar.[9]

The changes in the appearance of the spectrum on lowering the temperature arise from a combination of two effects similar to those postulated to occur in $RSPF_4$ derivatives:[10] (i) a slowing down of the pseudorotational exchange process, which tends to make all the fluorine atoms magnetically equivalent, and (ii) the onset of hindered rotation around the P–N bond. While the factors which slow pseudorotation of fluorophosphoranes are difficult to rationalize,[11] the equivalence of all the fluorine atoms in $(CH_3)_2NPF_4$ well below room temperature[12] suggests that intramolecular hydrogen bonding between the amino proton and one of the axial fluorine atoms takes place in CH_3NHPF_4. It has been shown that the pseudorotation rate depends on the ease with which the axial fluorine atoms can be deformed from their equilibrium positions.[13] Hydrogen bonding would hinder both this process and the ease with which rotation around the P–N bond takes place. The fluorine atoms in $C_2H_5NHPF_4$ and *tert*-C_4H_9-$NHPF_4$, which both contain more bulky groups than CH_3NHPF_4, are equivalent at room temperature;[1] the different energy barrier for these compounds is tentatively ascribed to the dependence of the degree of hydrogen bonding on the electron-withdrawing effects of the alkyl groups. Since one set of triplets due to an axial fluorine atom is further split into a doublet by coupling with the amino proton (confirmed from the ^1H nmr spectrum), it seems reasonable to assign this resonance to the fluorine atom which is the closest to the amino proton.

The further fine structure observed for each fluorine resonance (Figure 2) indicates coupling to other nuclei and the presence of second-order effects (which accounts for the approximate values given for some of the parameters in Table I), similar to those observed in the room-temperature nmr spectrum of $(NH_2)_2PF_3$.[14]

The assignments given for the peaks in the ir spectrum of CH_3NHPF_4 (Table II) have been made on the basis of the complete analysis for CH_3PF_4[15] and the partial analyses for $(CH_3)_2NPF_4$[2,3] and CH_3SPF_4.[16] Three strong absorption bands are expected in the PF stretching region. There is no peak in the region of the spectrum where the PN stretching mode was observed for $(CH_3)_2NPF_4$ but the slight asymmetry of the two bands centered at 958 cm^{-1} suggests that this might arise from the juxtaposition of two peaks of almost equal intensity, one of which is due to ν_{PN}.

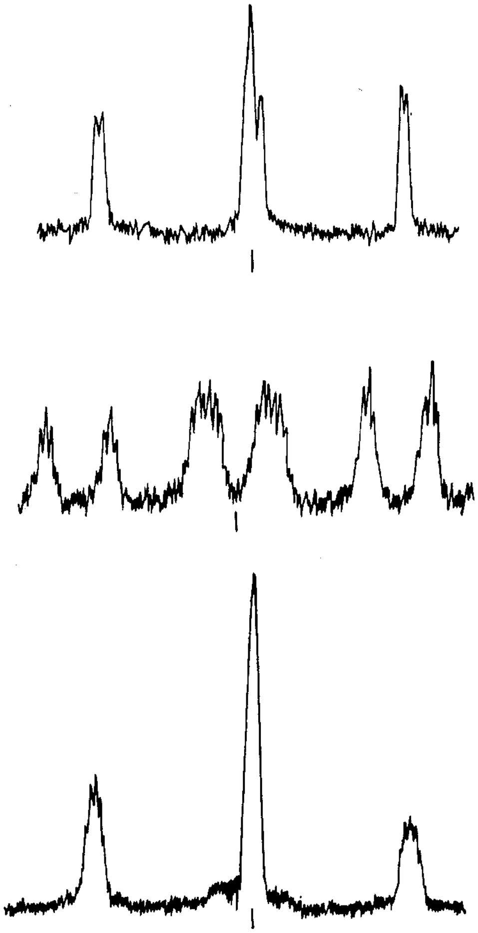

Figure 2.—Expansion of resonances at 53, 63, and 91 ppm.

TABLE II

IR SPECTRUM OF CH_3NHPF_4

3495 m		ν_{NH}
3003 w		ν_{CH}
2964 w		
2921 vw		
2855 vw		
1478 w		$\delta_{as\ CH_3}$
1440 m		δ_{NH}
1171 s		ν_{CN}
962 vs		$\nu_{as\ PF_2(e)}$
954 vs		ν_{PN}
867 vs	PQR	$\nu_{as\ PF_2(a)}$ and $\nu_{sym\ PF_2(e)}$
567 m	PQR	$\nu_{sym\ PF_2(a)}$
533 m	PQR	$\delta_{out\text{-}of\text{-}plane\ NPF_2(e)}$
504 m	PQR	$\delta_{in\text{-}plane\ PF_2(e)}$
473 w	PQR	ρ_{PF_4}

The mass spectrum of CH_3NHPF_4 is straightforward and shows little evidence for extensive rearrangement processes. A weak peak due to HPF_3^+ is probably formed by a process similar to that outlined for dimethylaminophosphines.[17] The most abundant ion is formed by the cleavage of the P–N bond in the molecular ion. Metastable ions indicate that the molecular ion can lose a hydrogen atom, presumably through the cleavage of a C–H bond as has been observed for amines,[18] and that the ion formed by the loss of a fluo-

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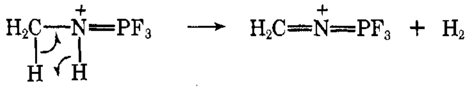
rine atom from the molecular ion can eliminate a molecule of hydrogen



$$H_2C—\overset{+}{N}=PF_3 \longrightarrow H_2C=\overset{+}{N}=PF_3 + H_2 \qquad (2)$$

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Nitrile Complexes of Zerovalent Nickel

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Although nitrile complexes of a variety of metals in higher oxidation states have been well known for a long time,[1] nitrile complexes of metals in the zerovalent state are much more rare, the best known examples being $(CH_3CN)_nM(CO)_{6-n}$ where $n = 1, 2,$ or 3 and M = Cr, Mo, or W.[2] We wish to report the first examples of nitrile complexes of zerovalent nickel, of stoichiometry $(RCN)NiL_3$ where L is $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ and R is CH_3, CH_2CH_3, $n\text{-}C_4H_9$, or C_6H_5.

