Table II

Infrared Frequencies[a]

Compound	P-O, N-O, As-O, S-O str freq		H-bond freq		
	Complex	Free Ligand			
[H((CH₃)₂SO)₂]AuCl₄	937 s	1053 s	1240 w,b	1150 w, b	750 s, b
[H((C₆H₅)₃PO)₂]AuCl₄	1100 s	1192 s	1225 w, b		850 s, b
[D((C₆H₅)₃PO)₂]AuCl₄	762 s	1192 s			<600 s, b
NaAuCl₄·4(C₆H₅)₃PO	1206 m, 1185 s	1192 s			
[H((C₆H₅)₃AsO)₂]AuCl₄	770 s	881 s	1280 w, b		1030 s, b
[H(C₅H₅NO)₂]AuCl₄	1245 s	1265 s (CS₂)[b]	1280 w, b		770 s, b
[H((CH₃)₃NO)₂]AuCl₄	937 m	940 s (CHBr₃)[c]	1065 m, b		860 s, b

[a] All values are in wave numbers. Abbreviations: s, strong; m, medium; w, weak; b, broad. [b] Reference 10. [c] Reference 12.

The role of the two ligand molecules seems then to be the stabilization of the acid proton by hydrogen bonding. The infrared data displayed in Table II support this conclusion. The P–O, As–O, and S–O stretching frequencies have all shifted to lower frequencies which is characteristic of complex formation through the oxygen atom. In the deuterated compound the band at 1100 cm⁻¹ is greatly diminished and a new strong band appears at 762 cm⁻¹. If this frequency is the P–O stretching frequency, it suggests that this vibration is strongly coupled with the proton. The sodium salt which crystalizes with four phosphine oxide molecules shows infrared frequencies almost identical with those of the free ligand. These data perhaps suggest that the ligands are simply filling holes in the crystal structure. However, in light of some recent studies indicating complex formation between phosphine oxides and alkali metal ions,[4,9] this conclusion should not be accepted without further evidence. The N–O stretching frequencies are affected as when complexed to other species.[10,11] The N–O frequencies of the complexes are compared to the free-ligand frequencies in solution where there should be less association.[10,12]

A second set of absorptions in the infrared also points to hydrogen bonding between the ligands and the proton in these compounds. A strong and broad but well-defined band appears in the region 750–1030 cm⁻¹ accompanied by one or more much weaker and broad bands in the region 1065–1280 cm⁻¹. Upon deuteration of the phosphine oxide complex, both of the broad bands disappear and only the tail of a strong, broad band below 600 cm⁻¹ was observed. These bands must then be associated with the hydrogen bond vibrations. Hadzi[7] attributes similar infrared activity to the formation of symmetrical hydrogen bonds. The infrared spectra of the complexes reported here are indeed very similar to but better defined than those reported for such compounds as HCl·2(C₆H₅)₃PO. With the hydrogen halides a 1:1 adduct is also reported with the halide ion associated with the proton. With tetrachloroauric acid the noncoordinating, large anion

AuCl₄⁻ allows the maximum coordination of the proton and assists in the stabilization of the large cation.

The preparation of a similar compound with the ligand triphenylphosphine sulfide, (C₆H₅)₃PS, was attempted. The compound trichloro(triphenylphosphine sulfide)gold(III), (C₆H₅)₃PSAuCl₃,[13] was isolated. This result might have been predicted if one considers that the soft sulfide donor has the choice of the hard proton or the soft gold(III).

These results lend support to the existence of protonic complexes in these compounds. The formulas of these compounds should then be written to indicate the ligands, point of attachment, such as [H((C₆H₅)₃PO)₂]-AuCl₄.

(13) I. M. Keen, *J. Chem. Soc.*, 5751 (1965).

Contribution from the Departments of Chemistry,
The University of South Dakota,
Vermillion, South Dakota 57069,
and North Texas State University, Denton, Texas 76203

Octahedral Metal Carbonyls. XVI.[1] A Kinetic Investigation of the Second Step of the Reaction of o-Phenanthrolinetetracarbonylmolybdenum with Lewis Bases

By Douglas Shrader, Earl P. Ross, Robert T. Jernigan, and Gerard R. Dobson[2]

