substituent bonds. In this view, the carbonyls function as "π ballasts" in their influence on the metal–substituent bonding properties.

Since the rate law for reaction of (phen)[$P(OC_2H_5)_3$]$Mo(CO)_3$ with triethyl phosphite was known, reactions of this substrate with other Lewis bases were studied. Reaction of (phen)[$P(OC_2H_5)_3$]$Mo(CO)_3$ with *n*-octylamine at 136° or with cyclohexylamine in refluxing mesitylene for long periods of time ($\gtrsim$20 hr) gave no evidence for the formation of tetrasubstituted products—the infrared spectra of reaction solutions indicated the reactant to be present at the end of the reaction periods. Thus it would appear that neither the substrate nor the presumed intermediate in which one carbonyl is dissociated is susceptible to attack by non-π-bonding Lewis bases. These observations provide further evidence for the dominance of π-bonding effects in highly substituted metal carbonyl complexes. Indeed it would seem almost axiomatic to expect π bonding to increase in importance relative to σ bonding as the degree of substitution—and thus the negative charge at the metal—increases.

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cis-Trifluorodiamidophosphorus(V)

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The new and interesting compound *cis*-trifluorodiamidophosphorus(V), $PF_3(NH_2)_2$, is prepared by the gas-phase reaction between phosphorus pentafluoride and ammonia. The interaction between these two reactants has been reported as early as 1876[1] and more recently in 1953.[2] These earlier workers reported a variety of solid products of the general composition $xPF_5 \cdot yNH_3$ where $5 \geq x, y \geq 1$. The results included in this work are substantially different than those reported earlier. These workers have observed the reaction (unbalanced)

$$PF_5 + NH_3 \longrightarrow PF_3(NH_2)_2 + NH_4PF_6 + \text{solids}$$

under the conditions detailed in the experimental part.

Experimental Section

Apparatus.—A standard Pyrex-glass vacuum apparatus was used for the manipulation of volatile reagents.

Reagents.—The PF_5 and NH_3 were obtained from the Matheson Co.

Synthesis of $PF_3(NH_2)_2$.—This reaction was performed by placing the PF_5 in a 1.1-l. Pyrex reactor equipped with a stopcock and admitting the NH_3 very slowly at a pressure greater than the contents of the reactor. The best yields were obtained using between a 2:1 and 3:1 NH_3 to PF_5 ratio. In a typical reaction, the reactor was charged with 17.9 mmol of PF_5 and the NH_3, 40.0 mmol, was slowly admitted. The reaction was rapid. After all the NH_3 was admitted, the mixture was allowed to stand for 15 min and then condensed at −196°. The products were then allowed to warm slowly while pumping through a trap held at −45°. The $PF_3(NH_2)_2$ (0.884 g, 7.36 mmol, 41.1% yield) was collected in this trap. The yield is based on the quantity of PF_5 employed. Ammonium hexafluorophosphate was a product, identified by its infrared spectrum.

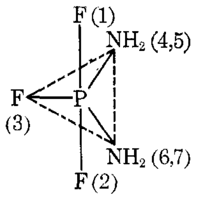
Analyses.—An F & M Model 185 analyzer was used to determine hydrogen and nitrogen. For phosphorus, the compound was burned in an oxygen flask. The residue was absorbed in 6 *N* HNO_3 and the phosphate was determined spectrophotometrically as phosphovanadomolybdate.[3] The fluorine was analyzed by reduction of the compound with lithium in *n*-propylamine. The fluoride was distilled as H_2SiF_6 and titrated with thorium nitrate. *Anal.* Calcd for $F_3H_4N_2P$: F, 47.5; H, 3.33; P, 25.8. Found: F, 47.1; H, 3.08; P, 25.5. The molecular weight by vapor density measurement was 127 (calcd 120), and the compound melted at 40–41°. The vapor pressure at 40.8° was found to be 22.8 mm and at 59.7° to be 44.6 mm at which point slow decomposition to NH_3 was observed.

Spectroscopy. A. Nmr Spectra.—The ^{19}F, ^{31}P, and ^1H nmr spectra were taken with a Varian Model V4310 spectrometer operating at 40 Mc for the fluorine and proton spectra and at 12.8 Mc for the phosphorus. Samples were measured at ambient temperature in 5-mm o.d. Pyrex tubes using trichlorofluoromethane and tetramethylsilane as internal standards for the fluorine and proton spectra, respectively, and phosphoric acid as an external standard for the phosphorus spectrum. Acetonitrile solutions containing 25% solute by volume were used for the measurements. The parameters are listed in Table I using the model accordant with the data. Refer to Figures 1 and 2. A calculated spectrum using the experimental coupling constant parameters for the seven nuclei designated in I was obtained using the LACOON-III program by Botherby with an IBM 360-40 computer (Figure 2).

