

Contribution from the Department of Chemistry, The University of Alberta,
Edmonton, Alberta, Canada T6G 2G2

Phosphoranes. 8. Dynamic ^{13}C NMR Studies of a Series of Fluxional Tetraalkylphosphoranes $(\text{CF}_3)_3\text{CH}_3\text{PY}$ [$\text{Y} = \text{F}, \text{Cl}, \text{OCH}_3, \text{SCH}_3, \text{N}(\text{CH}_3)_2$]

RONALD G. CAVELL,* J. ANDREW GIBSON, and KWAT I. THE

Received December 29, 1977

The averaging process which equilibrates the two distinct trifluoromethyl group environments in tris(trifluoromethyl)methylphosphoranes $(\text{CF}_3)_3\text{CH}_3\text{PY}$ [$\text{Y} = \text{F}, \text{Cl}, \text{OCH}_3, \text{SCH}_3, \text{N}(\text{CH}_3)_2$] has been examined by variable-temperature, fluorine-decoupled ^{13}C NMR spectroscopy and the observed spectra compared to those calculated by the line shape program DNMR3 to yield thermodynamic activation parameters. The free energy of activation, ΔG^\ddagger_{298} , ranges from 9.5 to 16.5 kcal/mol in the order $\text{F} < \text{Cl} < \text{OCH}_3 < \text{SCH}_3 < \text{N}(\text{CH}_3)_2$. The dimethylamino derivative has also been analyzed by temperature-dependent ^{31}P NMR spectroscopy. The compound $(\text{CF}_3)_3\text{P}(\text{CH}_3)_2$ which does not exhibit any observed fluxional behavior up to $+90^\circ\text{C}$ is assigned $\Delta G^\ddagger_{298} < 16.5$ kcal/mol. The scrambling of CF_3 environments in these compounds is probably best described by means of related multiple-step pathways consisting of sequential steps of Berry-type processes.

Introduction

The permutational processes which operate in five-coordinate phosphoranes have been of interest for many years, from both the experimental¹ and theoretical^{2,3} points of view. As a continuation of our series^{4,5} on the chemistry and stereochemistry of monofunctionally substituted phosphoranes, we have investigated the intramolecular scrambling of CF_3 groups in a series of tetraalkylphosphoranes, specifically the tris(trifluoromethyl)methylphosphoranes,⁵ $(\text{CF}_3)_3\text{CH}_3\text{PY}$ [$\text{Y} = \text{F}$ (**1**), Cl (**2**), OCH_3 (**3**), SCH_3 (**4**), $\text{N}(\text{CH}_3)_2$ (**5**)]. The related molecule,⁶ $\text{Y} = \text{CH}_3$ (**6**), which does not show NMR fluxionality to the highest accessible temperature, is reasonably included in the series.

Results and Discussion

A. Ground-State Structures. All of the compounds discussed herein displayed characteristic ^{13}C NMR spectra exhibiting, except in the case of **5** and **6**, observable fluxional behavior at $+33^\circ\text{C}$. The latter (**6**) appeared to be static up to $+90^\circ\text{C}$ whereas in the case of **5**, fluxional behavior was prominent in the spectrum at $+55^\circ\text{C}$. At appropriate reduced temperatures slow-exchange-limited ^{13}C NMR spectra (Table I) were obtained which allowed the assignment of each compound to one of two (assumed) trigonal-bipyramidal ground-state structures (Figure 1A,B) on the basis of relative magnitudes of the $^1J_{\text{PC}(\text{F})}$ and $^2J_{\text{PF}}$ coupling constants.⁴⁻⁷

The CH_3 group and the groups $\text{Y} = \text{OCH}_3, \text{SCH}_3$, and $\text{N}(\text{CH}_3)_2$ appear to preferentially occupy the equatorial plane of the trigonal bipyramid with two CF_3 groups residing in the axial position and one in the remaining equatorial position leading to ground-state structure B. The axial CF_3 substitution site is characterized by small $^1J_{\text{PC}(\text{F})}$ and $^2J_{\text{PF}}$ values while equatorial CF_3 groups have large $^1J_{\text{PC}(\text{F})}$ and $^2J_{\text{PF}}$ values presumably reflecting a greater proportion of "s" character in the equatorial P-C bonds.⁹ The ^{13}C NMR spectrum of $(\text{CH}_3)_4\text{POCH}_3$ ¹⁰ shows similar relative magnitudes of $^1J_{\text{PC}}$ which can be associated in the same way with axial and equatorial CH_3 groups. The magnitudes of $^1J_{\text{PC}(\text{H})}$ in the present system are comparable throughout and are similar to the values for the three equatorial CH_3 groups in $(\text{CH}_3)_4\text{P-OCH}_3$ ¹⁰ and for $(\text{CH}_3)_3\text{PF}_2$.¹¹ The CH_3 groups in the latter are, according to an electron diffraction study,¹³ equatorial. Thus, in keeping with the ground-state structure B, the slow-exchange ^{13}C spectra of compounds **3-6** consisted of a doublet of doublets of intensity ratio 1:2 with the larger $^1J_{\text{PC}(\text{F})}$ coupling constants associated with the unit intensity signal and the smaller $^1J_{\text{PC}(\text{F})}$ with the more intense signal.

The slow-exchange ^{13}C NMR spectra of both of the halogenophosphoranes **1** and **2** also show a 1:2 intensity ratio of signals with the reversed pattern of coupling constants; the larger $^1J_{\text{PC}(\text{F})}$ value is associated with the more intense signal.

