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(14) The ^{11}B{^{1}H} NMR spectrum of XIIb displayed a >BH$_2$ triplet at 32.8 ppm (J_{BP} = 77 Hz) and a >B(CH$_3$)$_2$ triplet at 23.2 ppm (J_{BP} = 71 Hz) in a ratio of 2:1 (all shifts are shielded with respect to external BF$_3$·O(C$_2$H$_5$)$_2$); the ^{1}H-coupled spectrum consisted of a well-resolved triplet for the >B(CH$_3$)$_2$ and a triplet of triplets (J_{BH} = 99 Hz) for the >BH$_2$ groups.
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Phosphoranes. 7. Chemistry and Stereochemistry of Monofunctionally Substituted Tetraalkylphosphoranes, $(CH_3)_2(CF_3)_2PY$ [Y = F, Cl, OCH_3, SCH_3, and $N(CH_3)_2$], Including a Second Example of Individual Nonequivalence of Fluorine Atoms in a Trifluoromethyl Group Attached to Phosphorus[1]

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Methylation of (CF$_3$)$_2$PCl$_3$ with excess (CH$_3$)$_4$Pb leads to dimethylated molecular phosphoranes, (CF$_3$)$_2$P(CH$_3$)$_2$Cl, which can be fluorinated (with SbF$_3$) to (CF$_3$)$_2$P(CH$_3$)$_2$F, converted to the derivatives (CF$_3$)$_2$(CH$_3$)$_2$PECH$_3$ (E = O and S) by means of the silyl reagent (CH$_3$)$_3$SiECH$_3$, and converted to (CF$_3$)$_2$(CH$_3$)$_2$PN(CH$_3$)$_2$ with (CH$_3$)$_2$NH. NMR spectroscopic studies strongly suggest molecular phosphorane structures in which halogens (X = F and probably Cl) and CF$_3$ groups occupy axial positions in the trigonal bipyramid. Alkaline hydrolysis of all compounds results in the formation of 2 mol of CF$_3$H and the (CH$_3$)$_2$PO$_2$$^-$ ion, whereas neutral hydrolysis yields 1 mol of CF$_3$H and CF$_3$(CH$_3$)$_2$PO. The very low temperature (−110 °C) ^{19}F NMR spectrum of (CH$_3$)$_2$(CF$_3$)$_2$PSCH$_3$ consists of an [AB$_2$]$_2$P spectral pattern with $^2J_{PF_A}$ = 19.4, $^2J_{PF_B}$ = 9.5, and $^2J_{F_AF_B}$ = 108 Hz, showing that F atom equivalence within both CF$_3$ groups has been destroyed, presumably as the result of steric interactions with the SCH$_3$ group.

Introduction

Extension of methylation reactions to bis(trifluoromethyl)halogenophosphoranes leads to a series of tetraalkylphosphoranes with two methyl and two trifluoromethyl substituents which are complementary to the monomethylated tetraalkylphosphoranes[1] reported earlier. In these and related[2-5] systems, we have found that temperature-dependent ^{19}F (and also ^{1}H, ^{31}P, and ^{13}C) NMR spectroscopy appears to indicate the position of the substituent in the five-coordinate molecular framework. This and related work have led to an empirical axial preference series.[6] Herein we describe the preparation, characterization, and substitutional preferences in the series (CH$_3$)$_2$(CF$_3$)$_2$PY, where Y = F, Cl, OCH$_3$, SCH$_3$, and N(CH$_3$)$_2$, and an interesting case of magnetic nonequivalence of the F atoms in the (axial) CF$_3$ NMR of (CH$_3$)$_2$(CF$_3$)$_2$PSCH$_3$ at very low temperatures.

Results and Discussion

Synthesis. The action of (CH$_3$)$_4$Pb on (CF$_3$)$_2$PCl$_3$ leads to (CH$_3$)$_2$(CF$_3$)$_2$PCl or CH$_3$(CF$_3$)$_2$PCl$_2$^{3} according to the reaction conditions (eq 1 and 2). Reaction 1 therefore provides an alternative route to the latter compound first synthesized by direct oxidative chlorination of CH$_3$(CF$_3$)$_2$P.[3]

$$(CF_3)_2PCl_3 + (CH_3)_4Pb \rightarrow CH_3(CF_3)_2PCl_2 + (CH_3)_3PbCl \qquad (1)$$

$$(CF_3)_2PCl_3 + 2(CH_3)_4Pb \rightarrow (CH_3)_2(CF_3)_2PCl + 2(CH_3)_3PbCl \qquad (2)$$

Fluorination of the chlorophosphorane was smoothly effected by SbF$_3$ at ordinary temperatures (eq 3), and the silyl reagents (CH$_3$)$_3$SiOCH$_3$ and (CH$_3$)$_3$SiSCH$_3$ converted the chloro- or fluorophosphorane to the methoxy or methylthio derivative in good yields (eq 4).

$$(CH_3)_2(CF_3)_2PCl \xrightarrow{SbF_3} (CH_3)_2(CF_3)_2PF \qquad (3)$$

$$(CH_3)_2(CF_3)_2PX + (CH_3)_3SiECH_3 \rightarrow (CH_3)_2(CF_3)_2PECH_3 + (CH_3)_3SiX \qquad (4)$$

X = F or Cl; E = O or S

Both of the resultant derivatives appear to be stable at ordinary temperatures, in contrast to the dimethylamino derivative, (CH$_3$)$_2$(CF$_3$)$_2$PN(CH$_3$)$_2$, prepared by direct dimethylaminolysis (eq 5), which appeared to decompose readily in the vacuum system whenever transfer was attempted.

$$(CH_3)_2(CF_3)_2PCl + 2(CH_3)_2NH \rightarrow (CH_3)_2(CF_3)_2PN(CH_3)_2 + (CH_3)_2NH_2Cl \qquad (5)$$

Because of this unexpected instability, only NMR spectral characterization of the aminophosphorane was achieved.

Neutral hydrolysis of all of the stable phosphoranes yielded 1 molar equiv of CF$_3$H, leaving CF$_3$(CH$_3$)$_2$PO in solution (eq 6). The phosphine oxide, CF$_3$(CH$_3$)$_2$PO,[7] a volatile crystalline solid, was synthesized independently from CF$_3$(CH$_3$)$_2$PCl$_2$ and H$_2$O and from CF$_3$(CH$_3$)$_2$PCl$_2$ and [(CH$_3$)$_3$Si]$_2$O.

$$(CF_3)_2(CH_3)_2PX + H_2O \rightarrow CF_3H + CF_3(CH_3)_2PO + HX \qquad (6)$$

Alkaline hydrolysis of the phosphoranes yielded 2 molar equiv of CF$_3$H, with the (CH$_3$)$_2$PO$_2$$^-$ ion remaining in solution (eq 7).

$$(CF_3)_2(CH_3)_2PX + 2H_2O \xrightarrow{OH^-} 2CF_3H + (CH_3)_2PO_2^- + H^+ + HX \qquad (7)$$

Mass Spectroscopy. In keeping with the typical behavior of pentacoordinate fluorophosphoranes[8] and trifluoromethylphosphoranes,[1,3-5] parent molecular ions were not observed in the mass spectra of any of these tetraalkyl-

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Table I. Mass Spectral Data[a] of $(CF_3)_2P(CH_3)_2X$