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

Nucleus	Chem shift, δ, ppm	Coupling constants, cps					
		J_{P-F_a}	J_{P-F_e}	$J_{F_a-F_e}$	J_{H-F_a}	J_{H-F_e}	J_{P-H}
^{19}F	51.3 (1,2) 77.3 (3)	672	860	40	20	1.7	...
^{31}P	58.6	652	848	...	...	...	...
^1H	3.14	...	...	...	*Ca.* 20	...	*Ca.* 20



I

B. Infrared Spectrum.—The infrared spectrum was obtained with a Perkin-Elmer Model 621 grating infrared spectrometer using a 10-cm path length gas cell with cesium bromide windows

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[1] (a) T. E. Thorpe, *Chem. News*, **32**, 232 (1876); (b) T. E. Thorpe, *Proc. Roy. Soc.* (London), **25**, 122 (1876); (c) T. E. Thorpe, *Ann. Chem.*, **182**, 201 (1876).

[2] S. Johnson, Ph.D. Thesis, Purdue University, June 1953.

[3] I. M. Kolthoff, P. J. Elving, and E. B. Sandell, "Treatise on Analytical Chemistry," Part II, Vol. 5, Interscience Publishers, Inc., New York, N. Y., 1961, p 370.

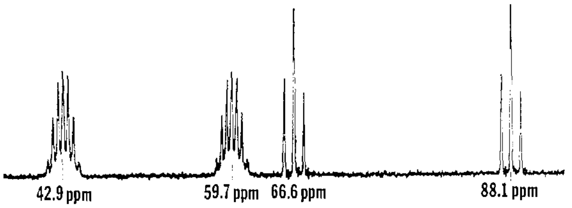

Figure 1.—The ^{19}F nmr spectrum of $PF_3(NH_2)_2$.

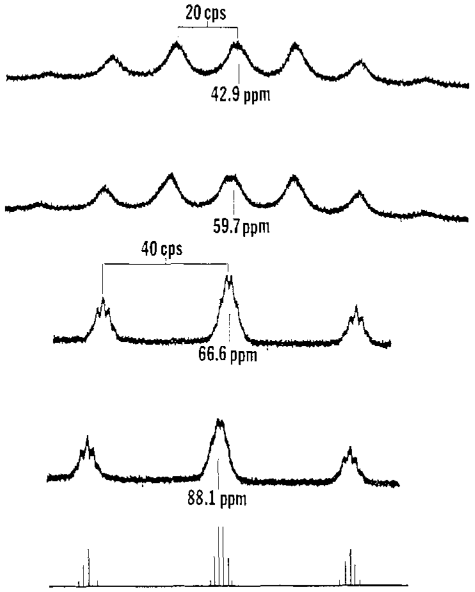

Figure 2.—Expanded recording of the complex resonances at 42.9, 59.7, 66.6, and 88.1 ppm under the same sweep conditions. The calculated line pattern of the resonance at 88.1 ppm is included.

at 8 mm pressure. Bands are at 3580 (w) and 3475 (w) (N–H stretch); at 1571 (m, complex) (N–H bend); at 1093 (wm, triplet), 1039 (s, complex), 972 (vs, triplet), 920–870 (w, complex), 860–760 (ms, complex), 712 (w, multiplet) (P–F stretch); and at 548 (m, triplet), 520–480 (w, multiple bands), 392 (wm, complex), 348 cm^{-1} (m, complex) (unassigned).

C. Mass Spectrum.—The spectrum was obtained with a Consolidated Engineering Corp. 61-620 spectrometer having a heated-inlet system and operating at 100 eV. The results are included in Table II.