Thus both **1** and **2** appear to have the same ground-state structure, A, in which the halide and one CF_3 group occupy the axial position and the remaining pair of CF_3 groups occupy equivalent equatorial locations along with the CH_3 group. While structure A for **2** violates the electronegativity rule,¹⁴ it does not seem reasonable to propose different ground-state structures for **1** and **2** in view of the similarity of their ^{13}C spectra. Similar conclusions were reached in the analogous $(\text{CF}_3)_2(\text{CH}_3)_2\text{PY}$ system.¹⁵

It is notable that in all of the compounds considered herein the axial ^{13}C (CF_3) resonances lie downfield of the equatorial CF_3 resonances for a given compound; however, the chemical shifts, as usual, do not exhibit a regular trend within the series. For example, axial CF_3 ^{13}C chemical shifts increase in the order $\text{Cl} < \text{SCH}_3 < \text{OCH}_3 < \text{F} < \text{CH}_3 < \text{N}(\text{CH}_3)_2$ whereas the equatorial shifts increase in the order $\text{Cl} < \text{F} < \text{SCH}_3 < \text{OCH}_3 < \text{CH}_3 < \text{N}(\text{CH}_3)_2$. Although similar, the trends are not parallel even within this limited series indicating that the ^{13}C chemical shift values are not useful for structural predictions.

B. Activation Parameters from Dynamic NMR. At temperatures above those reported in Table I all compounds (except **6**) showed evidence for intramolecular scrambling of CF_3 environments. The signals broadened considerably and in most cases finally sharpened to a simple doublet with chemical shift and coupling constant values equal to the weighted averages of the values obtained from the low-temperature-limited spectra. Thus $^1J_{\text{PC}(\text{F})_{\text{ax}}}$ and $^1J_{\text{PC}(\text{F})_{\text{eq}}}$ have the same sign and are probably positive.^{4,11}

Because solvent and solubility limitations were substantial in the case of **5**, a separate fit of the variable-temperature ^{31}P NMR spectrum was used to supplement the ^{13}C NMR data.

We have considered the rearrangement process to be intramolecular because of the solvent and concentration independence of the rearrangement process in these and similar compounds.^{4,5,15-18} The most plausible intermolecular process which could cause exchange of CF_3 environments would seem to be breaking the P-Y bond to form the intermediate phosphonium ion $(\text{CF}_3)_3\text{PCH}_3^+$; however, this process may be readily discounted in all but **2** since $^1J_{\text{PF}}$ coupling in **1** and long-range $^3J_{\text{PH}}$ couplings in **3-5** are preserved in ^1H , ^{19}F , or ^{31}P NMR spectra under fast-exchange conditions.^{4,5,15} The consistency of the results and the acceptable values of the resultant ΔS^\ddagger (note especially the low ΔS^\ddagger value for **2**) obtained throughout strongly suggest that an intramolecular fluxional process of a very similar type prevails throughout the series.

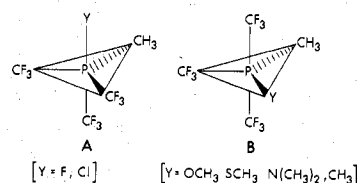
Line shapes for various rates of exchange for ^{13}C NMR spectra were computed with DNMR3¹⁹ on the basis of a VVWQ system for two equivalent CF_3 groups (axial or equatorial as



Table I. NMR Parameters for $(CF_3)_3CH_3PY$

compound	T, °C	$^1J_{PC}(H)$, Hz		$\delta(^{13}C(H))$, ^a		$^1J_{PC}(F)$, Hz (rel intens)		$\delta(^{13}C(F))$, ^a (rel intens)		$^2J_{PF}$, ^b Hz (rel intens)	
		ax	eq	ax	eq	ax	eq	ax	eq	ax	eq
1 $(CF_3)_3CH_3PF$	+27	100		+27.5		177		+124.13		102.6	
2 $(CF_3)_3CH_3PCI$	-108	72		+21.1		161		+123.90		101	
3 $(CF_3)_3CH_3POCH_3$ ^g	+33	71		+11.4		134		+126.5 ^d		101	
4 $(CF_3)_3CH_3PSCH_3$ ^h	+31	72		+12.5		n.o. ^e		n.o. ^e		n.o. ^f	
5 $(CF_3)_3CH_3PN(CH_3)_2$ ⁱ	-90	87		+11.7		21.5 (2)		+126.2 (2)		34 (2)	
6 $(CF_3)_3P(CH_3)_2$	+33	80		+15.8		49 (2)		+131.2 (2)		36 (2)	
	+33					<8 (2)		+124.4 (1)		23.5 (2)	
								+127.4 (1)		35 (1)	
								+124.4 (1)			135 (2)
								+126.9		62 (2)	
								+126.2 (2)			108.5 (1)
								+131.2 (2)			106 (1)
								+128.8 (2)			110 (1)
											114 (1)

^a Vs. ^{13}C of tetramethylsilane; positive values indicate shifts to low field of standard. ^b From ^{19}F spectra (ref 5). ^c Experimental "averaged" spectral values. ^d At +50 °C. ^e n.o. = not observed; limiting fast-exchange spectrum was not attained at +70 °C, and solvent limitations precluded further increase of temperature. ^f Not observed; axial-equatorial distinction preserved at +33 °C. ^g ^{13}C signal of OCH_3 appears as a simple doublet; $\delta(^{13}C) = +58.72$, $^2J_{PC} = 13.4$ Hz. ^h ^{13}C signal of SCH_3 at -70 °C appears to be an overlapping doublet of septets at $\delta(^{13}C) = +15.5$, with possible coupling constants: $^2J_{PC} = 9$ Hz, $^1J_{Creq} = 4.5$ Hz. ⁱ ^{13}C signal of $N(CH_3)_2$; singlet (fwhm = 9 Hz), $\delta(^{13}C) = 39.9$.