	X				
m/e	F	Cl	OCH_3	SCH_3	Assignment[b]
231				0.1[c]	$(CF_3)_2P(CH_3)_2{}^{32}S$
215			0.7[c]		$(CF_3)_2P(CH_3)_2O$
203	0.6[c]	0.35			$(CF_3)_2P(CH_3)F$
200	0.4	0.35	0.5		C_3F_7P
199	1.9[c]	0.35[c]	10.0[c]	3.4[c]	$(CF_3)_2P(CH_3)_2$
198	0.4				$(CF_3)_2P(CH_3)CH_2$
177				3.4[c]	$CF_3P(CH_3)_2{}^{32}SCH_3$
165			0.7		$C_3F_4H_6OP$
162			0.7		$C_3F_4H_3OP$
161			13.5		$CF_3P(CH_3)_2(OCH_3)$
156		1.1			CF_3PH_2FCl
153	6.6[c]	1.9	0.5		$C_2H_3F_5P$
150	0.6				C_2F_5P
149	19.0[c]	3.0	5.9	1.7	$CF_3PF(CH_3)_2$
147			0.5		$C_3H_7F_3OP$
142		0.7			$F_4P^{35}Cl$
131		3.0			C_2F_4P
130	0.2		1.4	1.3	$C_3F_3H_6P$, $C_2F_3H_2OP$, $C_2F_2H_5{}^{32}SP$
129	2.5	0.7	0.2		$C_3H_5F_3P$, C_2F_3HOP
127		0.35			$C_3H_6F^{35}ClP$
115			0.7		CF_3PCH_3, $C_2H_6F_2OP$
112			0.2		$C_2H_3F_2OP$
111			9.5		$C_2F_2H_2OP$
103	5.8	1.1	0.2		F_3PCH_3
100	0.6				CF_3P
99	17.1	5.8	8.3	3.2	$C_2H_6F_2P$
93				4.7	$C_2H_6P^{32}S$
92		0.35	0.7		C_3H_6FP, C_3H_9OP
91		0.7	0.2		C_3H_5FP, C_3H_8OP
90				1.3	C_3H_4FP, C_2H_3PS
88				7.7	F_3P, C_2HPS
86				7.7	CH_5F_2P, C_2PS
84	0.6				CH_4F_2P
81	0.2	4.2	2.1		CF_2P
80		0.7	1.9	1.3	C_2H_6FP
79	3.1	0.7	1.2	0.9	C_2H_5FP
78	3.1		0.2		C_2H_4FP
77		10.0	8.8	0.9	C_2H_3FP, C_2H_6OP, CHSP
76	1.2				C_3H_9P
73			0.2	0.9	C_3H_6P, C_2H_2OP
69	9.9	13.8	4.7	3.4	CF_3, F_2P
67		0.7			$HP^{35}Cl$
65	8.7	7.3	3.6	2.6	CH_3FP
64	1.4	0.35	0.2		CH_2FP
63	0.4		1.9	0.9	CH_4OP, PS
62			0.2		CH_3OP, PCF
61	0.6	1.1	2.6	2.1	C_2H_6P
59	1.0		1.7	1.7	C_2H_4P, CHOP
58	0.4		0.7		COP
57	1.4		1.4	0.9	C_2H_2P
56	0.2				HC_2P
53				6.0	H_2SF, H_3PF
51	3.5	4.3	1.0	17.5	HPF, CF_2H, SF, $H_4C^{35}Cl$
50	1.7	1.8	0.5	0.9	PF, CF_2, $H_3C^{35}Cl$
49		1.8	1.0	1.3	POH_2, $H_2C^{35}Cl$
48				6.4	POH, CH_4S
47		4.4	3.1	8.1	CH_4P, PO, CH_3S, $C^{35}Cl$
46		0.35	1.2	1.7	CH_3P, C_2H_6O, CH_2S, C_2H_3F
45	4.8	1.8	3.6	5.5	CH_2P, C_2H_5O, C_2H_2F
44	1.4	1.4	0.7	0.9	CHP, C_2H_4O, C_2HF
41	1.0	0.35	0.2		C_3H_5, HC_2O
40		0.35	0.5		C_3H_4, C_2O
38		5.5			$H^{37}Cl$
37		0.35			^{37}Cl
36		15.8			$H^{35}Cl$
35		1.1			^{35}Cl
32			2.3		CH_3O, HP, HCF
31		2.5			P, CF

[a] Expressed as percent of total ionization, which is the sum of all ions with *m/e* ≥ 30 and intensity <1% of base peak. [b] Reasonable structural formulas are quoted for some ions merely for ease of recognition. [c] Identity confirmed by mass measurement. See Table II.

phosphoranes but all showed an ion at *m/e* 199, which was identified as $(CH_3)_2(CF_3)_2P^+$ by mass measurement. In addition, the spectra showed fragments corresponding to $CF_3(CH_3)_2PF^+$, arising in the spectrum of $(CH_3)_2(CF_3)_2PF$, $C_4H_6F_6OP^+$ ($CH_3(CF_3)_2POCH_3{}^+$?) in the spectrum of $(CH_3)_2(CF_3)_2POCH_3$, and $C_4H_6F_6SP^+$, in the case of

Table II. Mass Spectra Data of $(CF_3)_2P(CH_3)_2X$

Compound	Ion[a]	Mass	
		Calcd	Found
$(CF_3)_2P(CH_3)_2F$	$(CF_3)_2P(CH_3)F^+$	202.9861	202.9863
	$(CF_3)_2P(CH_3)_2{}^+$	199.0111	199.0109
	$(CF_3)(CH_3)PF_2{}^+$	152.9893	152.9889
	$(CF_3)P(CH_3)_2F^+$	149.0143	149.0139
$(CF_3)_2P(CH_3)_2Cl$	$(CF_3)_2P(CH_3)_2{}^+$	199.0111	199.0109
$(CF_3)_2P(CH_3)_2OCH_3$	$(CF_3)_2P(CH_3)OCH_3{}^+$	215.0061	215.0067
	$(CF_3)_2P(CH_3)_2{}^+$	199.0111	199.0119
$(CF_3)_2P(CH_3)_2SCH_3$	$(CF_3)_2P(CH_3)_2S^+$	230.9832	230.9828
	$(CF_3)_2P(CH_3)_2{}^+$	199.0111	199.0107
	$(CF_3)P(CH_3)_2SCH_3{}^+$	177.0115	177.0116

[a] Structural formulas are given solely for convenience of identification.

Table III. Infrared Spectra Data of $(CF_3)_2P(CH_3)_2X$[a]

X				
F	Cl[b]	OCH_3	SCH_3	Assignment
	3000 w	3020 w	3020 w	ν(C–H)
	2940 m	2990 w	2940 w	
	2880 w			
1430 vw	1410 m	1465 w	1430 w	δ_{as}((P)C–H)
1370 w		1330 w	1330 w	
1310 w	1310 m	1310 w	1300 w	δ_s((P)C–H)
		1260 w		
1210 vs	1200 vs	1200 vs	1165 vs	ν(C–F)
1175 s	1180 vs		1120 s	
1160 vs	1150 vs	1150 sh	1110 s	
1090 vs	1090 s	1115 vs	1090 vs	
		975 s		P–O–C
990 m	970 s		970 m	δ(P–C(H))
920 m	930 s	920 w	900 w	
860 m	870 m	850 m	845 w	ν_{as}(P–C(H))
780 m	760 m	735 m	745 w	δ_s(C–F)
725 w				
675 m	665 m		670 w	ν_s(P–C(H))
630 vs				ν(P–F)
		590 w		
540 w	550 w	545 m	540 w	δ_{as}(C–F)
505 w		490 s	470 m	ν(P–C(F))
455 m				
430 w	430 s			
	410 s			
	370 s			

[a] Gas-phase spectra at +25 °C unless otherwise noted. All values are in cm^{-1}. Abbreviations and symbols are: s = strong, m = medium, w = weak, v = very, sh = shoulder, ν = stretch, δ = deformation, s = symmetric, and as = asymmetric. [b] Obtained at approximately +70 °C.