The preparation and properties of the three-coordinate nickel complex $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ (abbreviated NiL_3) have been previously reported.[3] Addition of an alkyl nitrile to a red-orange toluene solution of NiL_3 causes an immediate loss of color, attributed to the rapid reaction

$$RCN + NiL_3 \overset{K_1}{\rightleftharpoons} (RCN)NiL_3 \qquad \text{fast} \qquad (1)$$

The stoichiometry of the adduct is shown by a ^{31}P nmr experiment in which valeronitrile was added to 0.06 mmol of NiL_3 in 0.3 ml of toluene. Addition of 0.03 mmol of RCN (RCN:Ni ratio 0.5:1) caused the sharp resonance of NiL_3 at −128.5 ppm (85% H_3PO_4)[4] to shift to −129.2 ppm. More RCN (RCN:Ni = 1:1) again gave a single sharp line, further shifted downfield to −130.7 ppm. Excess RCN (RCN:Ni = 2:1) had no further effect on the ^{31}P spectrum. Addition of free L to the same solution gave a second resonance at −130.0 ppm, the chemical shift of free ligand alone.[4] These observations show that (1) reaction 1 must be fast enough to average resonances of L in NiL_3 and in $(RCN)NiL_3$, (2) the reaction has an appreciable equilibrium constant, (3) species with more than one RCN are not involved, and (4) free ligand is not in rapid exchange with complexed.[5,6] With the addition of a large excess of L a new resonance at −129.3 ppm, assigned to NiL_4,[4] grew at the expense of the resonance due to $(RCN)NiL_3$, showing displacement of RCN according to reaction 2. Similar results were obtained with benzonitrile, except that C_6H_5CN was less easily displaced.

$$(RCN)NiL_3 + L \rightleftharpoons NiL_4 + RCN \qquad (2)$$

Spectrophotometric experiments in which aceto-, propio-, or valeronitrile was added to a benzene solution of NiL_3 showed the disappearance of absorbance above 400 mμ and an isosbestic point at 356 mμ, as shown in Figure 1. Values of K_1 determined in a thermostated cell given as a function of temperature are: 10°, 510 ± 40; 25°, 230 ± 20; 40°, 120 ± 25. A plot of log K_1 against $1/T$ gives $\Delta H° = -9 \pm 1.5$ kcal/mol and $\Delta S° = -19 \pm 5$ eu.

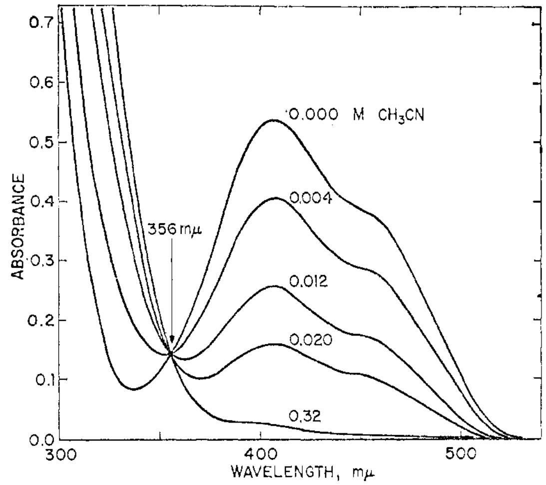

Figure 1.—Selected spectra for the addition of CH_3CN to 1.14×10^{-2} *M* $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ in benzene at ambient temperature; 0.1-mm cell.

The spectra with added benzonitrile were different, with an isosbestic point at 425 mμ; the final yellow-orange solution with excess C_6H_5CN showed an absorbance maximum at 396 mμ (ϵ 5.8 × 10^3 cm^{-1} M^{-1}). For benzonitrile $K_1 \approx 1000 \pm 400$ M^{-1}, in benzene at ambient temperature. The longer wavelength electronic band and the larger formation constant of benzonitrile compared to those of the alkyl nitriles are presumed to be consequences of electron delocalization which includes the benzene ring of the aromatic nitrile.

Infrared spectra of toluene solutions containing NiL_3 and excess CH_3CN showed a band at 2266 cm^{-1} due to ν_{CN} in $(CH_3CN)NiL_3$ in addition to a band of free CH_3CN at 2256 cm^{-1} ($\Delta\nu_{CN} = +10$ cm^{-1}). A similar solution with benzonitrile showed bands of $(C_6H_5CN)NiL_3$ and C_6H_5CN at 2217 and 2229 cm^{-1}, respectively ($\Delta\nu_{CN} = -12$ cm^{-1}). This is one of the few reported cases of a shift of ν_{CN} to lower frequency on complexation of benzonitrile.[7]

Analytically pure samples of $(RCN)NiL_3$ have not yet been prepared, owing to the ease with which they

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(5) This behavior can be contrasted with that when C_2H_4 is added to a solution of NiL_3. In that case the reaction is $C_2H_4 + NiL_3 \rightleftharpoons (C_2H_4)NiL_2 + L$ and rapid exchange of free ligand with complexed occurs.[6]

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