

This system may be compared with $\text{Co}^{\text{III}}(\text{d}^6)/\text{Co}^{\text{II}}(\text{d}^7)$ reactions such as those involving $\text{Co}(\text{en})_3^{2+/3+}$, $\text{Co}(\text{phen})_3^{2+/3+}$, and $\text{Co}(\text{sep})_3^{2+/3+}$ (en = ethylenediamine, phen = phenanthroline, sep = sepulchrate). The cobalt self-exchange rate constants are much lower than k_1 for $\text{NiL}^{2+}/\text{NiL}^+$: for $\text{Co}(\text{en})_3^{2+/3+}$, $k = 3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$,³² for $\text{Co}(\text{sep})_3^{2+/3+}$, $k = 5.1 \text{ M}^{-1} \text{ s}^{-1}$,³³ and for $\text{Co}(\text{phen})_3^{2+/3+}$, $k = 45 \text{ M}^{-1} \text{ s}^{-1}$.³⁴ The slowness of the cobalt-exchange reactions may be accounted for in part by a consideration of the energy required for reorganization of the spin configurations.^{21,35}

An important contribution to the self-exchange reorganizational energy is made by the changes in metal-ligand lengths of the ground-state reactants in forming the Franck-Condon activated complex.³⁶ The differences in metal-nitrogen bond lengths between the reduced and oxidized forms of the nickel and cobalt complexes may be correlated with the electron-exchange parameters.

The crystal structure of a NiL^{2+} complex has not been published, but information on $\text{Ni}^{\text{IV}}\text{-N}$ bond lengths is available from the reported structure of a similar compound, bis[2-((2-aminoethyl)imino)-3-butanone oximate]nickel(IV) diperchlorate.⁶ The average $\text{Ni}^{\text{IV}}\text{-N}$ bond length is 1.948 Å, which is 0.14 Å shorter than the average $\text{Ni}^{\text{II}}\text{-N}$ distance in

a similar $\text{Ni}(\text{II})$ complex, bis[2,2'-iminobis(acetamidoxime)]nickel(II) chloride dihydrate.³⁷ Interpolation of these distances to an octahedral $\text{Ni}^{\text{III}}\text{N}_6$ species, for which crystallographic data are not yet available, yields a difference of ~ 0.07 Å between the Ni-N bond lengths between NiL^{2+} and NiL^+ . A similarity in Ni-N bond length changes in the $\text{Ni}(\text{IV})/\text{Ni}(\text{III})$ and $\text{Ni}(\text{III})/\text{Ni}(\text{II})$ oxime complexes is suggested by the similar self-exchange rates determined for these systems.³⁸ For $\text{Co}(\text{en})_3^{2+/3+}$ and $\text{Co}(\text{sep})_3^{2+/3+}$, the $\text{Co}(\text{II})/\text{Co}(\text{III})$ metal-nitrogen bond length differences are 0.21^{39,40} and 0.19 Å,³³ respectively, substantially larger than for $\text{NiL}^{2+/+}$, and probably are the source of a sizable barrier to electron exchange.

Further kinetic studies currently in progress of differing nickel(IV) and -(III) complexes reacting with one- and two-electron reductants may prove useful in identifying other contributions to the self-exchange rates for these systems.

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Hexacoordinate Phosphorus. 2. Formation and Dynamic Exchange Processes in Methyltris(trifluoromethyl)(dimethylcarbamato-*O,O'*)phosphorus(V)

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The reaction of CO_2 with $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ yields the neutral six-coordinate phosphorus carbamate $\text{CH}_3(\text{CF}_3)_3\text{P}-\text{O}_2\text{CN}(\text{CH}_3)_2$. Carbon-13 CO_2 exchange and $\text{HN}(\text{CD}_3)_2$ exchange in this compound have been studied in the absence and presence of the amine trap $(\text{CH}_3)_3\text{SiCl}$. The results indicate that the mechanism for formation of the carbamate as well as for carbon dioxide exchange is catalyzed by the presence of fortuitous free amine. Dynamic ^{19}F and ^{31}P NMR methods demonstrate the equivalency of the CF_3 groups at room temperature while at lower temperatures the solution structure corresponds to that determined in the solid state by X-ray methods. The barrier to the rearrangement process, which equilibrates the CF_3 groups, is independent of solvent or concentration and has been determined by line shape analysis of the $^{31}\text{P}\{^1\text{H}\}$ temperature-dependent spectra to be 13.5 ± 0.7 kcal. Evidence is also presented showing formation of an adduct between Me_3N and $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ in solution.