$(CH_3)_2(CF_3)_2PSCH_3$, consistent with the formulas of the parent phosphoranes. Mass spectral data are given in Tables I and II.

Infrared Spectroscopy. Infrared spectra (Table III) identify the major structural features in each compound. Notable is the very low value of the P–F stretch (630 cm^{-1}) in $(CH_3)_2(CF_3)_2PF$, characteristic of an axial stretching frequency.[9]

NMR Spectroscopy and Essential Stereochemistry. We assume, as before,[1,3-5] and in view of considerable supporting evidence,[9,10] that the basic molecular framework of these molecules is trigonal bipyramidal, although it is possible that significant distortions from this ideal geometry occur in such crowded molecules. The very low temperature (–110 °C) spectra of $(CH_3)_2(CF_3)_2PSCH_3$, as discussed below, may provide some support for an alternative framework such as the square pyramid; however, the inconsistencies which arise from this structure lead us to favor the trigonal bipyramid as the basic prevailing structure. The NMR spectral parameters are given in Table IV.

The normal-temperature ^{19}F NMR spectrum of $(CH_3)_2(CF_3)_2PF$ consisted of a unit intensity signal, comprising a major doublet (719 Hz) of septets with septet fine structure in each component, which is readily assigned to the signal arising from the unique F atom directly bound to P and coupled to two equivalent CF_3 and two equivalent CH_3 groups. The existence of the major doublet due to P–F coupling and the additional fine structure arising from the coupling of the unique F to the CF_3 and, in the normal-temperature ^1H NMR, the CH_3 group, supports the phosphorane formulation. The more intense ^{19}F NMR signal due to the CF_3 groups consisted of two regions of approximately equal relative intensity; a doublet of multiplets and a single broad multiplet peak. Cooling the sample to 0 °C gave much improved resolution, and the two regions could be readily assigned to two magnetically nonequivalent CF_3 groups coupled to P, the unique F, and each other (Figure 1). The low-field signal, a doublet of doublets of quartets with a relatively large $^2J_{PF}$ coupling constant, is assigned to the equatorial CF_3 group.[6] The high-field signal, an overlapping doublet of doublets of quartets with a relatively small $^2J_{PF}$ coupling constant, is assigned to the axial CF_3 group.[6] In both cases, the major doublet arises from coupling of a CF_3 group with the P atom, and the minor doublet arises from coupling with the unique F atom. The quartet structure arises from coupling of each CF_3 group with the 3 F atoms of the other CF_3 group. It is notable that the axial CF_3 group is observably coupled to the single F trans to it ($^3J_{FF}$), whereas in the cases investigated earlier,[3-5a] this

Table IV. NMR Data for $(CH_3)_2(CF_3)_2PX$

X	Temp, °C	Chemical shifts, ppm			Coupling constants, Hz				
		τ[a]	ϕ[b]	δ_P[c]	$^2J_{PF}$	$^2J_{PH}$	$^3J_{PH}$	$^4J_{FH}$	$^5J_{FH}$
F[d]	–20	8.10[e,f]	63.6[g,j]	166.3[l,m]	127.0[j]	15.5	–	*f*	–
			73.3[h,k]		20.0[k]				
			–4.1[i]						
Cl	+33	7.46[f,n]	63.0[o]	162.1[l,p]	79.0[q]	16.2			
	–90		65.0[o]		78.5[q]				
OCH_3	+33	8.35[r,s]	71.9[k,u]	182.6[l,p]	41.0[k]	12.0	–	0.8	–
		6.17[s,t]			–	–	13.7	–	1.2
$N(CH_3)_2$[v]	–30	8.29[r,s]	69.4[k,n]	190.4[l,p]	16.6[k]	12.5	–	0.7	–
		7.24[s,w]			–	–	12.2	–	1.3
SCH_3[y]	+33	8.12[r,s]	68.1[k,n,y]	197.4[l,p]	15.0[k]	13.0	–	0.8	–
		7.63[s,x]			–	–	19.6	–	2.0

[a] ppm vs. $(CH_3)_4Si$ (τ = 10.0). [b] ppm vs. CCl_3F, positive values indicating resonance to high field of standard. [c] ppm vs. P_4O_6,[22] positive values indicating resonance to high field of standard. [d] The ^1H spectrum at +33 °C is a very broad doublet. Other coupling constants at –20 °C are $^1J_{PF}$ = 719, $^3J_{FH}$ = 9.0, $^3J_{FCF(eq)}$ = 15.0 (cis), $^3J_{FCF(ax)}$ = 20.0 (trans), and $^4J_{FF}$ = 12.5 Hz. [e] Doublet of doublets. [f] $^4J_{FCPCH}$ not resolved. [g] Relative intensity = 1; double doublet of quartets. [h] Relative intensity = 1; overlapping double doublet of quartets. [i] Spectrum of F on P, doublet of broad lines. [j] CF_3 equatorial. [k] CF_3 axial. [l] Hydrogen-decoupled spectrum. [m] Doublet of quartets of quartets. [n] Broad doublet. [o] Doublet. [p] Septet. [q] Averaged CF_3 environment? [r] CH_3 on P. [s] Doublet of septets. [t] CH_3O group. [u] Doublet of multiplets broadening to singlet at –90 °C. [v] Compound unstable at room temperatures; see text. [w] $(CH_3)_2N$ group. [x] CH_3S group. [y] See text and Table V regarding the ^{19}F AB_2 spectrum at –110 °C.