Figure 1. Alternative ground-state structures for $(CF_3)_3CH_3PY$.Table II. Permutational Processes in $(CF_3)_3CH_3PY$ Phosphoranes

ground state A		ground state B	
sets ^b	modes ^c	sets ^b	modes ^c
No Observable Processes			
(1)(3)(4)		(1)(2)(3)	
(34)(1)	ee (M_3)	(12)(3)	aa (M_3)
Single Observable Process ^e			
(1 3 4)	ae	(1 2 3)	aae
(1 4 3)	ae	(2 1 3)	aae
(3)(14)	ae	(13)(2)	ae
(4)(13)	ae	(23)(1)	ae

^a A and E stand for axial and equatorial CF_3 groups, respectively, and the numbers represent the axial (1, 2) and equatorial (3, 4, 5) positions of the trigonal bipyramid. ^b Equivalent sets of CF_3 nuclei only are considered. ^c As described in ref 22. ^d Identical nonchanging line shapes are provided by either permutation and the NMR process cannot identify the existence of this process; hence a nonobservable process. ^e All of these permutations yield identical line shapes and therefore all permutations are equivalent.

appropriate), one CF_3 group in the opposite type of site, and a phosphorus nucleus (Q) assuming $J_{wv} = 0^{20}$ and random intramolecular scrambling of V- and W-type CF_3 groups such that, for example, the unique ^{13}C groups in either ground-state structure has a 0.5 probability of exchanging with each of the two equivalent CF_3 groups. Assuming Y and CH_3 to be fixed in their ground-state locations reduces the problem to a three-site permutation between two equivalent axial and one equatorial (B) or two equivalent equatorial and one axial (A) sites for CF_3 depending on the ground-state structure. The permutational sets are delineated in Table II. The analysis is also compatible with a series of intramolecular multistep aae pairwise cyclic permutations modes²² such as the Berry pseudorotation (BPR)²³ or the turnstile rotation (TR)²⁴ with various pivots, but a single-step²⁵ BPR (or TR) is not sufficient. Observed spectra and computed simulations for two examples (2 with ground state A and 4 with ground state B) are given in Figures 2 and 3. The analysis of the ^{31}P NMR spectra of 5 was based on equivalent permutational behavior using the program EXCHSYS.²⁶

The activation parameters were derived from a linear least-squares fit of the pseudo-first-order rate constants (k) at appropriate absolute temperatures (T , K) to the Arrhenius equation and the Eyring equation²⁷ yielding the activation parameters in Table III.

Fluxional behavior has not been observed for 6 up to +90 °C, a temperature limit imposed by solvent properties and potential decomposition of this compound. We can consider 6 to have the highest barrier of the $(CF_3)_3CH_3PY$ series although the possibility of degenerate processes cannot be ruled out.

Data obtained for 4 in two solvents gave ΔG^\ddagger values in reasonable agreement considering the narrower temperature range accessible with CD_2Cl_2 . The unconstrained E_a values varied within wider limits. For comparison purposes ΔG^\ddagger_{298} values will be considered since these values are more reliable²⁸

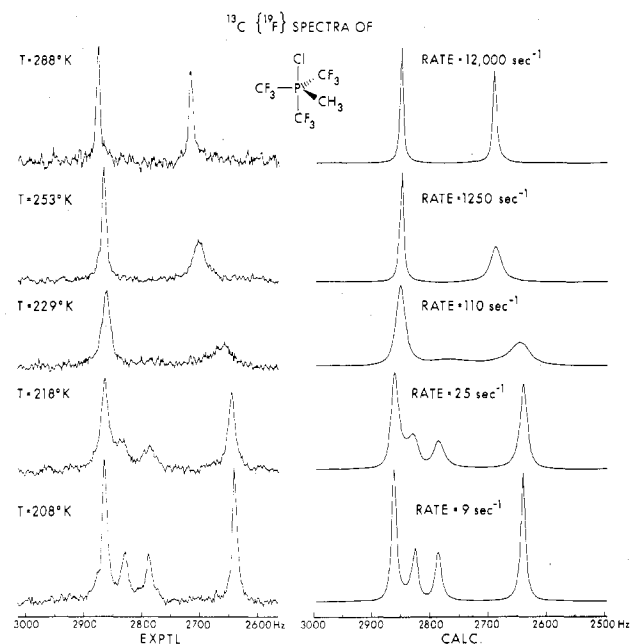


Figure 2. A selection of fluorine-decoupled Fourier transform ^{13}C NMR spectra of $(\text{CF}_3)_3\text{CH}_3\text{PCl}$ at various temperatures compared with those calculated for appropriate rates of exchange. The spectra were obtained in CD_2Cl_2 solution and the scale gives chemical shift in Hertz from ^{13}C of $(\text{CH}_3)_4\text{Si}$.