Introduction

In part 1,¹ the synthesis and the crystal and molecular structure of the hexacoordinate (carbamato)phosphorus(V) complex $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ was reported. This carbamate differs from the mono- and dithio analogues reported in the same paper in that the carbamate is fluxional in solution at ordinary temperatures whereas the sulfur-containing compounds are static. According to the crystal structure,¹ the carbamate is clearly six-coordinate in the solid state. The rather unusual fluxional behavior of this compound and the fact that these six-coordinate compounds can be formed by an "insertion" reaction involving the P-N bond of the phosphorane prompted us to investigate the fluxional process in

more depth and to evaluate the pathway for the formation of these molecules with the aid of isotopically labeled reagents. Of particular interest in this latter context are the divergent views expressed about the mode of CO_2 insertion in silicon-,² transition-metal-,³ and tin-based⁴ systems. Furthermore, it was of interest to ascertain whether this high-valent phosphorus compound resembled analogous transition-metal systems wherein similar reactions have been observed.

Experimental Section

General Procedures. Both the $^{13}\text{CO}_2$ (90.5 atom % ^{13}C) and $\text{HN}(\text{CD}_3)_2$ (99 atom % D) were obtained from Merck Sharp & Dohme. The solvent, CD_3CN , used in all the exchange experiments was dried

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by shaking with anhydrous CaSO_4 . Small quantities of $\text{N}(\text{CH}_3)_3$, $\text{HN}(\text{CH}_3)_2$, and $\text{N}(\text{C}_2\text{H}_5)_3$ were dried by shaking with LiAlH_4 in sealed tubes. Standard vacuum-line techniques were used to condense the weighed quantities of volatile and gaseous sample components (including solvents) onto weighed quantities of solid samples of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ previously placed in NMR tubes.

The exchange experiments were monitored by ^1H NMR spectroscopy (Varian A56/60) at 60.0 MHz or by ^{13}C NMR spectroscopy in the FT mode (Bruker HFX-90) at 22.6 MHz. Phosphorus spectra were recorded at 36.43 MHz in the pulsed FT mode also with the Bruker HFX-90 spectrometer. A Bruker temperature controller provided temperature control in the probe to within $\pm 1^\circ\text{C}$ ascertained by periodic calibration.

Preparation of Compounds. $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ and $\text{CH}_3(\text{CF}_3)_3\text{PO}_2^{13}\text{CN}(\text{CH}_3)_2$ were prepared as before¹ with CO_2 or $^{13}\text{CO}_2$ as appropriate. $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CD}_3)_2$ was prepared in the same manner as described³ for $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ except that $\text{HN}(\text{CD}_3)_2$ was used for aminolysis of $\text{CH}_3(\text{CF}_3)_3\text{PF}$. Its purity was confirmed by ^1H and ^{19}F NMR spectra.

Reactions. (a) $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ with CO_2 . A fresh solution of $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ (0.0402 g, 0.135 mmol) in CD_3CN and CO_2 (0.0121 g, 0.275 mmol) had reacted quantitatively to yield $\text{CH}_3(\text{C-F}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ by the time (15 min) an ^1H NMR spectrum could be recorded.

(b) $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ with CO_2 in the Presence of $(\text{CH}_3)_3\text{SiCl}$. Several NMR tubes containing these reactants in different concentrations were prepared by first allowing a solution of $\text{CH}_3(\text{CF}_3)_3\text{P-N}(\text{CH}_3)_2$ and $(\text{CH}_3)_3\text{SiCl}$ to mix a room temperature for about 15 min, after which CO_2 was added. The total volume for each sample was 0.25 mL. The initial ^1H NMR spectrum of each sample showed that no detectable amount of carbamate had been formed, but continued monitoring showed that carbamate was slowly formed in all samples. No significant dependence of the initial rate on the relative proportions was observed, but larger proportions of $(\text{CH}_3)_3\text{SiCl}$ appeared to substantially retard the long-term formation of carbamate.

(c) $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ with $\text{HN}(\text{CD}_3)_2$. The ^1H NMR spectrum of a mixture of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.0430 g, 0.126 mmol) and $\text{HN}(\text{CD}_3)_2$ (0.0126 g, 0.247 mmol) dissolved in CD_3CN , taken as soon as the carbamate had dissolved, showed that complete amine exchange had already occurred.