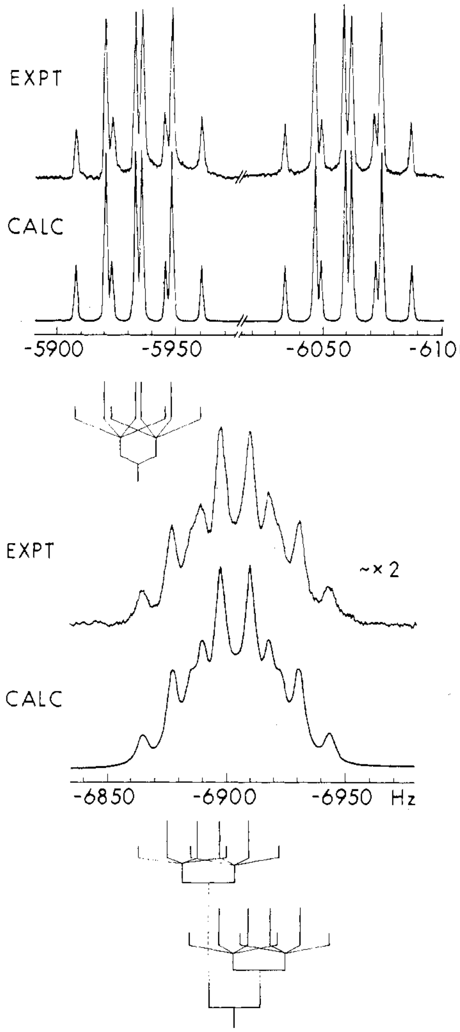

Figure 1. ^{19}F NMR (94.2 MHz) spectra of $(CH_3)_2(CF_3)_2PF$ (CF_3 region only) at 0 °C. The stick diagrams illustrate the origin of the coupling interactions, and the calculated spectra were obtained with the parameters given in Table IV. The scale values give chemical shifts in Hz vs. $CFCl_3$, with negative offset frequencies indicating resonance to high field of the standard.

coupling was either small or not observed. A value of 12 Hz was inferred[1] for $^3J_{FF}$ between the unique F and the CF_3 group trans to it in the case of $CH_3(CF_3)_3PF$ because of the improved agreement of the observed with the calculated spectrum. However, the complexity of the axial CF_3 spectrum arising from the several similar-valued coupling constants involved left some uncertainty.[1] Here, however, there is no such uncertainty, and because there is no a priori reason for $^3J_{FF}$ (trans) to be zero, it is clear that our previous inability[1,3-5a] to observe the trans $^3J_{FF}$ coupling constants was essentially due to the breadth and/or complexity of axial CF_3 group signals.

In the present case, all coupling constant assignments are confirmed by the excellent match of the observed ^{19}F spectrum with that calculated by means of the spectral simulation program NUMARIT[11] and by the $^{31}P\{^1H\}$ spectrum of $(CH_3)_2(CF_3)_2PF$ obtained at −20 °C (Figure 2), which consisted of a doublet of quartets of quartets due to coupling of P with the unique F, a large $^2J_{PF}$ coupling to the equatorial[6] CF_3 group, and a small $^2J_{PF}$ coupling to the axial[6] CF_3 group.

The normal-temperature ^1H NMR spectra of $(CH_3)_2(CF_3)_2PECH_3$ (E = O and S) showed two chemically shifted signals with a relative intensity ratio of 2:1. Each region consisted of a doublet of septets clearly assignable to the

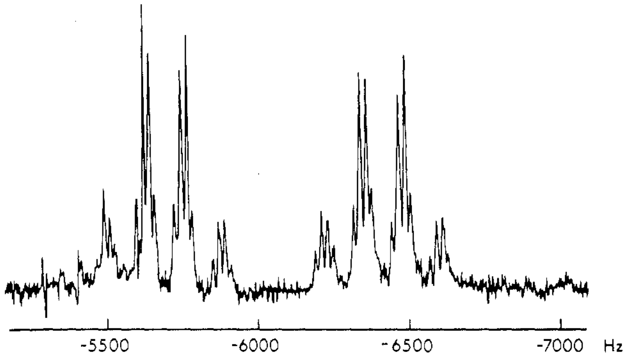

Figure 2. Proton-decoupled Fourier-transform ^{31}P (36.4 MHz) NMR spectra of $(CH_3)_2(CF_3)_2PF$ at −20 °C. Scale values give chemical shift in Hz from P_4O_6 (measured with the ^{19}F heteronuclear lock system) with negative offset frequencies indicating resonance to high field of the standard.

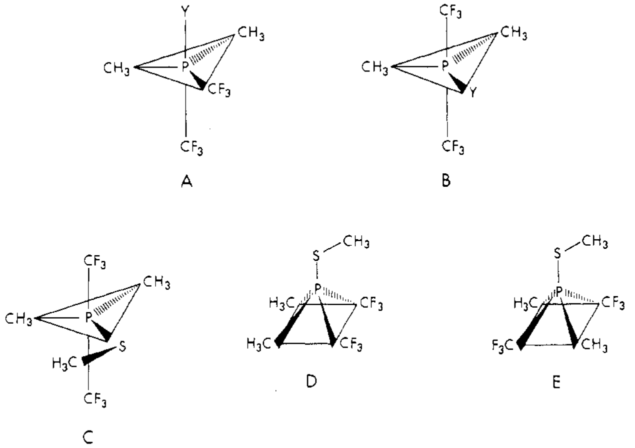

Figure 3. Ground-state structures of $(CH_3)_2(CF_3)_2PY$, A (Y = F and Cl) and B (Y = SCH_3, OCH_3, and $N(CH_3)_2$), and some possible alternative structures for $(CH_3)_2(CF_3)_2PSCH_3$ (C, D, and E).

$(CH_3)_2P$ and ECH_3 groups in the molecule. It is notable that the $^3J_{PSCH}$ coupling is significantly larger than the $^2J_{PCH}$ coupling in the compound $(CH_3)_2(CF_3)_2PSCH_3$, whereas in the other compounds the analogous values are nearly identical. In all cases, the substituent proton resonances (OCH_3, SCH_3, and $N(CH_3)_2$) appear to low field of the CH_3P signals.

Because of the room-temperature instability of $(CH_3)_2(CF_3)_2PN(CH_3)_2$, the ^1H spectrum was obtained only at −30 °C, where two equal-intensity regions, both showing a doublet of septets, were observed. Assignment of the appropriate signal in this case rests on the reasonable assumption that $N(CH_3)_2$ signals will be found to lower field (τ 7.2–7.4) of the CH_3 groups on P ($\tau \sim 8.0$). This assignment is consistent with previously investigated analogous systems,[1] and the $N(CH_3)_2$ chemical shifts are similar throughout the system.[1,3-5]

Assuming that the basic molecular structure is a trigonal bipyramid and that CH_3 groups will preferentially occupy equatorial sites,[9] the ground-state structure of $(CH_3)_2(CF_3)_2PF$ is A (Figure 3).

The NMR spectral data of the fluorophosphorane is also consistent with a square-pyramidal structure in which CF_3 groups occupy axial and basal positions and the remaining basal positions are occupied by F and two CH_3 groups, if we assume that the expected CH_3 nonequivalencies in this structure are too small to be observed. The similarity of observed NMR parameters of $(CH_3)_2(CF_3)_2PY$ with those observed for the $(CF_3)_3PXY$, $CH_3(CF_3)_2PXY$, and $CH_3(CF_3)_3PY$ series,[1-5] where the trigonal-bipyramidal structure was more easily justified, suggests, however, that the $(CH_3)_2(CF_3)_2PY$ system is also reasonably based on a trigonal-bipyramidal framework, and therefore we think that a square-pyramidal structure is unlikely for this system. With increased molecular complexity, however, distortions which destroy the idealized trigonal-bipyramidal geometry might become important, but we do not think that we have yet encountered a system which suffers such distortion that it is best considered a square pyramid.

At the lowest accessible temperature, −90 °C, the ^{19}F NMR spectrum of $(CH_3)_2(CF_3)_2PCl$ was unresolved, and therefore it is not possible to deduce the ground-state structure in this case. Tentatively we assign structure A (Figure 3) to $(CH_3)_2(CF_3)_2PCl$ rather than the alternative B since the former ground-state structure is in agreement with the apparent ground-state structure of other chlorophosphoranes[3-5] in which Cl appears to occupy an axial site. Apparently the barrier to CF_3 site interchange is smaller for $(CH_3)_2(CF_3)_2PCl$ than for $(CH_3)_2(CF_3)_2PF$. Attempts to resolve the problem of the Cl position in $(CH_3)_2(CF_3)_2PCl$ by means of ^{13}C NMR spectroscopy have to date been unsuccessful because of the poor solubility of the compound in suitable solvents.