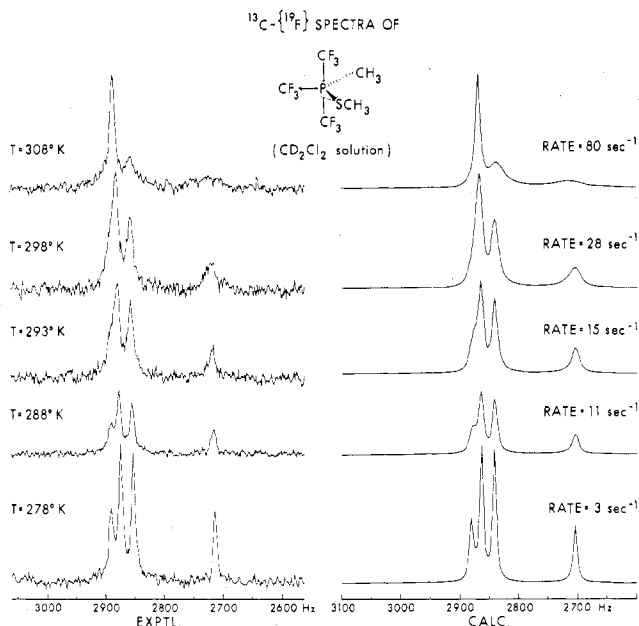


Figure 3. A selection of fluorine-decoupled Fourier transform ^{13}C NMR spectra of $(\text{CF}_3)_3\text{CH}_3\text{PSCH}_3$ at various temperatures compared with those calculated for appropriate rates of exchange. The spectra were obtained in CD_2Cl_2 solution and the scale gives chemical shifts in Hertz from ^{13}C of $(\text{CH}_3)_4\text{Si}$.

than the unconstrained values. The wide variations in the preexponential factor (A) which accompany unconstrained E_a values do not inspire confidence in these E_a values.²⁹ Barrier results obtained for **5** from either ^{13}C or ^{31}P NMR spectra are in good agreement

It is interesting that the ΔG^\ddagger_{298} values obtained in this series are similar to activation barriers determined elsewhere^{1,16} for the XPF_4 and X_2PF_3 ¹⁶⁻¹⁸ series despite the substantial difference in the nature of the substituents involved. Notably the ΔG^\ddagger_{298} values of the present series of compounds increase in the order $\text{F} < \text{Cl} < \text{OCH}_3 < \text{SCH}_3 < \text{N}(\text{CH}_3)_2 < \text{CH}_3$

Table III. Thermodynamic Parameters for Intramolecular Exchange^a

	solvent	temp range, °C	$A \times 10^{12}$	E_a , kcal	ΔH^\ddagger_T , kcal	ΔS^\ddagger_T , eu	$\Delta G^\ddagger_{T_{av}}$, kcal	T_{av}^b , K	ΔG^\ddagger_{298} , kcal
$(\text{CF}_3)_3\text{CH}_3\text{PF}$	CD_2Cl_2	-83 to -40	350 (± 180)	12.0 (± 0.3)	11.5 (± 0.2)	+6.7 (± 1)	10.1 (± 0.5)	210	9.6 (± 0.5)
$(\text{CF}_3)_3\text{CH}_3\text{PCl}$	CD_2Cl_2	-65 to +33	25 (± 0.9)	11.9 (± 0.1)	11.4 (± 0.1)	+1.2 (± 0.1)	11.2 (± 0.5)	236	11.1 (± 0.5)
$(\text{CF}_3)_3\text{CH}_3\text{POCH}_3$	CD_2Cl_2	-50 to +50	0.28 (± 0.08)	11.1 (± 0.1)	10.6 (± 0.2)	-8.0 (± 1)	12.7 (± 0.5)	274	12.9 (± 0.5)
$(\text{CF}_3)_3\text{CH}_3\text{PSCH}_3$	combined ^c	+5 to +70	52 (± 26)	16.8 (± 0.3)	16.2 (± 0.3)	+2.2 (± 1)	15.5 (± 1.0)	306	15.5 (± 1.0)
	CD_2Cl_2	+5 to +35	1800 (± 2200)	18.8 (± 0.7)	18.2 (± 0.7)	+9.3 (± 3)	15.5 (± 1.0)	294	15.5 (± 1.0)
	$\text{C}_6\text{D}_6\text{D}_2$	+20 to +70	52 (± 39)	16.8 (± 0.5)	16.2 (± 0.5)	+2.1 (± 1.5)	15.5 (± 0.7)	318	15.5 (± 0.7)
	CD_3CN	+35 to +75	0.1 (± 0.1)	14.1 (± 0.6)	13.5 (± 0.6)	-10.4 (± 2)	16.9 (± 0.8)	328	16.5 (± 0.8)
$(\text{CF}_3)_3\text{CH}_3\text{PN}(\text{CH}_3)_2$	$\text{C}_6\text{D}_6\text{CD}_3$ ^d	+30 to +90	0.0016 (± 0.0008)	11.7 (± 0.4)	11.0 (± 0.4)	-18.6 (± 1)	17.3 (± 0.5)	340	16.5 (± 0.5)

^a Obtained by a unconstrained least-squares fit of rate-temperature data obtained from ^{13}C NMR spectra unless otherwise indicated. The error limits quoted are those derived from statistical analysis. As discussed in the text, the error limits appropriate to E_a , A , ΔH^\ddagger , and ΔS^\ddagger are probably underestimated. An alternative approach to barrier analysis²⁹ gave E_a values comparable to the ΔG^\ddagger values herein. ^b These are not coalescence temperatures but rather the midpoints of the fitted region. ^c Data for two solvents below combined. ^d Obtained from line shape analysis of the ^{31}P spectrum.