(d) $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ with $^{13}\text{CO}_2$. Two samples of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.0380 g, 0.111 mmol, and 0.1095 g, 0.321 mmol) with CO_2 (0.0119 g, 0.265 mmol, and 0.0243 g, 0.541 mmol) were prepared for ^{13}C and ^1H NMR spectra, respectively. Both spectra showed that $^{13}\text{CO}_2$ was incorporated into the carbamate ligand in less than 15 min, the time to obtain a spectrum.

(e) $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ with $^{13}\text{CO}_2$ in the Presence of $(\text{C-H}_3)_3\text{SiCl}$. A CD_3CN solution of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.0410 g, 0.120 mmol) and $(\text{CH}_3)_3\text{SiCl}$ (0.0117 g, 0.108 mmol) was brought to room temperature for 15 min after which $^{13}\text{CO}_2$ (0.0113 g, 0.252 mmol) was then added. The ^1H and ^{13}C spectra showed that no $^{13}\text{CO}_2$ was incorporated into the carbamate ligand in 5 days. However, slow exchange did occur over a period of 19 months although equilibrium was not reached.

(f) $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ with $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CD}_3)_2$. The ^1H NMR spectrum of a freshly prepared solution containing $\text{CH}_3(\text{C-F}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.0397 g, 0.116 mmol) and $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CD}_3)_2$ (0.0401 g, 0.132 mmol) showed no formation of $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$. After the solution was monitored for 6 days, ^1H NMR integration showed that 11% of the $\text{N}(\text{CH}_3)_2$ group had been incorporated into $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CD}_3)_2$.

(g) $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ with $\text{HN}(\text{CD}_3)_2$. Monitoring a solution containing $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ (0.0885 g, 0.298 mmol) and $\text{HN}(\text{CD}_3)_2$ (0.0195 g, 0.382 mmol) by ^1H NMR showed that about 5% amine exchange had occurred in 25 h. After 43 h the ^1H NMR spectrum showed that aminolysis of one CF_3 group had occurred, generating CF_3H and a species containing a $\text{CH}_3(\text{CF}_3)_2\text{P}$ function in the solution. With a 3:1 amine:aminophosphorane reacting ratio, elimination of one CF_3 group as CF_3H was essentially complete in 16 h.

Sample Preparation for Dynamic NMR. Four samples of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ were prepared for temperature-dependent ^{31}P spectra. Sample A contained $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.162 g, 0.475

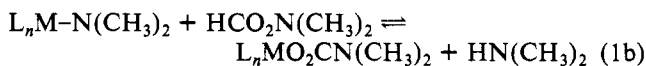
mmol), $(\text{CH}_3)_3\text{N}$ (0.629 g, 10.7 mmol), CD_3CN (0.350 g), and $((\text{CH}_3)_3\text{Si})_2\text{NCH}_3$ (0.037 g, 0.211 mmol), sample B contained $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.221 g, 0.648 mmol), $(\text{C}_2\text{H}_5)_3\text{N}$ (0.541 g, 5.36 mmol), and CD_3CN (0.833 g), sample C contained $\text{CH}_3(\text{C-F}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ (0.280 g, 0.821 mmol), $(\text{CH}_3)_3\text{SiCl}$ (0.233 g, 2.15 mmol), and CD_3CN (1.025 g), and sample D contained approximately 20% $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$, 20% CF_2Cl_2 , and 60% CD_3CN . Hydrolysis products accounting for approximately 40% of the ^{31}P signal intensity were present in sample B as the $(\text{C}_2\text{H}_5)_3\text{N}$ had not been dried for this experiment. In spite of this complication the barrier derived for the remaining carbamate in B was essentially equivalent to those given in Table II. In fitting the spectra of these samples, the line width at half-maximum ranged from 2.5 to 5.0 Hz, from the lowest to the highest temperature.

The NMR data in Table I were obtained on a sample containing $\text{CH}_3(\text{CF}_3)_3\text{PO}_2^{13}\text{CN}(\text{CH}_3)_2$ (0.0679 g, 0.199 mmol), $(\text{CH}_3)_3\text{N}$ (0.7807 g, 13.2 mmol), and CD_3CN (0.3641 g). In spite of the precaution to exclude water, the ^{31}P NMR spectrum still showed about 5% hydrolysis products.