The ^{19}F NMR spectra of the remaining phosphoranes [Y = OCH_3, SCH_3, and $N(CH_3)_2$] appear to be consistent with the trigonal-bipyramidal ground-state structure B (Figure 3). At normal temperatures (+33 °C) a broad doublet or a doublet of unresolved multiplets was observed due to coupling of equivalent (or nearly equivalent) CF_3 groups to P and to the protons of the methyl groups. The values of $^2J_{PF}$ are remarkably small (15–41 Hz), suggesting[6] that the CF_3 groups are located in the axial positions in keeping with the relative axial preference series.[6]

Equivalent CF_3 environments, as apparently presented by the phosphoranes $(CH_3)_2(CF_3)_2PY$ [Y = OCH_3, SCH_3, and $N(CH_3)_2$], are of course also consistent with a square-pyramidal geometry in which both CF_3 groups reside in the basal plane and the unique substituent Y occupies the apex. The relative magnitude of $^2J_{PF}$ values in all of these compounds would be interpreted by associating the smaller values of $^2J_{PF}$ with CF_3 groups in the basal plane and the larger values with the axial CF_3 substituent as in $(CH_3)_2(CF_3)_2PF$ (vide supra). Molecules which have two equivalent CF_3 groups which are characterized[1-5] by a relatively large value of $^2J_{PF}$ would then require that the larger value of $^2J_{PF}$ be associated with basal substitution, thus forcing abandonment of the correlation of the $^2J_{PF}$ value with the position of the CF_3 group in the molecular framework. Since many analogous systems[1,3-6,12] provide a consistent correlation of $^2J_{PF}$ with the apparent location of the CF_3 group in the trigonal-bipyramidal framework and since there is no clear evidence in the present system to warrant the rejection of either the assumption of trigonal-bipyramidial geometry or the correlation of $^2J_{PF}$ with position within this geometry, we think that it is reasonable to interpret the present set of NMR parameters in a manner which is consistent with previous interpretations[1,3-6] which have been based on the trigonal-bipyramid geometry.

If we assume that the equivalence of the CF_3 groups in the system $(CH_3)_2(CF_3)_2PY$ [Y = OCH_3, SCH_3, and $N(CH_3)_2$] is due to their location in equivalent geometrical positions in the ground-state structure, then, regardless of whether that ground state is trigonal bipyramidal or square pyramidal, positional interchange processes would not be observable, and the ^{19}F NMR spectra of these molecules would be essentially temperature invariant. If, however, the observed equivalence of CF_3 environments arises from positional interchange processes[13,14] affecting the CF_3 groups, then we would expect that the relatively high barriers to such interchange which appear to prevail for the Y = OCH_3, SCH_3, and $N(CH_3)_2$ derivatives[1,3-6] would have permitted resolution of the CF_3 environments with relatively little temperature reduction; i.e., the various environments would likely be distinguishable between 0 and −40 °C. The ^{19}F NMR spectra of the present series of compounds $(CH_3)_2(CF_3)_2PY$ [Y = OCH_3, SCH_3, and $N(CH_3)_2$] change in this temperature region but in a manner markedly different from that attributed earlier[1-5] to positional interchange processes in the trigonal bipyramid, and it appears that in these compounds the CF_3 groups reside in geometrically equivalent positions, most likely the axial positions of the trigonal bipyramid, and that the spectral changes are best explained by cessation of other dynamic averaging processes such as P–O, P–S, or P–N bond rotation. Since the barriers to these processes appear to be lower than the barrier to CF_3 positional interchange,[1-5,12] these effects will be important at only very low temperatures. Such processes provide the best understanding of the rather remarkable very low temperature NMR spectral behavior of compounds $(CH_3)_2(CF_3)_2PY$ [Y = OCH_3, SCH_3, and $N(CH_3)_2$].

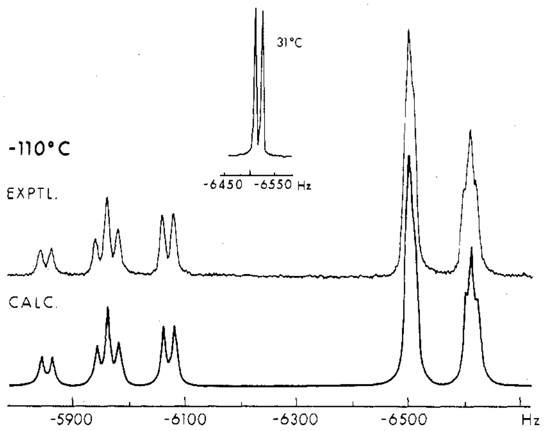

Figure 4. ^{19}F (94.2 MHz) spectrum of $(CH_3)_2(CF_3)_2PSCH_3$ at −110 °C compared with the calculated $[AB_2]_2P$ spectrum using the parameters given in Table V. The scale gives chemical shifts in hertz from $CFCl_3$, with negative offset frequencies indicating resonance to high field of standard.

Table V. A_3 and AB_2 Parameters of CF_3 Groups in $(CH_3)_2(CF_3)_2PSCH_3$

Temp, °C	ϕ, ppm	$^2J_{PF_A}$, Hz	$^2J_{PF_B}$, Hz	$^2J_{F_AF_B}$, Hz	$\Delta\nu$, Hz	$J_{AB}/\Delta\nu$
−110	63.6	19.4	-	108	570[b]	0.19
	69.7	-	9.5			
+33 (expl)	68.1	15.0		-	-	-
+33 (calcd)[a]	67.6	12.8				

[a] Weighted averages. [b] At 94.2 MHz.

Magnetic Nonequivalence within Axial CF_3 Groups. The clearest example is provided by the ^{19}F spectrum of $(CH_3)_2(CF_3)_2PSCH_3$ in which the simple doublet pattern observed at +33 °C collapses to a broad singlet below −40 °C. At −110 °C the spectrum is resolved into multiplets which can be analyzed as an $[AB_2]_2X$ spin system (Figure 4). The corresponding $^{31}P\{^1H\}$ spectrum at similar temperatures can be assigned as a first-order triplet of quintets, consistent with an A_2B_4 fluorine spin system. The low-temperature parameters (Table V) give a weighted average $^2J_{PF}$ value of 12.8 Hz, which is in reasonable agreement with the normal-temperature value of 15.0 Hz, strongly suggesting that the basic geometry of the system has not changed but rather that the observed spectrum arises because the six F atoms of the (axial) CF_3 groups are no longer magnetically equivalent and have been replaced by