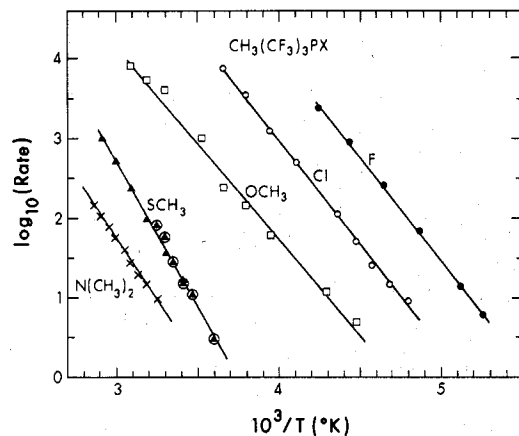


Figure 4. Arrhenius plots for $(\text{CF}_3)_3\text{CH}_3\text{PY}$. All data were obtained on one solvent system (F in $\text{CFCl}_3 + \text{CD}_2\text{Cl}_2$; Cl and OCH_3 in CD_2Cl_2 ; $\text{N}(\text{CH}_3)_2$ in CD_3CN) except for Y = SCH_3 where data obtained on $\text{c-C}_6\text{D}_{12}$ (\blacktriangle) and in CD_2Cl_2 (\bullet) are plotted on the same straight line. The points represent experimental data and the solid lines are computer-calculated least-squares equations.

which is the order of the axial preference series⁷ and which is in turn paralleled by the order of the inductive parameter σ_I of the groups indicated. These parallels may be coincidental. Unfortunately $(\text{CF}_3)_4\text{PCH}_3$, which would position CF_3 in the above series, has not been prepared to date.

In the XPF_4 system, the order of increasing barrier, deduced from a combination of line shape analysis and temperature ranges at which fluxionality ceases is¹⁷ $\text{F}, \text{CH}_3 < \text{Cl} < \text{H}, \text{SR} < \text{N}(\text{CH}_3)_2$. Except for the position of CH_3 , this order agrees with our order for tetraalkylphosphoranes. The positions of F and CH_3 are deduced, rather unreliably, by the fact that these two systems remain fluxional at the lowest temperatures attainable,^{16,17} approximately -160 to -180 °C.

The order of the barrier to fluorine permutational exchange in X_2PF_3 , deduced similarly,¹⁶ is $\text{F} \sim \text{CF}_3 < \text{Br}, \text{Cl} < \text{H} < \text{CH}_3 < \text{C}_6\text{H}_5 < \text{N}(\text{CH}_3)_2$ which is substantially different from the order for tetraalkylphosphoranes and XPF_4 systems. Again $(\text{CF}_3)_2\text{PF}_3$ and F_2PF_3 (i.e., PF_5) are assigned low barriers because equivalent fluorine NMR environments are preserved to the very lowest attainable temperatures.

Although the analysis of the NMR spectra involves the "jump" model, which is compatible with single-step M_2, M_4 modes²² or multistep BPR²³ and TR²⁴ processes but which does not provide detailed mechanistic data, the constraints of the system yield some insight into the rearrangement process. In addition, the apparent connection of the barriers with the substituent parameter suggests a possible common origin. It is notable that the barriers exhibit a regular relationship even though two different ground-state structures are involved.

Single-step processes which can be associated with the allowed permutational modes require that CH_3 and Y substituents remain fixed in their indicated ground-state locations during the rearrangement. There does not seem to be any reason either of these groups, CH_3 or Y, would remain fixed in this molecule while CF_3 moves to effect the rearrangement; therefore it is more reasonable to consider the rearrangement process to be a multistep process traversing higher energy isomers of the ground state structure. While several pathways can be envisaged involving various alternate allowed modes, we consider herein only a sequence of reasonable BPR (or equivalent TR) processes, in keeping with the conclusion that F exchange in R_2NPF_4 involves a BPR-type process.¹⁷ The observable permutational requirements are also satisfied by a series of BPR processes.

Fast nonobservable processes cannot be ruled out by the present data. For example the aeae (i.e., BPR)²³ mode with

a CH_3 pivot results in the rearrangement of isomer A into isomer B (Figure 1). If this process is rapid, a fast-exchange NMR spectrum in which the CF_3 groups appear to exist in a 1:2 relative intensity ratio will be observed, but the parameters derived therefrom would represent population weighted averages of true axial and equatorial values. We cannot, therefore, assert without qualification that the low-temperature-limiting spectra described herein represent parameters characteristic of A or B isomers. It is, however, probable that the A and B isomers of any one compound have significantly different energies and hence, at the lower limits of temperature, the relative populations of the two isomers will be different. It is upon this expected difference that the assignment of the ground-state structure is based. Although we are confident that our ground-state assignments represent the dominant constituent of the particular system, it is interesting to note that 3 which is the closest member of the series to the "crossover" point of the axial preference series wherein structures change from the ground state A to B has somewhat anomalous $^1J_{\text{PC}(\text{F})}$ values; the "axial" value is the largest and the equatorial value is the smallest of those so assigned. We cannot, therefore, exclude the possibility that the ground state of 3 contains a significant proportion of A in rapid exchange with the presumably dominant form B giving population-weighted averages of both structures to the $^1J_{\text{PC}(\text{F})}$ values obtained. Such a process must be rapid even at very low temperatures; otherwise the A and B isomers would be distinguishable in the mixture. In such a case, the relative populations of A and B and consequently coupling constants and chemical shifts should vary with temperature. Since the high-temperature averaged values of both parameters are within 1 Hz and 1 ppm of the weighted averages of the low-temperature values and since line shape analyses could be accomplished on the basis of only one isomer (B) with no discernible need to include significant proportions of the other isomer, we think that 3 exists as a single dominant isomer of structure B.

The expectation of different stabilities for each isomer upon which our assignment is based is qualitatively supported by semiempirical and ab initio molecular orbital calculations on five-coordinate phosphorus systems which suggest that an isomer of preferred stability exists.^{2,3,30,31} For the multistep rearrangement processes proposed here the observed barriers represent the greatest barrier encountered, and it is likely that the observed barriers represent those formed between less stable intermediates and the transition states involved in the interconversion. Because multistep BPR processes appear to be involved, several intermediates are possible and it is possible that the barriers are significantly influenced (or controlled) by the relative stabilization of the trigonal-bipyramidal isomers. Considering, for the sake of simplicity, only the four possible trigonal-bipyramidal isomers³² of the system, we assign the ground state on the basis of the low-temperature-limiting spectrum as described above. The least stable isomer is the trigonal-bipyramidal structure in which both CH_3 and either Y (if the ground state is B) or CF_3 (if the ground state is A) are also axial [e.g., structures C or D, respectively, of Figure 5].