Results and Discussion

In the absence of an amine trap, labeled $^{13}\text{CO}_2$ was rapidly incorporated (complete equilibration was achieved in less than 15 min) into the carbamate ligand of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CNMe}_2$ in CD_3CN solution. Similar rapid uptake of CO_2 by $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ occurred in the absence of an amine trap. In the presence of an amine trap, $(\text{CH}_3)_3\text{SiCl}$, no detectable incorporation of $^{13}\text{CO}_2$ into the bound carbamate occurred over 5 days although over long periods of time slow exchange of $^{13}\text{CO}_2$ did occur. Related to this latter observation is the fact that samples of $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$ and CO_2 in the presence of the amine trap also slowly formed carbamate, but the initial rates of formation and the final concentrations attained after very long periods (3 weeks) appeared to be independent of the initial concentration ratios of aminophosphorane and CO_2 .

The lack of a specific rate dependence and the retardation of the rate of uptake or exchange by an amine trap strongly suggest that the pathway for "insertion" of CO_2 into the P-N bond follows the formation of carbamate (ion or carbamic acid, HCO_2NMe_2) in solution by the action of CO_2 on "fortuitous amine" and the displacement of the bound amino substituent by free carbamate ligand (eq 1), as suggested by Breederveld²



for the insertion reaction of an aminosilane. The $\text{CH}_3(\text{C-F}_3)_3\text{PN}(\text{CH}_3)_2$ "insertion" reaction is also parallel to the behavior of transition-metal amides wherein a similar pathway was suggested³ on the basis of the known reaction of CO_2 with amine.⁶

The fact that slow exchange and slow uptake of CO_2 occurred even in the presence of the amine trap suggests that the trapping agent employed was not totally effective. In fact, it is unlikely that an "absolute" amine trap can ever be found because the trap must bind the amine strongly whereas this process is likely to be a typical equilibrium situation and, furthermore, the bound amine-trap complex must be unreactive in the system. The discrepancy in behavior in the reaction of CS_2 with $(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$ studied by George and Lappert⁴ wherein the amine trap was found to be without effect, which led to the suggestion that their reaction proceeded via a concerted pathway, may be resolved by realizing that the amine trap may not have been adequate to sufficiently inhibit the free amine in their system.

The displacement of the carbamate group on phosphorus by amine implied by the reversibility of reaction 1b was

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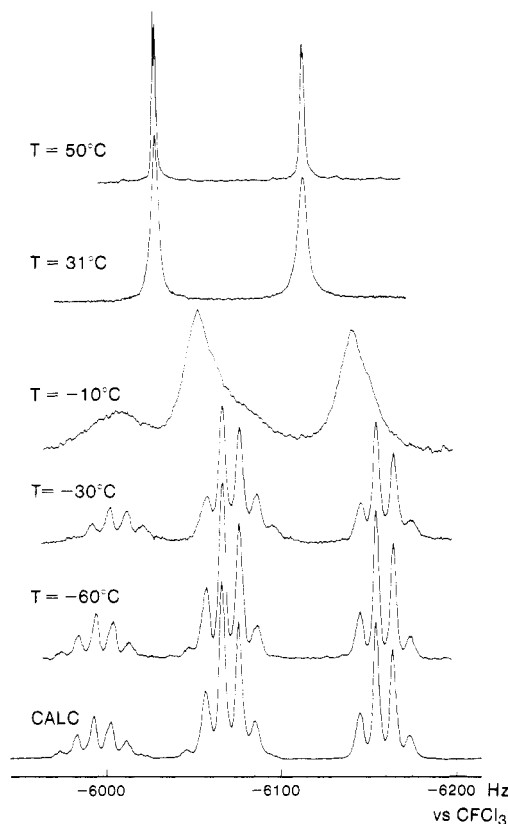
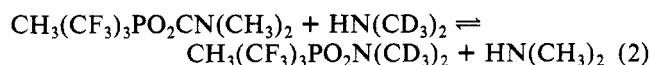
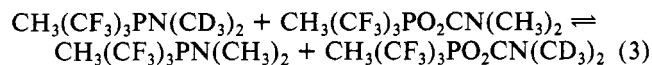


Figure 1. Variation of the ^{19}F (CW, 94.1-MHz) NMR spectrum of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ in CFCl_3 solution through the temperature range $+50$ to -60°C . The first-order calculated spectrum for two CF_3 environments (two "axial", one "equatorial") is shown in comparison to the limiting spectrum obtained at -60°C . The chemical shift scale is given in hertz relative to the solvent standard, CFCl_3 , with negative values indicating resonance to high field of the standard.