Angelici and Graham have investigated the kinetics of reactions of (phen)M(CO)₄ (phen = o-phenanthroline; M = Cr, Mo, W) with Lewis bases (L) to give, as sole products, (phen)(L)M(CO)₃ complexes[3,4]

$$\text{(phen)M(CO)}_4 + \text{L} \longrightarrow \text{(phen)(L)M(CO)}_3 + \text{CO} \quad (1)$$
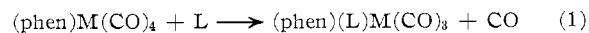
For M = Mo, W, these reactions were found to proceed by way of a two-term rate law[4]

$$\text{rate} = k_1[\text{(phen)M(CO)}_4] + k_2[\text{(phen)M(CO)}_4][\text{L}] \quad (2)$$

A mechanism involving two parallel processes, rate-

(9) K. B. Yatsimirski, M. I. Kabachnik, Z. A. Sheka, T. Ya. Medved, E. I. Sinyavskaya, and Yu. M. Polikarpov, *Teor. i Eksperim. Khim., Akad. Nauk Ukr. SSR*, **4**, 446 (1968); *Chem. Abstr.*, **69**, 100083 (1968).

(10) S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

(11) S. H. Hunter, V. M. Langford, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc., A*, 305 (1968).

(12) S. Kida, *Bull. Chem. Soc. Japan*, **36**, 712 (1963).

(1) Part XV: G. R. Dobson and L. A. H. Smith, *Inorg. Chem.*, **9**, 1001 (1970).

(2) To whom correspondence concerning this work should be addressed at the latter address.

(3) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

(4) J. R. Graham and R. J. Angelici, *ibid.*, **6**, 992 (1967).

determining dissociation of CO and nucleophilic attack of L on the substrate

(phen)(L)M(CO)₃
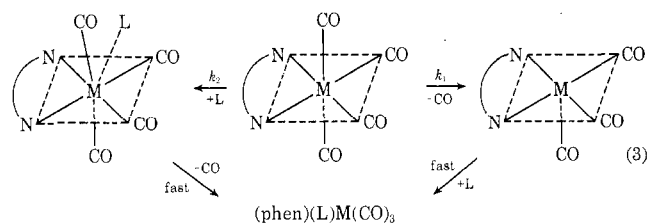
was proposed to explain the kinetic data.

Houk and Dobson reported reaction 1 to proceed further, under forcing conditions, with replacement by L of 1 additional mol of carbon monoxide to give (phen)(L)₂M(CO)₂ products[5,6]

$$(phen)(L)M(CO)_3 + L \longrightarrow (phen)(L)_2M(CO)_2 + CO \quad (4)$$
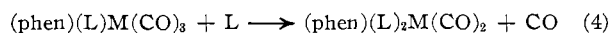
So that a comparison between the two consecutive steps of these reactions could be made and the effect on complex reactivity of the replacement of CO by L in a highly substituted metal carbonyl system could be determined, the kinetics of reaction 4 (for M = Mo) have been investigated.

Experimental Section

Infrared spectra were recorded on a Beckman IR-12 or Perkin-Elmer 621 spectrophotometer and were calibrated against the known bands of polystyrene. Chemical analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Triethyl phosphite and mesitylene were distilled over sodium at reduced pressure employing a spinning-band column. The triethyl phosphite thus purified was found to be free of volatile impurities by gas chromatographic analysis. Tri-*n*-butylphosphine, generously supplied by the Carlisle Chemical Works, and triphenyl phosphite were fractionally distilled at reduced pressure.

Both the substrates, (phen)(L)Mo(CO)₃, and the products, (phen)(L)₂Mo(CO)₂, were prepared by methods similar to those previously reported;[5,6] the substrates were generally prepared in refluxing benzene rather than in higher boiling aromatic solvents. Substrates and colored products for L = P(OC₂H₅)₃, P(*n*-C₄H₉)₃, and P(OC₆H₅)₃ were characterized through their characteristic carbonyl stretching spectra and through elemental analyses (carbon, hydrogen), which differed from the calculated values by not more than 0.3% (absolute) for each complex.

Because the high reaction temperatures necessarily limited the choice of solvents and because of low substrate solubility in several prospective nonpolar solvents and for reasons detailed below, the reactions were monitored at two wavelengths of the visible spectrum. It was thus possible to employ substrate concentrations of *ca.* 2 × 10⁻⁵ *M* in the study.