Within the constraints of BPR or equivalent processes, there are a limited number of possible exchange pathways. Molecules with ground state B can be equilibrated in a two-step BPR via the intermediate C. In this case, however, C is the least stable trigonal-bipyramidal isomer and more reasonable paths might be $\text{B} \rightleftharpoons \text{D} \rightleftharpoons \text{A}^* \rightleftharpoons \text{B}^*$ or $\text{B} \rightleftharpoons \text{A} \rightleftharpoons \text{D}^* \rightleftharpoons \text{B}^*$ involving multistep BPR processes with successive Y, CF_3 , and CH_3 or CH_3 , CF_3 , and Y pivots, respectively. Similarly molecules with ground state A can avoid the least stable trigonal bipyramid D^* (through which equilibration can be

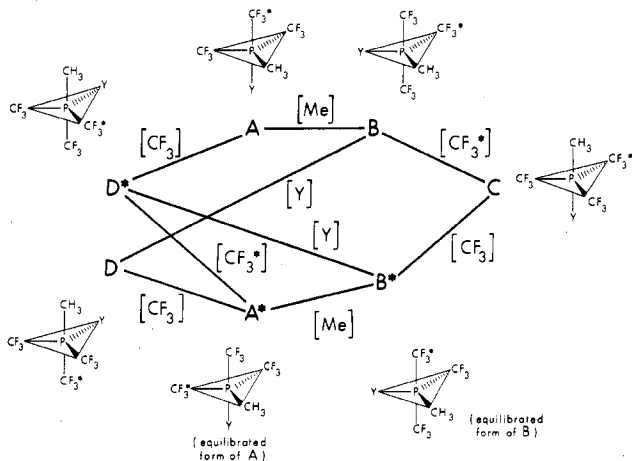


Figure 5. Some postulated exchange pathways for $(\text{CF}_3)_3\text{CH}_3\text{PY}$ based on the possible trigonal-bipyramidal isomers available in the system. The pivot for a BPR process is shown enclosed in square brackets above the line connecting two TBP isomers connected by a single-step BPR permutation. The unique CF_3 in each of the major ground states A or B is labeled (*) for identification, and the label is preserved to show the new position of this unique CF_3 in the new isomer following BPR.

achieved in two steps) by traversing the route $A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons B^* \rightleftharpoons A^*$.³³

The equivalent TR mechanisms for these BPR transformations may provide more attractive routes for equilibration which avoid the formal intermediates illustrated in Figure 5. The NMR results obtained herein, however, do not allow a choice between mechanisms of rearrangement.

Experimental Section

Compounds 1–6 were prepared as described elsewhere.^{5,6} The ^{13}C spectra were recorded on samples of the compound dissolved, when possible, in CD_2Cl_2 solution sealed under vacuum in 5 or 10 mm o.d. sample tubes. The ^{13}C signal of the solvent, which was to high field of the compounds, was used as a field–frequency lock and an internal chemical shift standard. Shift values were corrected to ^{13}C of $(\text{CH}_3)_4\text{Si}$. Fluorine-19 decoupling was used in order to reduce the complexity of the spectrum, and for this reason fluorinated solvents were generally avoided since these fluorinated solvents were perturbed by the modulated ^{19}F decoupler and produced signals close to the $^{13}\text{CF}_3$ region of interest. Aromatic solvents which have ^{13}C resonance signals which obscure the $^{13}\text{CF}_3$ region of interest were also avoided. Little or no Overhauser enhancement of the ^{13}C signals was obtained because coupled nuclei remain in the molecules^{9,34,35} in these molecules. This effect and the presence of other possible intensity-reducing mechanisms such as quadrupolar and possibly also scalar relaxation processes^{34,35} necessitated the use of relatively high sample concentrations, especially in the case of the chloride where signal/noise ratios were poor even at high concentrations. Considerable care was necessary to ensure that optimum solution concentrations and spectrometer conditions existed in order that spectra with an acceptable S/N ratio were obtained while at the same time the necessary low temperatures could be achieved without solidification of the sample. In all cases the ^{13}C NMR spectra of 1–5 were adequate for the line shape analysis although the latter provided the greatest difficulty due to solvent and solubility limitations.

A mixed solvent, $\text{CFCl}_3\text{--CD}_2\text{Cl}_2$, was required for 1 in order to obtain the necessary very low temperature spectra, and a suitable spectrometer setting was employed to avoid the modulation problem mentioned above. Two different solvents, CD_2Cl_2 and C_6D_{12} , were used for studies of 4; the latter solution extended the upper limit of the accessible temperature range. The results indicate that the exchange processes are solvent and concentration independent.

For measurement of ^{13}C NMR spectra the ^{19}F decoupler was set precisely at the ^{19}F resonance frequency of the CF_3 groups of the compound in question. This was extremely important since, in the intermediate exchange region, the spectra were broad and measurement

of half-height width was not an effective method of determining decoupling efficiency. Off-resonance decoupling, even only 200 Hz from the required value, sometimes produced serious intensity distortions in the spectra. Random tests were made to ensure that decoupling was at maximum efficiency. In the case of compound 1 setting the decoupler at the trifluoromethyl group frequency was sufficiently effective in removing residual $^1\text{J}_{\text{CF}}$ coupling.