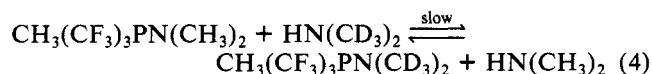
demonstrated by the fast exchange of $\text{N}(\text{CH}_3)_2$ groups by deuteriomethylated dimethylamine, $\text{N}(\text{CD}_3)_2$ (eq 2), which



reached complete equilibrium within 15 min at 25°C in CD_3CN . While we cannot entirely rule out a nucleophilic displacement of $\text{N}(\text{CH}_3)_2$ by $\text{N}(\text{CD}_3)_2$ on the carbon of the carbamate bound to phosphorus, it seems more reasonable to involve the process represented by eq 1a to effect the H-D exchange on the free carbamate. The deuterium-labeled aminophosphorane $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CD}_3)_2$ also slowly exchanged its deuterated $\text{N}(\text{CD}_3)_2$ groups with those bound to the carbamate (eq 3) with about 10% of the aminophosphorane



containing $\text{N}(\text{CH}_3)_2$ substituents after 143 h at 25°C . Again, free amine and free carbamate are most likely involved. Separate experiments showed that free amine itself did not react (eq 4) very quickly with the aminophosphorane since no



exchange of amino group with deuterioamine groups was observed within 15 min at 25°C , in contrast to the more rapid exchange process depicted by eq 2, but this system suffers a competitive secondary substitution process wherein a CF_3 group was slowly displaced as CF_3H , forming a species con-

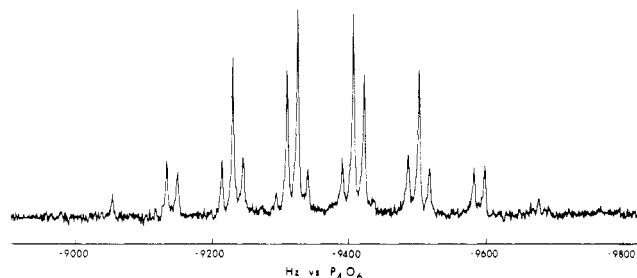


Figure 2. Limiting ^{31}P (FT, 36.4-MHz) proton-decoupled NMR spectrum of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ at -35°C in CFCl_3 solution. The chemical shift scale is given in hertz relative to the standard, P_4O_6 , negative values indicating resonance to high field of the standard.

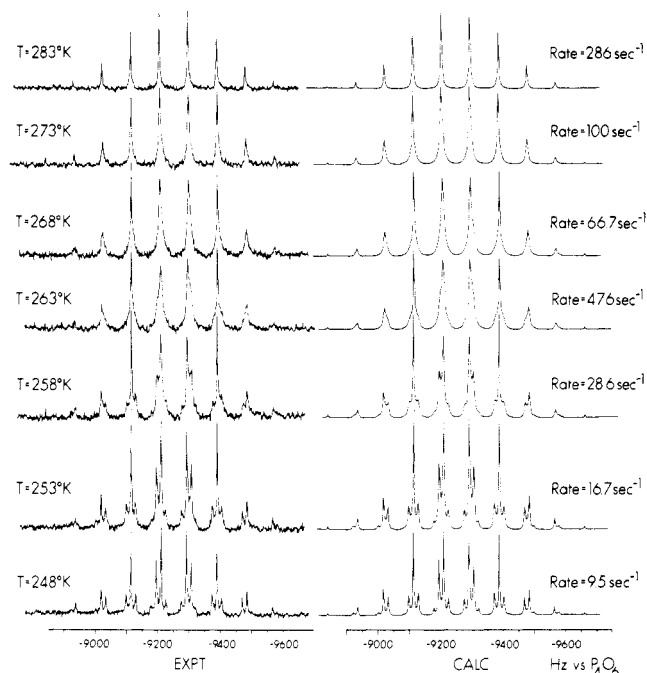


Figure 3. Observed and calculated $^{31}\text{P}\{^1\text{H}\}$ (FT, 36.4-MHz) NMR spectra for dynamic exchange of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ through the temperature range 283–248 K. The chemical shift scale is the same as for Figure 2.

taining a $\text{CH}_3(\text{CF}_3)_2\text{P}$ functionality as indicated by NMR. This second reaction is dependent on the relative concentration of amine, suggesting that it may involve a nucleophilic attack at phosphorus. The sluggish character of the exchange of the P-N compound with free amine clearly implicates species such as the carbamate in the above facile exchanges. The propensity of the phosphorus carbamate to suffer rapid exchanges can be understood from the fluxional process discussed below.