Only for the reaction of (phen)[P(OC₂H₅)₃]Mo(CO)₃ with triethyl phosphite did it prove possible to complete a detailed kinetic investigation of reaction 4. For L = P(C₆H₅)₃, the reaction product, (phen)[P(C₆H₅)₃]₂Mo(CO)₂, could not be obtained under conditions employed in kinetic runs (see below). With P(OC₆H₅)₃, extensive decomposition was noted during the course of kinetic runs. For P(*n*-C₄H₉)₃, the formation of a second colored product which did not contain carbonyls and was not (phen)[P(*n*-C₄H₉)₃]₄Mo but which has not further been characterized precluded a detailed kinetic investigation. Procedures employed in the determination of rates of reaction of (phen)-[P(OC₂H₅)₃]Mo(CO)₃ with triethyl phosphite are typical of those employed in the attempts outlined above.

This reaction was monitored in mesitylene solvent over a temperature range of 100–136° employing a Beckman DU-2

direct-reading uv–visible spectrophotometer and a 1-cm quartz cell under pseudo-first-order reaction conditions (large excess of triethyl phosphite). The absorbance of a ligand–solvent blank was subtracted from each measurement. Under the reaction conditions employed it was found that in addition to the expected (phen)[P(OC₂H₅)₃]₂Mo(CO)₂, *trans-* and *cis-*[P(OC₂H₅)₃]₃Mo-(CO)₃ were also obtained as reaction products. These were independently synthesized through use of published procedures[7] and were then identified in reaction solutions as follows: mesitylene solvent was removed from the *t*∞ solutions of trial kinetic runs, and the infrared spectra of the residues dissolved in hydrocarbon solvent were compared to the carbonyl stretching spectra (hydrocarbon solvent) for each isomer.

Since both *trans-* and *cis-*[P(OC₂H₅)₃]₃Mo(CO)₃ were found to be colorless, it was possible to determine the concentrations of both substrate and colored product at given times during the course of the reactions from absorbance data taken at two wavelengths (580 and 650 nm).[8] Both substrate and colored product were found to obey Beer's law over the concentration range employed at both 580 and 650 nm in mesitylene; molar absorptivities (ε) were determined from these data. The preparation of reaction solutions and sampling procedures have previously been described.[9] Plots of ln (c_r) *vs.* *t* were linear to at least 2 half-lives. Least-squares analyses were performed on data at three temperatures; limits of error given for $\Delta H_2{}^{\ddagger}$ are one standard deviation.

Results and Discussion

Rate data for the reaction of (phen)[P(OC₂H₅)₃]-Mo(CO)₃ with triethyl phosphite are given in Table
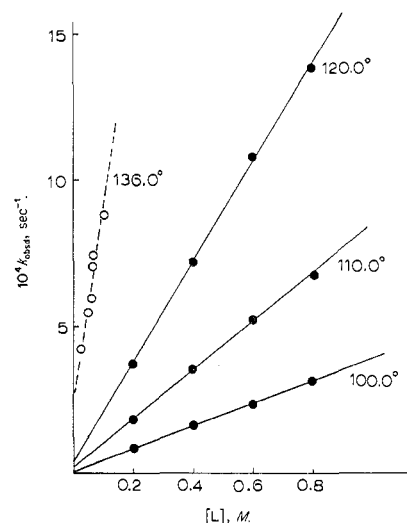
Figure 1.—Plots of k_{obsd} *vs.* [L] for the reaction of (phen)-[P(OC₂H₅)₃]Mo(CO)₃ with triethyl phosphite in mesitylene at various temperatures.

I. Plots of k_{obsd} *vs.* [L] (Figure 1) show the reaction to obey a two-term rate law

rate = k_1[(phen){P(OC₂H₅)₃}Mo(CO)₃] +
k_2[(phen){P(OC₂H₅)₃}Mo(CO)₃][L]   (5)

The presence of the relatively small first-order term was confirmed through kinetic runs at low ligand concentrations at 136° (dashed plot, Figure 1). Since

(5) L. W. Houk and G. R. Dobson, *J. Chem. Soc., A*, 317 (1966).

(6) L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966).

(7) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

(8) The concentrations for r = reactant and p = colored product, (phen)-[P(OC₂H₅)₃]₂Mo(CO)₂, are given by

$$c_p = \frac{A^{650}\epsilon_r^{580} - A^{580}\epsilon_r^{650}}{\epsilon_r^{580}\epsilon_p^{650} - \epsilon_p^{580}\epsilon_r^{650}}; \quad c_r = \frac{A^{580}\epsilon_p^{650} - A^{650}\epsilon_p^{580}}{\epsilon_r^{580}\epsilon_p^{650} - \epsilon_p^{580}\epsilon_r^{650}}$$

See, *e.g.*, D. A. Skoog and D. W. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1963, pp 661–664.