The ^{13}C spectra were collected with a Bruker HFX 90 spectrometer operating in FT mode at 22.6 MHz. Fluorine decoupling frequencies were generated by a HP 5110B frequency synthesizer multiplied by 3 by the Bruker console prior to amplification by the Bruker broad-band decoupler and further modulated by the imposition of 4167-Hz sidebands. Typical settings for data acquisition were 4000 pulses, 8- μs pulse widths, and 0.8-s pulse intervals. Temperature control was provided by the Bruker temperature controller ascertained by calibration to be within ± 1 $^\circ\text{C}$ of the values quoted. No detectable temperature gradients existed along the sample tube in the sample-containing region.

Compound 5 ($X = \text{N}(\text{CH}_3)_2$) appeared “rigid” at ambient temperature and heating to the temperature limit of CD_2Cl_2 in thin-wall 10-mm NMR tubes (~ 50 $^\circ\text{C}$) produced only slight broadening of the spectrum. CD_3CN proved to be a satisfactory solvent up to $+80$ $^\circ\text{C}$. Because line shape analysis of the ^{13}C NMR spectra of 5 was less reliable because of difficulties in obtaining spectra at the higher temperatures, the ^{31}P NMR spectra were also analyzed. These spectra were obtained on the Bruker instrument operating in FT mode at 36.4 MHz with ^1H decoupling. The sample of compound 5, dissolved in toluene- d_8 contained in a 5 mm o.d. tube, was placed inside a 10 mm o.d. thin-wall tube containing D_2O reference lock. Typical settings for data acquisition were 900 pulses, 10- μs pulse widths, and 0.8-s pulse intervals.

Compound 6 ($Y = \text{CH}_3$) did not display any features in the ^{19}F , ^{13}C , or ^{31}P spectra, indicative of exchange of CF_3 groups up to $+90$ $^\circ\text{C}$.

Acknowledgment. We thank the National Research Council of Canada and The University of Alberta for financial support of this work. J.A.G. acknowledges with thanks the award of a NRC postdoctoral fellowship. We thank Dr. T. Nakashima, Mr. G. Bigam, and Mr. T. Brisbane for their help with the spectral measurements. We also thank Dr. Larry Vande Griend for additional ^{13}C and ^{31}P NMR studies on $(\text{CF}_3)_3\text{CH}_3\text{P-N}(\text{CH}_3)_2$.

Registry No. 1, 56396-13-5; 2, 56420-21-4; 3, 56350-99-3; 4, 63715-50-4; 5, 63715-49-1; 6, 57539-04-5; ^{13}C , 14762-74-4.

References and Notes

- J. P. Jesson and E. L. Muetterties in “Dynamic Nuclear Magnetic Resonance Spectroscopy”, L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975.
- J. A. Altmann, K. Yates, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **98**, 1450 (1976).
- (a) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94**, 3035 (1972); (b) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972); (c) J. B. Florey and L. C. Cusachs, *ibid.*, **94**, 3040 (1972); (d) A. Stritch and A. Veillard, *ibid.*, **95**, 5574 (1973).
- R. G. Cavell, J. A. Gibson, and K. I. The, *J. Am. Chem. Soc.*, **99**, 7841 (1977).
- (a) K. I. The and R. G. Cavell, *Inorg. Chem.*, **16**, 2887 (1977); (b) *J. Chem. Soc., Chem. Commun.*, 279 (1975).
- K. I. The and R. G. Cavell, *J. Chem. Soc., Chem. Commun.*, 716 (1975).
- R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J. Chem. Soc., Chem. Commun.*, 19 (1974).
- P. R. Wells, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, **6**, 147 (1968); S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *ibid.*, **10**, 1 (1973).
- J. W. Emsley, J. Feeney, and L. H. Sutcliffe, “High Resolution Nuclear Magnetic Resonance Spectroscopy”, Vol. 1 and 2, Pergamon Press, London, 1966.
- H. Schmidbaur, W. Buchner, and F. H. Köhler, *J. Am. Chem. Soc.*, **96**, 6208 (1974).
- H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Commun.*, 671 (1970).
- A. J. Downs and R. Schmutzler, *Spectrochim. Acta, Part A*, **23**, 681 (1967).
- H. Yow and L. S. Bartell, *J. Mol. Struct.*, **15**, 209 (1973).
- E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).
- R. G. Cavell and K. I. The, *Inorg. Chem.*, **17**, 355 (1978).
- C. G. Moreland, G. O. Doak, L. B. Littlefield, N. S. Walker, J. W. Gilge, R. W. Braun, and A. H. Cowley, *J. Am. Chem. Soc.*, **98**, 2161 (1976).