Fluxional Behavior. At -60°C the two CF_3 environments expected from the solid-state structure of the carbamate are observed in the NMR spectrum: a unit intensity group consisting of a doublet of septets and a group of twofold relative intensity consisting of a doublet of quartets. At 94.1 MHz, the two midfield members of each group overlap, creating a complex structure, which is however readily fitted by first-order analysis (Figure 1). At ordinary temperatures, the ^{19}F spectrum is a simple doublet due to rapid interchange of CF_3 environments. Similarly, the ^{31}P NMR spectrum is fluxional, showing a 10-line pattern at 33°C and a quartet of septets at -40°C (Figure 2). The limiting spectra at low temperatures are compatible with the solid-state structure.¹

Line shape fitting of ^{31}P NMR spectra (Figure 3) obtained in various solutions over the temperature range 248–293 K with the program EXCHSYS⁷ to the Arrhenius and Eyring⁸

Table I. ^1H and ^{13}C NMR Data^{a,b} for $\text{CH}_3(\text{CF}_3)_3\text{PY}$

Y	r^c	$^3J_{\text{PNCH}}$	$^5J_{\text{FCPNCH}}$	$^3J_{\text{CNCH}}$	$^2J_{\text{POC}}$	$\delta(^{13}\text{C})^d$
$\text{N}(\text{CH}_3)_2$	7.52 ^e	13.2	1.0			
$\text{O}_2\text{CN}(\text{CH}_3)_2$	7.30 ^f					
$\text{O}_2^{13}\text{CN}(\text{CH}_3)_2$	7.30 ^f					

^a ^{19}F and ^{31}P NMR data are given in ref 1. One of the $^2J_{\text{PF}}$ values given therein in Table III for $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ at -45°C is in error. The correct values are J (intensity ratio) = 95.5 (2) and 80.6 (1) Hz. ^b Values of chemical shifts and coupling constants are in ppm and Hz, respectively. ^c $\text{N}(\text{CH}_3)_2$ group relative to external $(\text{CH}_3)_4\text{Si}$; $\tau = 10.0$. ^d Relative to ^{13}C of $(\text{CH}_3)_4\text{Si}$, a positive value indicates a shift to low field of the reference. ^e Doublet of multiplets. ^f Singlet under measurement conditions. ^g Doublet.

Table II. Activation Barrier to CF_3 Permutational Interchange in $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$ ^a

compd	ΔG^\ddagger , kcal	ΔG^\ddagger , kcal	ΔG^\ddagger , kcal	ΔH^\ddagger , kcal	ΔS^\ddagger , eu	temp range, K	E_a , kcal	$10^{-12}A$, s ⁻¹	E_a (constrained) ^c	sample
compd	13.4 ± 0.5	13.4 ± 0.5 (266)	12.8 ± 0.3	12.8 ± 0.3	-2.2 ± 1.3	248–293	13.3 ± 0.3	5.1 ± 3.4	13.9 ± 0.1	20% soln in $\text{CD}_3\text{CN}/\text{CF}_3\text{Cl}_2$ (3/1) (D)
compd + amine trap	13.5 ± 0.9	13.6 ± 0.5 (275)	14.9 ± 0.6	14.9 ± 0.6	4.6 ± 2.2	263–293	15.4 ± 0.6	15.8 ± 17.5	14.1 ± 0.1	30% soln in $\text{CD}_3\text{CN} + \text{Me}_3\text{SiCl}$ (amine trap) (C)
compd + base + trap	13.4 ± 0.6	13.4 ± 0.5 (269)	13.7 ± 0.4	13.7 ± 0.4	1.2 ± 1.4	253–293	14.3 ± 0.4	27.5 ± 20.0	14.1 ± 0.3	$\text{Me}_3\text{N}/\text{carbamate}$ (20/1) in $\text{CD}_3\text{CN} + (\text{Me}_3\text{Si})_2\text{NMe}$ (amine trap) (A)

^a By line shape analyses of the ^{31}P NMR spectrum.⁷ The error limits are those derived from statistical analyses. ^b T is the average temperature of the fitting range, not a coalescence temperature. ^c Obtained by fitting the data to the idealized Arrhenius equation for an intramolecular process with $A = 10^{13.2} \text{ s}^{-1}$.