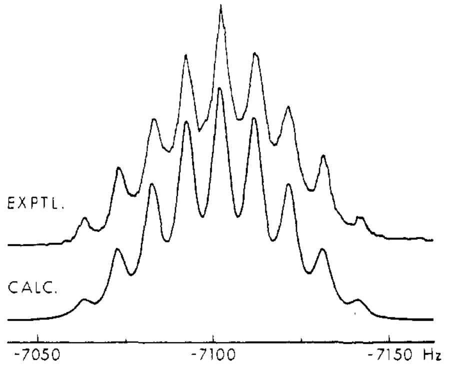

Figure 5. Fourier-transform proton-decoupled ^{31}P (36.4 MHz) NMR spectrum of $(CH_3)_2(CF_3)_2PSCH_3$ and −110 °C. The pattern, which can be analyzed in first order as an overlapping triplet of quintets, was also calculated from the parameters given in Table V. Scale values give chemical shifts in hertz from P_4O_6 (measured with the ^{19}F heteronuclear lock system), with negative offset frequencies indicating resonance to high field of the standard.

two different groups of two and four F atoms each, a conclusion which is supported by the agreement of the weighted average of the chemical shifts of F_A and F_B with the experimental average. The agreement of weighted average values also indicates that the relative signs of $^2J_{F_A}$ and $^2J_{F_B}$ are the same. It seems reasonable then to attribute the destruction of magnetic equivalence to a process such as the cessation of P–S bond rotation in $(CH_3)_2(CF_3)_2PSCH_3$ coupled with an interference with the axial CF_3 groups such that, in effect, the CF_3 groups are no longer freely rotating. No such clear spectral pattern was observed in the very low temperature spectra of $(CH_3)_2(CF_3)_2POCH_3$ or $(CH_3)_2(CF_3)_2PN(CH_3)_2$; however, these spectra became complex at very low temperatures in a manner reminiscent of analogous systems encountered earlier[1,3-5] wherein the spectrum comprised a large number of transitions spread over 500 to 1000 Hz. The resolution of clear and assignable spectral patterns from the restricted rotation of angular substituents such as OCH_3, SCH_3, and perhaps also $N(CH_3)_2$ is therefore rare, and to date only the present case, $(CH_3)_2(CF_3)_2PSCH_3$, and the compound $CH_3(CF_3)_2P(OCH_3)_2$[3] have yielded tractable spectra. Even in these cases, however, the stereochemical significance of these spectra is not clear.

The nonequivalence of the axial F atoms in F_4PSCH_3 was attributed[16] to the cessation of rotation about the P–S bond, restraining the SCH_3 group in or near to the axial plane of the molecule. Similar behavior has been noted in $(CF_3)_2PF_2SCH_3$[17] and $CF_3(CH_3)PF_2SCH_3$.[17] Proposing the analogous structure for $(CH_3)_2(CF_3)_2PSCH_3$ leads, however, to the prediction that only one of the axial CF_3 groups would likely be affected by the proximity of the CH_3 group of SCH_3, but the experimental evidence (especially the ^{31}P spectrum, Figure 5) clearly indicates that both CF_3 groups are equally affected by whatever process is responsible for the creation of magnetic nonequivalence. The square-pyramidal ground-state structure D (Figure 3) in which CF_3 substituents are mutually cis allows equal perturbation of CF_3 environments by a "frozen" SCH_3 group; however, we have rejected the square-pyramidal structure for reasons given above. In addition, D is not the most reasonable square-pyramidal structure for this molecule. Minimization of steric interactions would be most likely provided by structure E (Figure 3), but E, like the structure based on the trigonal bipyramid (B), cannot provide a general equality of CF_3 environments when SCH_3 rotation ceases.

A third possibility is that these effects arise not from the interaction of the axial CF_3 groups with the CH_3 group on sulfur but rather as a result of interactions of the lone pairs on sulfur[18] with the polar (i.e., C–F) bonds in the molecule. A trigonal-bipyramidal structure in which S lone-pair density lies equally above and below the trigonal plane such that both CF_3 groups are equally perturbed can be readily visualized. Similar structures can be invoked to account for the behavior of $(CF_3)_2CH_3P(OCH_3)_2$,[3] where a similar effect was also clearly observed but was readily rationalized on the basis of equivalent steric interaction between the two CF_3 groups and the two OCH_3 groups. The interactions which give rise to the AB_2 spectra may be quite different in the two molecules, and thus there may be no need to visualize a comparable mechanism for the creation of magnetically nonequivalent environments. It should be noted that, while $^2J_{AB}$ is comparable in both cases, the relative magnitudes of chemical shift and coupling constants of A and B nuclei are reversed. In the present case, $(CF_3)_2(CH_3)_2PSCH_3$, $\phi_{F_A} < \phi_{F_B}$ and $^2J_{F_A} > {}^2J_{F_B}$, whereas in $(CF_3)_2CH_3P(OCH_3)_2$[3] $\phi_{F_A} > \phi_{F_B}$ and $^2J_{F_A} < {}^2J_{F_B}$, where A consistently represents the unique nucleus of the CF_3 group. $^2J_{AB}$ is similar in both cases. This difference may be due to the entirely different electronic environments provided by each case or may indicate that the interaction which destroys the magnetic equivalence is different in each case.

Table VI. Hydrolysis of $(CF_3)_2(CH_3)_2PY$

Y	Quantity of compound, g (mmol)	Quantity of liberated CF_3H, g (mmol)	Species in solution by NMR
		(A) Neutral	
Cl	0.142 (0.61)	0.042 (0.60)	$CF_3(CH_3)_2PO$[a]
F	0.127 (0.58)	0.040 (0.57)	$CF_3(CH_3)_2PO$,[a] F^-
OCH_3	0.219 (0.95)	0.067 (0.96)	$CF_3(CH_3)_2PO$[a]
SCH_3	0.084 (0.34)	0.024 (0.34)	$CF_3(CH_3)_2PO$[a]
		(B) Alkaline	
Cl	0.164 (0.71)	0.097 (1.38)	$(CH_3)_2PO_2^-$
F	0.177 (0.81)	0.111 (1.59)	$(CH_3)_2PO_2^-$
OCH_3	0.114 (0.49)	0.069 (0.99)	$(CH_3)_2PO_2^-$
SCH_3	0.082 (0.33)	0.046 (0.66)	$(CH_3)_2PO_2^-$

[a] See parameters in Table VII.

Some insight into this problem might be provided by the behavior of the CH_3 group ^1H NMR signals in both systems since if these effects arise from steric interaction between CF_3 and the CH_3 protons of the ECH_3 group, the NMR signals of these protons should also demonstrate magnetic nonequivalence. On the other hand, if the effects arise from the interaction of the lone pairs with the polar C–F bonds, then the CH_3 groups on P will be nonequivalent as the result of interactions with the SCH_3 groups, in this case lying in or near the equatorial plane. Unfortunately the ^1H NMR spectrum (100 MHz) obtained at the lowest accessible temperatures, as in the previous case,[3] did not demonstrate sufficient resolution to identify individual magnetic environments within the CH_3 groups. Since these effects are likely to be small, high-field (270–300 MHz) ^1H NMR spectroscopy may be required to resolve the problem.

Experimental Section

All reactions were done in sealed tubes, and standard vacuum techniques were used throughout. $(CF_3)_2PCl_3$,[19] $(CH_3)_3SiOCH_3$,[20] and $(CH_3)_3SiSCH_3$[21] were prepared according to published methods. $(CH_3)_4Pb$ (as a 70% solution in toluene) was purchased from Alfa Inorganics and was used without further purification, as was $(CH_3)_2NH$. SbF_3 (Alfa) was sublimed twice before use to remove oxide and water impurities which caused contamination of the fluoride with various phosphine oxides.

Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using a 9-cm gas cell with KBr windows. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. ^1H and ^{19}F NMR spectra were recorded at 60.0 and 56.4 MHz, respectively, on a Varian A56/60, or at 100 and 94.2 MHz, respectively, on a Varian HA-100 instrument. ^{31}P spectra were recorded at 36.4 MHz with a Bruker HFX-90-Nicolet 1085 spec-

Table VII. NMR Parameters of the Hydrolysate Species and the Phosphine Oxide

Compound	Medium[a]	Y	ϕ_F,[b] ppm	τ[c]	$^2J_{PF}$, Hz	J_{PH}, Hz	J_{FH}, Hz	Identity
$(CF_3)_2(CH_3)_2PY$[g]	H_2O	Cl	75.7[d]	8.10[e]	91	14.9	0.8	$CF_3(CH_3)_2PO$[j]
	H_2O	F	76.0[d]	8.13[e]	92	15.0	0.8	
	H_2O	OCH_3	76.1[d]	8.16[e]	89	14.6	0.8	
	H_2O	SCH_3	75.9[d]	8.16[e]	92	14.7	0.8	
$CF_3(CH_3)_2PCl_2$[g]	H_2O	Cl	76.2[d]	8.06[e]	90	14.3	0.8	
$(CF_3)_2(CH_3)_2PY$[g]	Alkaline H_2O	All	-	8.70[f]	-	14.2	-	$(CH_3)_2PO_2^-$
$CF_3(CH_3)_2PO$[h-j]	H_2O	-	76.2[d]	8.06[e]	91	14.3	0.8	
	$CFCl_3/CD_2Cl_2$	-	77.1[d]	8.44[e]	86	14.0	0.8	

[a] Solvent. Unless otherwise noted neutral water was used for hydrolysis. Resultant X = Cl and F solutions were acidic; all others had pH close to neutral. [b] ppm vs. $CFCl_3$, positive values indicating resonance to high field of standard. [c] τ scale: ppm vs. Me_4Si, for which τ = 10.0. [d] The ^{19}F spectrum is a doublet of septets. [e] The ^1H spectrum is a doublet of quartets. [f] The ^1H spectrum is a simple doublet and the only coupling constant is $^2J_{PH}$. [g] Compound taken for hydrolysis. [h] Independently synthesized and dissolved in the solvent indicated. [i] σ (^{31}P) +60.0 ppm vs. P_4O_6[22]; quartet spin-splitting pattern. [j] Parameters in agreement with those of ref 7.

trometer operating in the pulsed FT mode. All spectra were recorded on samples which consisted of an approximate 10% solution of the compound in $CFCl_3$ and CF_2Cl_2. ^{19}F chemical shifts were measured relative to internal $CFCl_3$ solvent, or external $CFCl_3$ (capillary) in cases where other solvents were used. ^1H chemical shifts were measured relative to internal tetramethylsilane (Me_4Si). ^{31}P NMR spectra were measured with respect to the heteronuclear ^{19}F lock signal and then converted to the P_4O_6 scale[22] by means of the appropriate conversion factor. For the $CFCl_3$ lock reference, P_4O_6 was established as 118 ppm to high field of the machine zero by measurement against an external capillary of P_4O_6. Each instrument was equipped with a variable-temperature controller which was established as accurate to within ±1 °C of the temperature indicated on the controller by calibration.

Hydrolysis in Neutral Media. A quantity of the compound was treated with approximately 1 cm^3 of degassed distilled water in vacuo in a sealed tube for 48 h at room temperature. Highly volatile products were removed under vacuum and the hydrolysate solution was examined by ^1H and ^{19}F NMR spectroscopy. Reaction quantities and results are given in Table VI. NMR parameters of the hydrolysate species identified below as $CF_3(CH_3)_2PO$ are given in Table VII.

Hydrolysis in Alkaline Media. A quantity of the compound was treated with approximately 1 mL of 10% solution according to the above procedure. Quantities and results are given in Table VI, and NMR parameters of the hydrolysate species, identified[23] as $(CH_3)_2PO_2^-$, are given in Table VII.

Preparation of Dimethylbis(trifluoromethyl)chlorophosphorane, $(CF_3)_2P(CH_3)_2Cl$. Bis(trifluoromethyl)trichlorophosphorane, $(CF_3)_2PCl_3$[18] (2.248 g, 8.21 mmol), was condensed with tetramethyllead, $(CH_3)_4Pb$ (4.967 g, 70% solution in toluene), into a 50-mL tube, which was sealed. A white solid was formed gradually upon warming to room temperature. After 2 days of reaction with shaking, the volatile products were separated by vacuum fractionation and identified as dimethylbis(trifluoromethyl)chlorophosphorane (0.898 g, 3.84 mmol, 47%), mp 65–67 °C (uncorrected), which was trapped at −35 °C, and a more volatile mixture of $CH_3(CF_3)_2PCl_2$, $(CH_3)_4Pb$, and toluene (2.367 g), according to the NMR spectrum. $(CH_3)_3PbCl$ remained in the reaction tube. A trace amount of an unidentified, noncondensable gas was also observed.

Preparation of Dimethylbis(trifluoromethyl)fluorophosphorane. $(CF_3)_2P(CH_3)_2Cl$ (0.384 g, 1.64 mmol) and excess freshly sublimed SbF_3 gave, after shaking for 24 h at room temperature, dimethylbis(trifluoromethyl)fluorophosphorane (0.344 g, 1.58 mmol, 96%); mp 16–17 °C (uncorrected).

Preparation of Dimethylbis(trifluoromethyl)methoxyphosphorane. Method A. A mixture of $(CH_3)_2(CF_3)_2PCl$ (0.377 g, 1.61 mmol) and $(CH_3)_3SiOCH_3$ (0.194 g, 1.86 mmol) gave, after shaking for 3 h at room temperature, dimethylbis(trifluoromethyl)methoxyphosphorane, $(CH_3)_2(CF_3)_2POCH_3$ (0.360 g, 1.57 mmol), which was trapped at −45 °C, and a more volatile unseparated mixture of $(CH_3)_3SiCl$ and $(CH_3)_3SiOCH_3$ (0.206 g), identified by NMR spectra.

Method B. $(CH_3)_2(CF_3)_2PF$ (0.134 g, 0.61 mmol) and $(CH_3)_3SiOCH_3$ (0.086 g, 0.82 mmol) gave, after shaking for several hours at room temperature, $(CH_3)_2(CF_3)_2POCH_3$ (0.137 g, 0.60 mmol), which was trapped at −51 °C, $(CH_3)_3SiOCH_3$ (0.0251 g, 0.02 mmol), which was trapped at −96 °C, and $(CH_3)_3SiF$ (0.057 g, 0.62 mmol), which was trapped at −196 °C.

Preparation of Dimethylbis(trifluoromethyl)dimethylaminophosphorane. $(CH_3)_2(CF_3)_2PCl$ (0.237 g, 1.01 mmol) and $(CH_3)_2NH$ (0.136 g, 3.01 mmol) in diethyl ether solvent (0.978 g) gave, after warming slowly from −196 °C to room temperature, a mixture of diethyl ether and $(CH_3)_2NH$ (1.0440 g), which passed a −78 °C trap, and an unstable compound, trapped at −45 °C, which appeared by NMR spectroscopy to be dimethylbis(trifluoromethyl)dimethylaminophosphorane. This product decomposed rapidly when vacuum transfer to a weighing tube was attempted.