TABLE II

MASS SPECTRUM

m/e	Assigned species	Rel abund	m/e	Assigned species	Rel abund
14	N^+	1.2	69	PF_2^+	14.4
15	NH^+	2.0	84	PF_2NH^+	29.2
16	NH_2^+	7.9	85	$PF_2NH_2^+$	3.0
20	HF^+	3.7	88	PF_3^+	2.4
31	P^+	9.2	103	PF_3NH^+	3.7
46	PF^+	7.2	104	$PF_3NH_2^+$	100.0
50	PF^+	3.2			

Discussion

The compound $PF_3(NH_2)_2$ is the first amido derivative of PF_5 to be reported, although the alkylamido compounds have been described.[4] This compound is unstable above 59.7° but can be handled at ambient conditions without noticeable decomposition. It has vapor pressure lower than that expected based on its molecular weight. This may be due to intermolecular association by hydrogen bonding, but vapor density measurements indicate the gas phase is monomeric.

The nmr spectrum of this compound is complex. Eight nuclei in this compound interact with each other. The ^{19}F spectrum (Figure 1) shows two sets of multiplets. The lower field set is a pair of septets centered at 51.3 ppm while the high field set is a pair of triplets at 77.3 ppm with each multiplet showing additional fine structure. The integrated area ratio of the lower field to higher field resonances is 1.997:1. These data are consistent with a trigonal-bipyramidal structure with two fluorine atoms occupying apical sites. However, a tetragonal pyramid is not ruled out. The coupling constants in Table I show that the coupling between the phosphorus and apical fluorine nuclei (J_{P-F_a} = 672 cps) is smaller than that between phosphorus and the equatorial fluorine (J_{P-F_e} = 860). These numbers as well as $J_{F_a-F_e}$ are of the same order and magnitude as those reported for bis(dialkylamino)- and dialkyltrifluorophosphoranes.[5,6]

The low-field pair of septets originate from two lines caused by phosphorus to fluorine coupling (J_{P-F_a} = 672 cps). Each shows further splitting due to the overlapping of a doublet ($J_{F_a-F_e}$ = 40 cps) of quintets (J_{F_a-H} = 20 cps). A doublet of doublets can be obtained by proton decoupling and a doublet of quintets by homodecoupling. The high-field set of triplets arise from phosphorus–fluorine coupling (J_{P-F_e} = 860 cps) and from coupling with the two apical fluorines. The triplets show 40-cps spacing and also show fine structure due to coupling between the equatorial fluorine and the hydrogen nuclei J = 1.7 cps (Figure 2). Saturation at the proton frequency does simplify the fluorine spectrum. The pair of septets is reduced to doublets (J = 40 cps) while the complex triplets are also simplified but in this case the low-intensity members appear as singlets and the central high-intensity member as a closely spaced doublet. Although the observed fine structure cannot be predicted on the basis of first-order splitting, a partial computer calculated spectrum employing the first-order measured coupling constants does reproduce the observed spectral patterns (Figure 2).

The ^{31}P spectrum is a pair of triplets and the measured coupling constants from this spectrum approximate those obtained from the fluorine spectrum. The proton spectrum appears as a broad resonance due to the ^{14}N quadrupole interaction. However, upon decoupling the ^{14}N, a crude 1:2:3:1 quartet is observed with the absorptions split by *ca.* 20 cps. This can be explained if it is assumed that the P–H coupling constant also is *ca.* 20 cps and the quartet is due to an overlap of a doublet (J = 20 cps) of triplets (J = 20 cps).

The mass spectrum (Table II) shows the expected

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[4] R. Schmutzler, *Angew. Chem., Intern. Ed. Engl.*, **3**, 753 (1964).

[5] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[6] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

fragments; however, the molecule ion was not observed. The ion corresponding to $m/e = 84$ exhibiting a high relative intensity may be a protonated phosphonitrilic fluoride monomer, $PF_2{=}NH^+$. It is further observed from this table that ions containing the NH_2 group are more stable than those with one hydrogen less. The exception is that presumed to be the phosphonitrilic derivative which shows a considerably higher relative abundance than $PF_2NH_2^+$.