Table III. NMR Parameters^a of the Proposed Adduct of $\text{CH}_3(\text{CF}_3)_3\text{PO}_2^{13}\text{CN}(\text{CH}_3)_2$ and $(\text{CH}_3)_3\text{N}$

$\delta(^{31}\text{P})^b$	ϕ^{F^c} (intens)	$\delta(^{13}\text{C})^d$	J_{PCF}	J_{FCPCF}	$J_{\text{PO}^{13}\text{C}}$
61.6 (1)			107.7		
+198.1	67.4 (2)	161.7	41.2	13.4	<1 ^e

^a Recorded at 0°C . Chemical shifts and coupling constants are in ppm and Hz, respectively. ^b Relative to P_4O_6 . The chemical shift of 85% H_3PO_4 is +112 ppm (high field) of P_4O_6 (Chapman, A. C.; Horner, J.; Mowthorpe, D. J.; Jones, K. T. *Chem. Commun.* 1965, 121). ^c Relative to CFCl_3 . ^d Relative to $(\text{CH}_3)_4\text{Si}$. ^e The line widths at half-maximum in the ^{13}C and ^{31}P NMR spectra are 9.5 and 3.6 Hz, respectively.

equations gave the barrier data in Table II. We regard the ΔG^\ddagger values to be the more reliable⁹ parameters, and our conclusions are so based. It is interesting to note that ΔS^\ddagger values are satisfyingly small. The chemical shift does not change significantly through the temperature range, and the barrier is apparently independent of concentration and of the presence of a potential coordinating base (R_3N) or traces of moisture. Amine (or water) traps also appear to be without effect on the barrier. Thus, the process appears to be unimolecular. The most reasonable process responsible for the fluxional behavior seems to be transformation of the carbamate to a monodentate ligand rendering the phosphorus atom five-coordinate and therefore subject to typical pseudorotatory processes (i.e., Berry pseudorotation) of such centers. The average value of the barrier, $13.5 \pm 0.7 \text{ kcal/mol}$, is typical of that found for CF_3 permutations on a five-coordinate center found in related systems.¹⁰ The suggestion of a partial dissociation process is supported by the appearance of bands in solution infrared spectra that are suggestive of a terminal $\text{C}=\text{O}$ stretch.¹ The essential temperature independence of the ^{31}P NMR chemical shift and its very high value, considerably higher than that usually found for five-coordinate phosphorus centers,¹⁰ suggest that the pentacoordinate species is present in only very low concentrations. It is surprising that coordinating ligands do not appear to affect the barrier, and this result might be suggestive of a nondissociative, six-coordinate twist permutational mechanism. In the absence of both definitive indications and precedent, we favor the dissociative process as the more reasonable and rationalize the lack of effect of amines on the barrier on the grounds of their inability to form stable or prominently persistent complexes.

Base Adducts of the (Carbamato)phosphorus(V) Compound. Although the barrier to the fluxional process was unaffected by amine bases, there was some evidence for an adduct formed between the (carbamato)phosphorus(V) complex and Me_3N , but this species was formed in only relatively small amounts leaving the bulk of the (carbamato)phosphorus(V) complex unaffected in the solution. NMR parameters of this proposed adduct with $(\text{CH}_3)_3\text{N}$ are given in Table III, the six-coordinate or higher coordinate nature of the species is suggested by the high-field ^{31}P NMR chemical shift. Notably, a 2:1 ratio of CF_3 groups is present with coupling constants typical of the system. We think that the most likely formulation is a six-coordinate complex with a monodentate carbamate ligand and the base in the plane containing the unique CF_3 and the CH_3 group. The smaller $^2J_{\text{PF}}$ value is therefore assigned to the trans CF_3 groups.

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A stronger donor such as $(\text{CH}_3)_3\text{P}$ gave an insoluble precipitate; thus no evidence of donor-acceptor interactions could be gleaned from potential phosphorus-phosphorus couplings.

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Registry No. $\text{CH}_3(\text{CF}_3)_3\text{PO}_2\text{CN}(\text{CH}_3)_2$, 65013-32-3; CO_2 , 124-38-9; $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CD}_3)_2$, 85650-39-1; $\text{HN}(\text{CD}_3)_2$, 14802-36-9; $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2$, 63715-49-1; $(\text{CH}_3)_3\text{SiCl}$, 75-77-4; $^{13}\text{CO}_2$, 1111-72-4; $\text{CH}_3(\text{CF}_3)_3\text{PO}_2^{13}\text{CN}(\text{CH}_3)_2$, 85650-40-4; Me_3N , 75-50-3.