(9) G. C. Faber and G. R. Dobson, *Inorg. Chem.*, **7**, 584 (1968).

Table I

Rate Data for the Reaction of (phen)[P(OC$_2$H$_5$)$_3$]Mo(CO)$_3$
with Triethyl Phosphite in Mesitylene Solvent

Temp, °C	[P(OC$_2$H$_5$)$_3$], M	$10^4 k_{obsd}$, sec^{-1}	$10^4 k_2$, M^{-1} sec^{-1}
100.0	0.2055	0.88	3.74
	0.3977	1.65	
	0.6027	2.34	
	0.7995	3.13	
110.0	0.1998	1.84	8.14
	0.3995	3.55	
	0.5791	5.24	
	0.8052	6.74	
120.0	0.2009	3.72	17.1
	0.3994	7.20	
	0.6026	10.8	
	0.7976	13.9	

it was possible to determine concentrations of substrate and colored product at given times (see Experimental Section), the relative amounts of colored and colorless products formed could also be found. The observed ratios of products formed, [(phen){P(OC$_2$-H$_5$)$_3$}$_2$Mo(CO)$_2$]/(*trans*- and *cis*-{ P(OC$_2$H$_5$)$_3$}$_3$Mo(CO)$_3$], corresponded, within experimental error, to the ratios k_1/k_2[L], strongly suggesting the carbonyl-replacement product to be formed exclusively *via* the first-order path and the phen-replacement products exclusively through the ligand-dependent path

$$(phen)[P(OC_2H_5)_3]Mo(CO)_3 \quad (6)$$

(phen)[P(OC$_2$H$_5$)$_3$]$_2$Mo(CO)$_2$

trans- and *cis*-[P(OC$_2$H$_5$)$_3$]$_3$Mo(CO)$_3$
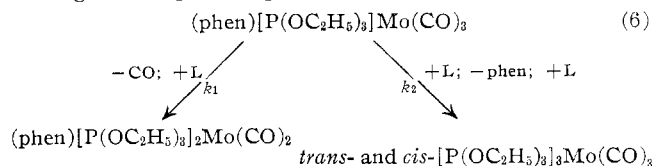
It has been shown[7] that equilibrium mixtures of *trans*- and *cis*-[P(OC$_2$H$_5$)$_3$]$_3$Mo(CO)$_3$ are formed from either isomer; thus it is not possible to say whether the *trans*- or *cis*-[P(OC$_2$H$_5$)$_3$]$_3$Mo(CO)$_3$ product is formed initially.

The relatively small first-order terms observed under the kinetic conditions employed resulted in large uncertainties in the first-order rate data and activation parameters. Nonetheless, from data at high temperatures and low ligand concentrations the entropy of activation as calculated is positive, as would be expected for a mechanism involving rate-determining dissociation of CO.

Two possible mechanisms would appear to be consistent with the kinetic and activation data for the ligand-dependent path ($\Delta H_2^{\ddagger}$ = 21.8 ± 0.4 kcal mol^{-1}; $\Delta S_2^{\ddagger}$ = −16.3 ± 1.0 eu). The first, involving nucleophilic attack of triethyl phosphite on the substrate to give a seven-coordinate activated complex or intermediate, followed by other, rapid steps to give the observed products, a mechanism analogous to the associative path envisioned in (2), would appear most plausible. The other possible path, involving reversible dissociation of one end of the phen ligand followed by attack of triethyl phosphite on the resulting five-coordinate species and which under certain conditions can also lead to ligand-dependent kinetics,[10]

(10) See, *e.g.*, J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965).

would appear less likely because of the rigidity of the phen ligand[11] and because product studies at low substrate and high ligand concentration confirmed (phen)[P(OC$_2$H$_5$)$_3$]$_2$Cr(CO)$_2$[6] to be the only product of the reaction of (phen)[P(OC$_2$H$_5$)$_3$]Cr(CO)$_3$ with triethyl phosphite. While there would be no apparent explanation for this observation were the reaction to proceed by initial reversible dissociation of one end of the phen ligand, it is readily rationalized in terms of inhibition of nucleophilic attack at the smaller Cr atom. There have been many instances in which the kinetic behavior of chromium carbonyl complexes differs from that observed for the corresponding molybdenum derivatives; in most cases such differences have been attributed to the smaller size of zerovalent Cr.[11]