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The Kinetics and Mechanism of the Oxidation of Iron(II) by Thiocyanatopentaamminecobalt(III) Ions. Comparisons with Related Systems[1]

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Comparisons of the effect of azide and thiocyanate on the rates of electron-transfer reactions involving metal ions and their complexes have been widely used as a basis for determining whether a particular reaction proceeds by an inner- or an outer-sphere mechanism.[2–4] If the metal centers of the oxidizing and reducing agents are hard and if transfer of the bridging group occurs during the reaction, then an inner-sphere reaction should proceed faster when the bridging group is azide then when it is isothiocyanate. This is principally due to the increased stability of a metal–nitrogen bond over a metal–sulfur bond.[4] Similar free energy considerations show that an inner-sphere reaction should proceed faster when the bridging group is thiocyanate than when it is either azide or isothiocyanate. This study is concerned with the kinetics and mechanism of the reaction of $(NH_3)_5CoSCN^{2+}$ with Fe^{2+} at 25.0° and 1.0 M ionic strength and comparisons of this reaction with other systems. Because of the favorable free energy change, it was expected that the rate of oxidation of iron(II) by $(NH_3)_5CoSCN^{2+}$ would be relatively rapid. This could allow identification of the primary iron(III) reaction product and thus establish the mechanism of the reaction. Because the rates of dissociation of FeX^{2+} complexes are rapid, an inner-sphere mechanism for reductions by iron(II) has only been unambiguously established in very few instances.[5]

Perchloric acid solutions containing $(NH_3)_5CoSCN^{2+}$ were prepared according to the procedure of Buckingham, Creaser, and Sargeson.[6] The concentrations of the cobalt(III) complex were determined spectrophotometrically using the known extinction coefficients.[6] The kinetics of the reduction of the $(NH_3)_5CoSCN^{2+}$ by iron(II) were studied under pseudo-first-order conditions with the iron(II) present in large excess. It was found that the reaction proceeds in two stages

$$(NH_3)_5CoSCN^{2+} + Fe^{2+} \xrightarrow[5H^+]{k_1} FeNCS^{2+} + Co^{2+} + 5NH_4^+ \quad (1)$$

$$FeNCS^{2+} \xrightarrow{k_2} Fe^{3+} + SCN^- \quad (2)$$

The first stage corresponds to the reduction of the cobalt(III) complex and was studied at relatively low iron(II) concentrations on a Cary 16K spectrophotometer. Two types of measurements were performed. In the first type the disappearance of $(NH_3)_5CoSCN^{2+}$ was followed at 288 nm, an absorbance maximum of the cobalt(III) complex (ϵ 1.56 × 10^4 at 288 nm).[6] Excess iron(III) was added in the second type of measurement and the formation of $FeNCS^{2+}$ was followed at 460 nm, an absorbance maximum of the iron(III) complex (ϵ 4.60 × 10^3 at 460 nm).[7] The solution concentrations and observed rate constants are summarized in Table I. The value of k_1 obtained from these measurements is 0.12 ± 0.01 M^{-1} sec^{-1} at 25.0° and 1.0 M perchloric acid.[8] It is also apparent from the data presented in Table I that the value of k_1 decreases with decreasing acidity. A similar dependence of the rate on the perchloric acid concentration has previously been found for the reaction of $CrSCN^{2+}$ with vanadium(II) and was ascribed there to a medium effect.[9] This medium effect could arise from the use of sodium perchlorate instead of lithium perchlorate to maintain the ionic strength.

The second stage of the reaction was studied at high iron(II) concentrations on the stopped-flow apparatus previously described.[10] In these experiments the formation of $FeNCS^{2+}$ and its subsequent decay were followed at 440 nm, the wavelength of the maximum ratio of the absorbance of $FeNCS^{2+}$ to that of $(NH_3)_5CoSCN^{2+}$. At λ 440 nm, $[Fe(II)] = 0.478$ M, and $[HClO_4] = 1.55$ M, a maximum in the absorbance *vs.* time curve was observed at $t = 0.6 \pm 0.1$ sec.[11] Ac-

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(3) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(4) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(5) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 5343 (1966).

(6) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

(7) The iron(III) concentration used in these measurements (3.53 × 10^{-2} M) was sufficiently large so that $[Fe^{3+}]$ remained essentially constant during a run, and the equilibrium between Fe^{3+}, SCN^-, and $FeNCS^{2+}$ was maintained throughout the course of the reaction.

(8) The data in Table I indicate that there may be a slight dependence of the rate constants on the iron(III) concentration. Such a dependence could occur if the aquation of $(NH_3)_5CoSCN^{2+}$ was catalyzed by iron(III). The $(NH_3)_5CoH_2O^{3+}$ produced in the catalyzed aquation would not react with iron(II) to any significant extent during the course of the Fe(II)–$(NH_3)_5CoSCN^{2+}$ reaction.

(9) M. Orhanovic, H. N. Po, and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968).

(10) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(11) The position of the maximum in the absorbance–time curve is very sensitive to traces of iron(III) in the iron(II).