- (17) M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutsch, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 5385 (1974).
- (18) R. G. Cavell, N. T. Yap, J. A. Gibson, L. Vande Griend, unpublished work.
- (19) G. Binsch and D. L. Kleier, "DNMR3, A Computer Program for the Calculation of Exchange Broadened NMR Spectra", Program 165, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- (20) This procedure is acceptable since there is a negligible chance of having two $^{13}\text{CF}_3$ groups in the same molecule in systems such as the present with natural-abundance carbon-13 nuclei.
- (21) W. Klemperer, in "Dynamic NMR Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975.
- (22) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 5662 (1972).
- (23) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
- (24) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971).
- (25) A one-step BPR effects a trigonal-bipyramidal (TBP) to TBP rearrangement (via the square-pyramidal transition state or intermediate). In all cases considered herein, the product is a distinctly different isomer of the system in contrast to XPY₄ systems and the product isomer must return to an equilibrated, indistinguishably rearranged form of the initial isomer. Preserving the pivot and reverting by the reverse BPR process implies that the product has a short lifetime on the NMR time scale or the BPR process is instantaneous, but in either case axial-equatorial interchange does not result. Changing the pivot in the rearrangement implies the existence of a TBP intermediate with a sufficiently long lifetime for the species to "forget" the originally employed pivot and execute a second BPR with an arbitrarily chosen pivot achieving the desired equilibration.
- (26) A locally adapted version of the program EXCHSYS described by J. K. Kreiger, J. M. Deutsch, and G. M. Whitesides, *Inorg. Chem.*, **12**, 1535 (1973). Details of the program are given in the thesis of J. K. Kreiger, MIT, Cambridge, Mass., 1971.
- (27) K. Laidler, "Chemical Kinetics", McGraw-Hill, New York, N.Y., 1950.
- (28) G. Binsch in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975.
- (29) Alternative analysis of the rate data assuming an intramolecular process with $\Delta S^\ddagger = 0$ and $A = 10^{13.2}$ yielded ΔH^\ddagger and E_a values which were within 0.5 kcal of each other. The resultant E_a values are within 1.0 kcal of and possess the same relative order as the ΔG^\ddagger_{298} values obtained by unconstrained least-squares analysis which are shown in Table III; thus the present comparisons based on ΔG^\ddagger_{298} are not altered of constrained intramolecular E_a values are used.
- (30) J. M. Howell, *J. Am. Chem. Soc.*, **97**, 3930 (1975); F. Keil and W. Kutzelnigg, *ibid.*, **97**, 3623 (1975); J. M. Howell, J. R. Van Wazer, and A. R. Rossi, *Inorg. Chem.*, **13**, 1747 (1974).
- (31) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).
- (32) Clearly square-pyramidal isomers are also possible and may well be more stable than some of the trigonal-bipyramidal isomers considered.^{2,3,30,31} In a complex system such as this one, the appropriate choice of structures is not clear; we make the simplifying assumptions that there is a "square pyramid" (regular or distorted) of higher energy² related to each of the TBP isomers shown which may be close to the transition-state geometry and that we can map a rearrangement through a series of isomers.
- (33) A single ae permutation of the equatorial CH₃ group and the axial CF₃ group effects the A → D conversion and achieves equilibration in a single step, and while such a process may be possible, it cannot be either a BPR or TR mechanism which are cyclic permutations of the type aeae in which an axial pair is swapped for an equatorial pair by means of an appropriate motion. Thus D* is accessible from A by BPR whereas D is not. Similarly one-step equilibration would be achieved by direct A → C transformation, a transformation not available by means of a BPR or TR process.
- (34) J. B. Stothers, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1972.
- (35) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971.

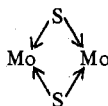
Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Synthesis and Characterization of Several Novel Molybdenum Complexes of Cyclic Polythiaethers. Crystal and Molecular Structure of *sym*-Dihydrosulfido-bis(μ -1,5,9,13-tetrathiacyclohexadecane)-dimolybdenum(II) Trifluoromethanesulfonate Dihydrate

JOHN CRAGEL, JR., VIRGINIA B. PETT, MILTON D. GLICK, and RICHARD E. DESIMONE*

Received December 27, 1977

The reaction of $[\text{Mo}_2(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_4](\text{CF}_3\text{SO}_3)_2$ with the cyclic polythiaether 1,5,9,13-tetrathiacyclohexadecane yields several products, three of which have been extensively characterized. They are *sym*-dihydrosulfido-bis(μ -1,5,9,13-tetrathiacyclohexadecane)-dimolybdenum(II) trifluoromethanesulfonate dihydrate (I), ethoxidoobis(1,5,9,13-tetrathiacyclohexadecane)- μ -oxo-dimolybdenum(IV) trifluoromethanesulfonate hydrate (II), and hydrosulfido(1,5,9,13-tetrathiacyclohexadecane)oxomolybdenum(IV) trifluoromethanesulfonate (III). These are the first complexes in which molybdenum is coordinated by a macrocyclic ligand. I is a completely sulfur-coordinated sulfur-bridged binuclear species, II an oxo-bridged binuclear species, and III a monomer. UV-visible, IR, NMR, and cyclic voltammetric data are presented. Complex I crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell of dimensions $a = 10.827(2)$ Å, $b = 11.921(2)$ Å, $c = 9.234(1)$ Å, $\alpha = 97.22(1)^\circ$, $\beta = 104.42(1)^\circ$, $\gamma = 108.21(2)^\circ$, and $V = 1069.5(4)$ Å³. Full-matrix least-squares refinement gave final discrepancy factors of $R_1 = 0.040$ and $R_2 = 0.067$ for 2637 data having $F^2 > 2.5\sigma(F^2)$. The molecular structure is highlighted by the presence of a



bridging unit with the bridging sulfurs each belonging to an intact macrocycle coordinated in the endo configuration. The Mo-Mo distance is 2.823 Å, and the metal-sulfur distances in the Mo coordination sphere imply that the bridge functions as a quite effective bonding unit. The other unique feature of this molecule is the presence of a terminal -SH group on each Mo atom, the first reported example of such an anion on a Mo^{II} complex.

Introduction

Complexes of macrocyclic ligands have in recent years received attention from an increasingly large share of inorganic chemists. Much of this attention has been devoted to nitrogen-containing macrocycles which have the obvious feature of serving as (sometimes) useful models for naturally occurring macrocyclic species.¹⁻⁵ More recently, oxygen-containing

macrocycles—the "crown ethers" and the bicyclic cryptates—have also been the focus of considerable interest, again mainly from a biological viewpoint.⁶⁻⁸ Large cyclic molecules containing sulfur as the heteroatom have received less attention than probably any class of macrocyclic species,⁹⁻¹³ although their potential utility in several areas should not be underestimated. We have been involved in a program of synthesis