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Mechanism of Iron(III) Complex Formation. Activation Volumes for the Complexation of the Iron(III) Ion with Thiocyanate Ion and Acetohydroxamic Acid

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Activation volumes (ΔV^\ddagger) for the complexation of the iron(III) ion with thiocyanate (SCN^-) and acetohydroxamic acid (Hahx) were determined by a high-pressure stopped-flow technique. The values of ΔV^\ddagger for reaction of Fe^{3+} are $-6.1 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ for SCN^- and $-10.0 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$ for Hahx, whereas the ΔV^\ddagger values of the FeOH^{2+} ion are $8.5 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$ for SCN^- and $7.7 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ for Hahx. Complexation of FeOH^{2+} is dissociatively activated but that of Fe^{3+} associatively. No apparent parallel relationship is observed between ΔV^\ddagger and corresponding ΔS^\ddagger values.

Introduction

The sign of activation volumes has been demonstrated to be useful for distinction between reaction pathways for iron(III) complexation with proton ambiguity.¹ The activation volumes so far available for iron(III) complex formation are relatively few,² and additional data are required to ascertain the general possibility of this criterion.

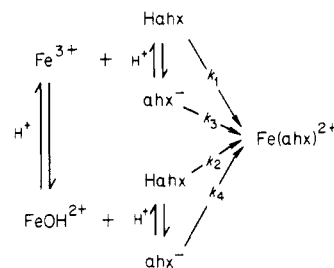
The reaction of the iron(III) ion with thiocyanate has no proton ambiguity. Although activation volumes for thiocyanate are available, the reported values do not agree with each other.^{2b,d} Thus we decided to reexperiment by using a high-pressure stopped-flow technique. Moreover, in order to review a relationship between activation volume and activation entropy, we selected the reaction for which the value of activation entropy is the smallest among the available values and investigated the pressure effect on the iron(III) complexation with acetohydroxamic acid.

Experimental Section

Reagents. The solutions of iron(III) perchlorate and sodium perchlorate were prepared as described previously.¹ Reagent grade sodium thiocyanate was twice recrystallized from distilled water. The thiocyanate solution was standardized by the Volhard method.³ Acetohydroxamic acid, CH_3CONHOH (Aldrich Chemical Co., Inc.), was recrystallized three times from ethyl acetate and dried in vacuo at room temperature.

Measurements. All the measurements were carried out in a room thermostated at $25 \pm 0.5^\circ\text{C}$. The temperature of the reaction solution was kept to within $\pm 0.1^\circ\text{C}$ by using a thermoelectric circulating bath. Ionic strength was maintained with sodium perchlorate and perchloric acid at 1.00 mol dm^{-3} for the system of acetohydroxamic acid (AHX or Hahx) and at 1.50 mol dm^{-3} for the thiocyanate system. Solutions were prepared at 25°C in molar ($\text{mol dm}^{-3} \equiv \text{M}$) concentration scale. The molar concentrations were converted to the pressure-independent molal ($\text{mol kg}^{-1} \equiv m$) scale, when necessary. Rates at high pressure

Scheme I



were measured by a high-pressure stopped-flow apparatus with spectrophotometric detection.^{1,4} Reactions were followed mainly at 500 nm in the AHX system and at 460 nm in the NaSCN system. Hydrogen ion concentrations were varied from 0.17 to 0.66 M for the AHX system and from 0.038 to 0.43 M for the SCN^- system.

Results

Reaction rates for the iron(III) complex formation were measured under the pseudo-first-order conditions where the concentration of the ligands was in large excess over that of the iron(III) ion. The backward reactions were completely negligible. In both systems the formation of higher complexes than the 1:1 iron(III) complex was observed. It was confirmed experimentally that the rate of the forward reactions was first order with respect to the respective total concentrations of iron(III) ion and ligands over the following concentration ranges: in the AHX system, $C_{\text{Fe}} = 2.8 \times 10^{-4}$ – $1.4 \times 10^{-3} \text{ M}$, $C_{\text{AHX}} = 0.08$ – 0.62 M ; in the SCN system, $C_{\text{Fe}} = 2.6 \times 10^{-5}$ – $3.9 \times 10^{-5} \text{ M}$, $C_{\text{SCN}} = 0.20$ – 0.54 M . Some experiments were also performed under excess iron(III) conditions where only the 1:1 complex was formed. The rate constants obtained were identical with those under the conditions of excess ligand concentrations. Thus, the step of the 1:1 complex should be rate limiting, and the formation of higher complexes must be faster.

Kinetics of Formation of the (Acetohydroxamato)iron(III) Complex. The rate of the formation reaction of the (aceto-

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