Preparation of Dimethylbis(trifluoromethyl)methylthiophosphorane. $(CH_3)_2(CF_3)_2PCl$ (0.314 g, 1.34 mmol) and $(CH_3)_3SiSCH_3$ (0.180 g, 1.50 mmol) gave, after shaking 30 min at room temperature, dimethylbis(trifluoromethyl)methylthiophosphorane, $(CF_3)_2(CH_3)_2PSCH_3$ (0.316 g, 1.29 mmol), which was trapped at −33 °C, and a more volatile mixture of $(CH_3)_3SiCl$ and $(CH_3)_3SiSCH_3$ (0.171 g).

Preparation of Dimethyl(trifluoromethyl)phosphine Oxide. Method A. About 2 mmol of $CF_3(CH_3)_2PCl_2$ (prepared from $CF_3(CH_3)PCl_3$ and $(CH_3)_4Pb$) was heated with excess $[(CH_3)_3Si]_2O$ in a sealed tube at room temperature for 3 days. Removal of the most volatile products, $(CH_3)_3SiCl$ and unreacted $[(CH_3)_3Si]_2O$, left a white, volatile, crystalline solid identified as the phosphine oxide $CF_3(CH_3)_2PO$ by elemental analysis and spectroscopic properties. (Anal. Calcd for $C_3H_6F_3PO$: C, 24.66; H, 4.14; F, 39.04; P, 21.23. Found: C, 24.52; H, 4.33; F, 40.39; P, 21.88.) NMR parameters in $CFCl_3/CD_2Cl_2$ mixed solvent and water were similar and are given in Table VII. Prominent peaks in the mass spectrum are the parent ion $C_3H_6F_3PO^+$ (*m/e*: calcd 146.0108, found 146.0112; relative intensity 4.8%) and $C_2H_6PO^+$ (*m/e*: calcd 77.0153, found 77.0156; relative intensity 100%).

Method B. Neutral hydrolysis of $CF_3(CH_3)_2PCl_2$ for 5 days at room temperature yielded a solution with NMR parameters (Table VII) characteristic of $CF_3(CH_3)_2PO$. The oxide was not isolated from this solution.

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Registry No. $(CH_3)_2(CF_3)_2PCl$, 64728-35-4; $(CH_3)_2(CF_3)_2PF$, 64728-34-3; $(CH_3)_2(CF_3)_2POCH_3$, 64728-33-2; $(CH_3)_2(CF_3)_2PSCH_3$, 64728-38-7; $(CH_3)_2(CF_3)_2PN(CH_3)_2$, 64728-37-6; $(CH_3)_3SiOCH_3$, 1825-61-2; $(CH_3)_3SiSCH_3$, 3908-55-2; $CF_3(CH_3)_2PO$, 26348-91-4; $(CF_3)_2PCl_3$, 353-77-5; $CF_3(CH_3)_2PCl_2$, 64728-36-5.

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Macrocycle-Promoted Oxygenation Reactions: Equatorial and Axial Ligand Effects

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Equilibrium data are reported for the complexation of dioxygen by the cobalt(II) complexes of 1,4,8,11-tetraazacyclotetradecane and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene in the presence of various trans axial donors including pyridine, imidazole, ammonia, cyanide, and coordinated water. A switch in preferred stoichiometry from 2:1 to 1:1 occurs from the saturated to unsaturated systems. Data for these systems are compared with previously investigated systems, and the equilibria are explained in terms of ligand donor properties. Spectroscopic characterization of these oxygenated species and their reactivity are briefly reported.

Introduction

There has been intense interest during the past several years in the properties of metal–dioxygen adducts.[1-3] While a wide variety of transition-metal complexes are known to bind dioxygen,[9] interest has largely centered on iron[2,4] and analogous cobalt[1-3] complexes, the former being of foremost biological interest and the latter appearing to function as excellent general models for metal–dioxygen binding.[1]

It is now widely[1-4] but not universally[5] accepted, largely on the basis of cobalt complex work, that dioxygen adds to metals via an "internal redox" reaction, i.e.

$$LM^{n+} + O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} LM^{(n+1)+}O_2^- \underset{K_2}{\overset{LM}{\rightleftharpoons}} LM^{(n+1)+}O_2^{2-}\text{-}LM^{(n+1)+}$$

in which the metal is formally oxidized and O_2 formally reduced.

Work from several laboratories, including those of Martell,[1] Basolo,[2] and others, have begun to clarify the structural and electronic effects which govern the position of equilibria K_1 and K_2, but much remains to be accomplished in this respect. To this end, we have begun a systematic study of the bonding of dioxygen by macrocyclic cobalt complexes.

While the potential of synthetic macrocyclic complexes for mimicking the biologically important porphyrin macrocycles has long been recognized,[6] few if any studies of macrocycle-promoted oxygenation reactions exist.[7] These ligands offer a number of advantages in mechanistic studies, including rigid stereochemical control, allowing individual parameterization of axial and equatorial ligand effects. Equatorial effects may be utilized to traverse a series of ligands from a fully saturated nitrogen donor (cyclam) to the fully unsaturated porphyrins and porphyrin analogues,[8] whereas axial effects may probe the sensitivity of oxygenation to direct differences in relative energy and occupancy of the d_{z^2} orbital with which O_2 combines.

The inert character of the equatorial ligand, with corresponding stereochemical control of ligand exchange, used to great advantage by Poon et al. in studies of Co(III) ligand exchange reactions, makes these systems ideal for investigating ligand-exchange reactions at an oxygenated metal center, as well as allowing simplified mechanistic studies of the conversion of CoO_2 to an irreversibly oxidized Co(III) complex. In order to carry out these mechanistic studies, good equilibrium data describing the oxygenated system must be available.

In the present paper, thermodynamic data are reported for the formation of oxygen adducts of cobalt promoted by 1,4,8,11-tetraazacyclotetradecane (abbreviated cyclam or (14)aneN_4) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (abbreviated Me_6(14)4,11-dieneN_4), a partially unsaturated analogue, which form two members of such a series.

Axial effects have been probed for the cyclam system utilizing H_2O, CN^-, imidazole, pyridine, and ammonia trans to coordinated O_2.

Experimental Section

Cyclam and Me_6(14)diene were obtained from Strem Chemicals, recrystallized from ethanol–water, and purity-checked by potentiometric titration. Spectrophotometric measurements were obtained on a Cary 14 spectrophotometer using matched quartz cells. Oxygenation equilibria were monitored using an oxygen-sensitive (polarographic) electrode (Yellow Springs Instrument Co.). Equilibria were characterized at a constant temperature of 25.0 ± 0.1 °C in the presence of 0.1 M KNO_3 as an electrolyte. In a typical experiment, ligand solution was air saturated, an initial instrument setting made, and a small known volume of air-saturated Co(II) solution added by syringe to the closed system. Typically 40 min was allowed to attain equilibrium (this time reflects the slow macrocycle complex formation with subsequent addition of O_2 being fast[1]). After the Co(II) macrocycle aquo complex had attained equilibrium with O_2, an aliquot of a stock solution of the trans axial ligand of interest was added by

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