Kinetic data for the first step of the reaction of (phen)Mo(CO)$_4$ with triethyl phosphite are not available, so a direct comparison of second-order rate data for the two consecutive steps cannot be made. The relative rates may be estimated, however, from data for the reaction of (phen)Mo(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ in 1,2-dichloroethane[4] and for the reaction of the very similar (2,2'-dipy)Mo(CO)$_4$ with P(OCH$_2$)$_3$CCH$_3$ and triethyl phosphite in the same solvent.[12] A consideration of these data and the effect upon rate of the different solvents indicates the second-order rate constants for the two steps should differ rather little, the first step being considerably less than two orders of magnitude faster than the second. This difference can be rationalized in terms of the increased steric requirements about the metal, or its reduced Lewis acidity in the second step. The observed replacement of CO in the first step but phen in the second is a more dramatic difference, but one less amenable to ready interpretation.

Although detailed kinetic studies of analogous reactions for L = P(OC$_6$H$_5$)$_3$ and P(n-C$_4$H$_9$)$_3$ could not be made, it was determined that no phen replacement occurred in these systems. Further, it was possible to determine the relative first-order rates for reaction 4 to vary with substituent L: (CO)[4] > P(OC$_6$H$_5$)$_3$ > P(OC$_2$H$_5$)$_3$ > P(n-C$_4$H$_9$)$_3$. This order is that to be expected if the effects of variations in ligand-to-metal π bonding on the metal–carbon bond to be broken are dominant and if the ease of dissociation of CO is largely determined by the relative energies of the Mo–CO bonds.[1,13] This order may be contrasted to the properties of the ligand–metal bonds in the very similar (phen)(L)Cr(CO)$_3$ complexes, as inferred from kinetic data. Here, the Cr–L bond strengths evidently vary in the order L = P(n-C$_4$H$_9$)$_3$ > P(OC$_2$H$_5$)$_3$ > CO > P(OC$_6$H$_5$)$_3$, and it has been concluded that the bond strengths are largely determined by the σ-bonding abilities of the ligands.[1] It would thus appear that the carbonyl ligands are more sensitive to changes in π bonding in substituent groups, while σ bonding is of greater importance to the strengths of metal–

(11) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

(12) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965).

(13) M. Graziani, F. Zingales, and U. Belluco, *Inorg. Chem.*, **6**, 1582 (1967).

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(OC₂H₅)₃]-Mo(CO)₃ with triethyl phosphite was known, reactions of this substrate with other Lewis bases were studied. Reaction of (phen)[P(OC₂H₅)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.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MEMPHIS STATE UNIVERSITY, MEMPHIS, TENNESSEE 38111,
AND THE ANORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT, GÖTTINGEN, GERMANY

cis-Trifluorodiamidophosphorus(V)

BY MAX LUSTIG AND HERBERT W. ROESKY

The new and interesting compound *cis*-trifluorodiamidophosphorus(V), PF₃(NH₂)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 xPF₅·yNH₃ 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)

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

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.

(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.

Reagents.—The PF₅ and NH₃ were obtained from the Matheson Co.

Synthesis of PF₃(NH₂)₂.—This reaction was performed by placing the PF₅ in a 1.1-l. Pyrex reactor equipped with a stopcock and admitting the NH₃ 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 NH₃ to PF₅ ratio. In a typical reaction, the reactor was charged with 17.9 mmol of PF₅ and the NH₃, 40.0 mmol, was slowly admitted. The reaction was rapid. After all the NH₃ 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 PF₃(NH₂)₂ (0.884 g, 7.36 mmol, 41.1% yield) was collected in this trap. The yield is based on the quantity of PF₅ employed. Ammonium hexafluorophosphate was a product, identified by its infrared spectrum.
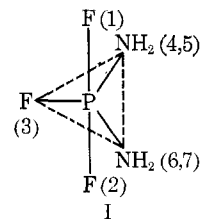
Analyses.—An F & M Model 185 analyzer was used to determine hydrogen and nitrogen. For phosphorus, the compound was burned in an oxygen flask. The residue was absorbed in 6 *N* HNO₃ and the phosphate was determined spectrophotometrically as phosphovanadomolybdate.[3] The fluorine was analyzed by reduction of the compound with lithium in *n*-propylamine. The fluoride was distilled as H₂SiF₆ and titrated with thorium nitrate. *Anal.* Calcd for F₃H₄N₂P: 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 NH₃ was observed.

Spectroscopy. A. Nmr Spectra.—The ¹⁹F, ³¹P, 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

TABLE I
NUCLEAR MAGNETIC RESONANCE SPECTRA

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

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).

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

I

(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.